

Review

Alkynyl compounds and nonlinear optics [☆]

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Abstract

The authors' studies of the nonlinear optical (NLO) properties of metal alkynyl complexes are summarized; structure–NLO property relationships are developed and attempts to “switch” optical nonlinearities of alkynyl complexes are described.
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Keywords: Acetylides; Alkynyl complexes; Nonlinear optics; Hyperpolarizabilities; Quadratic nonlinearities; Cubic nonlinearities

1. Introduction

The nonlinear optical (NLO) properties of materials have come under increasing scrutiny. This is because when light interacts with materials possessing NLO properties, the incident light can be changed and new electromagnetic field components produced (e.g., with differing phase, frequency, amplitude, polarization, path, etc). As a result, NLO materials have potential applications in optical signal processing, switching and frequency generation (making use of processes such as harmonic generation, frequency mixing, and optical parametric oscillation), and may also contribute to optical data storage, optical communication, and image processing [1]. There have been several reviews of the NLO properties of organometallics and/or coordination complexes that include a detailed discussion of the theory behind nonlinear optics and experimental procedures to measure NLO effects [1–5] and a comprehensive review of the NLO properties of alkynyl complexes

has recently appeared [6]; this detailed material will not be reproduced here (although a brief summary of the theory has been provided to clarify the subsequent discussion) – rather, the emphasis of the present account is on results from research by the authors' group in the field of organometallics for nonlinear optics.

An electric field E_{loc} acting on a molecule can distort the molecular electron density distribution $\rho(\mathbf{r})$, an effect that can be described in terms of changes in the dipole moment μ . Changes in the dipole moment induced by a weak field are linear with the magnitude of the field, but when E_{loc} is comparable in strength to the internal electric fields within the molecule, the distortion and the induced dipole moment should be treated as nonlinear functions of the field strength:

$$\mu = \mu_0 + \alpha E_{loc} + \beta E_{loc} E_{loc} + \gamma E_{loc} E_{loc} E_{loc} + \dots \quad (1)$$

The tensors α , β and γ defined by the above equation are the linear polarizability, the second-order or quadratic hyperpolarizability (the first hyperpolarizability) and the third-order or cubic hyperpolarizability (the second hyperpolarizability), respectively. Both μ and E_{loc} are vectors, α is a second-rank tensor (or a 3×3 matrix), β is a third-rank tensor (or a $3 \times 3 \times 3$ matrix), and γ is a fourth-rank tensor (or a $3 \times 3 \times 3 \times 3$ matrix). Many tensor components of α , β , and γ are equivalent by various symmetry rules or equal to zero. Polarizabilities are

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invariant with respect to all point group symmetry operations, so all the components of β vanish in centrosymmetric point groups.

The electric field of a light wave can be expressed as:

$$\mathbf{E}(t) = \mathbf{E}_0 \cos(\omega t).$$

Eq. (1) can therefore be written as:

$$\boldsymbol{\mu}(t) = \boldsymbol{\mu}_0 + \alpha \mathbf{E}_0 \cos(\omega t) + \beta \mathbf{E}_0^2 \cos^2(\omega t) + \gamma \mathbf{E}_0^3 \cos^3(\omega t) + \dots$$

It is readily apparent [from trigonometric relations such as $\cos^2(\omega t) = 1/2 + 1/2\cos(2\omega t)$] that nonlinear terms in the dipole moment expansion introduce contributions at different frequencies. The second-order (β) term introduces a time-independent (d.c.) contribution and a term oscillating at 2ω (second-harmonic generation), and provides a frequency mixing phenomenon if the input field is a sum of two components with different frequencies. A constant (d.c.) field may influence an oscillating field if the two are combined in a medium containing second-order nonlinear molecules [this is known as the electrooptic effect]. The cubic term in Eq. (1) leads to several NLO effects, one being oscillation of the induced dipoles at 3ω (third-harmonic generation). The magnitude of these effects depends on the magnitude of the NLO coefficients β and γ , so a major focus of studies has been to prepare materials with large NLO coefficients that are stable to processing and subsequent device operating conditions.

Inorganic salts were the initial focus of attention as NLO materials, after the invention of the laser made it possible to observe these effects, but the potential of organic molecules was soon realized and this became a major area of study. Unlike inorganics, for which lattice distortions (with a time domain of ns) contribute to the nonlinearity, organics can possess a purely electronic nonlinearity with a time domain of fs, they are more easily processable into films, and the ready access to systematically modified compounds permits structure–property studies and optimization of responses. Despite their potentially greater structural diversity and the accessibility of more than one oxidation state for the metal, organometallic complexes were curiously little explored until the mid-1980s [7], when Malcolm Green alerted organometallic chemists to the potential of organometallics in nonlinear optics [8]. In the next few years, the number of studies slowly increased, and (relevant to the present account) there were a few reports of the NLO properties of platinum and palladium alkynyl complexes and polymers [9–12], a variety of techniques (four-wave mixing, intensity dependent absorption, optical Kerr gate, and third-harmonic generation [3]) at a range of wavelengths revealing moderate cubic nonlinearities. The authors' entry into the arena of alkynyl complexes for nonlinear optics was prompted by a call

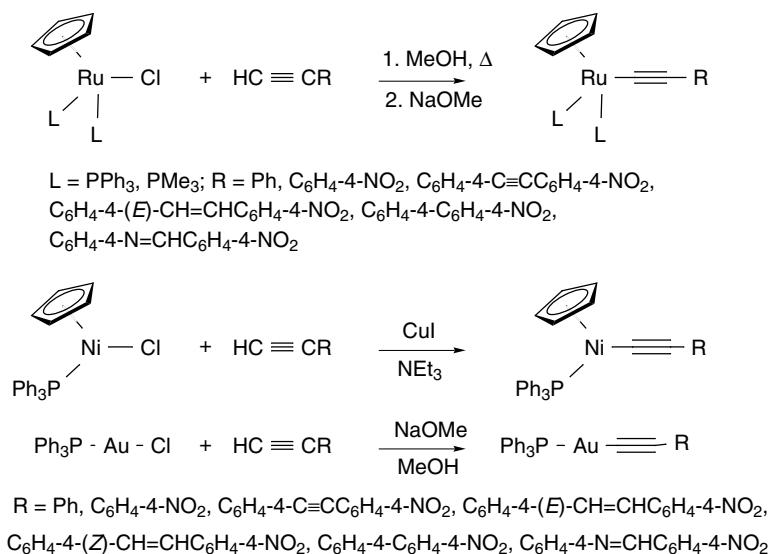
to arms for organometallic chemists by Seth Marder [13]. After securing some funding and an enthusiastic PhD student, we entered the fray.

2. Structure–quadratic NLO studies

Efficient organic NLO molecules such as *p*-nitroaniline have a donor–bridge–acceptor composition. Our first PhD student to enter this field, Ian Whittall, prepared an array of systematically varied ruthenium, nickel and gold complexes bearing alkynyl ligands with an appended nitro group. Alkynyl complexes with a 4-nitrophenyl group at the alkynyl ligand can be considered to have a similar composition to efficient organics, but one in which the donor group is a ligated metal; the possibility of modifying the ligand environment at the metal affords the attractive prospect of a tunable donor group. The suite of complexes that we studied (Scheme 1) was readily accessed by extending literature procedures that had been developed for the synthesis of the related phenylalkynyl examples by Michael Bruce [14–16].

Criteria for efficient organic NLO materials were being developed at the time, but far less was known of how to achieve substantial NLO effects in organometallic complexes, design criteria to achieving significant responses generally being those propagated from organic compound studies. While studying the NLO properties of ferrocenyl complexes, Seth Marder had suggested that more efficient compounds than ferrocenyl derivatives may be accessed by incorporating the metal into the plane of the chromophore π -system, and by incorporating some metal–chromophore multiple bonding [17]. Metal alkynyl complexes certainly satisfy the first suggested design criterion, so we sought evidence for π -bonding by structurally characterizing a large number of examples in a comprehensive study of M–C bond distances. The evidence was tantalizing – as expected, a decrease in M–C distance and increase in C \equiv C distance was observed upon introduction of nitro substituent to the alkynyl ligand, but differences were at the margin of statistical significance [18,19]. Complementary photoelectron spectroscopy studies on our compounds by Dennis Lichtenberger and density functional calculations on model compounds by John McGrady and Rob Stranger [20] were useful in evaluating this π -contribution to the overall metal–alkynyl bonding, suggesting that π -backbonding contributes at most 10% to the overall bonding interaction.

Armed with this evidence supportive of some π -interaction, we set about quantifying the NLO merit of our complexes. At the time, Tobin Marks and Mark Ratner had just reported using semi-empirical ZINDO (Zerner's intermediate neglect of differential overlap) to assess the NLO merit of ferrocenyl complexes computationally [21], so we obtained a license for the software and Ian



Scheme 1. Preparation of ruthenium, nickel and gold alkynyl complexes.

Whittall and Andrew McDonagh evaluated its performance with alkynyl complexes. It proved useful in reproducing trends in experimental data, but unreliable in reproducing the magnitude. Its greatest strength lay in assessing structural variations difficult or impossible to assess experimentally; we were able to examine the effect on quadratic NLO properties of M–C bond length modification (Fig. 1) and alkynyl ligand phenyl ring rotation (Fig. 2) – the results suggested that in order to optimize NLO response one should strive to minimize M–C distance, but that phenyl orientation was not a

crucial concern, the latter reassuring because the crystal engineering needed to organize a specific ring orientation was clearly going to be difficult [22–24].

The experimental quadratic nonlinearities of these complexes were evaluated in Leuven as the start of a fruitful collaboration with André Persoons and his group. At the time, they had just developed the hyper-Rayleigh scattering (HRS) procedure that greatly expanded the range of compounds for which quadratic nonlinearities could be measured (previously, the usual technique used had been electric field-induced second harmonic generation (EFISH), with which one can

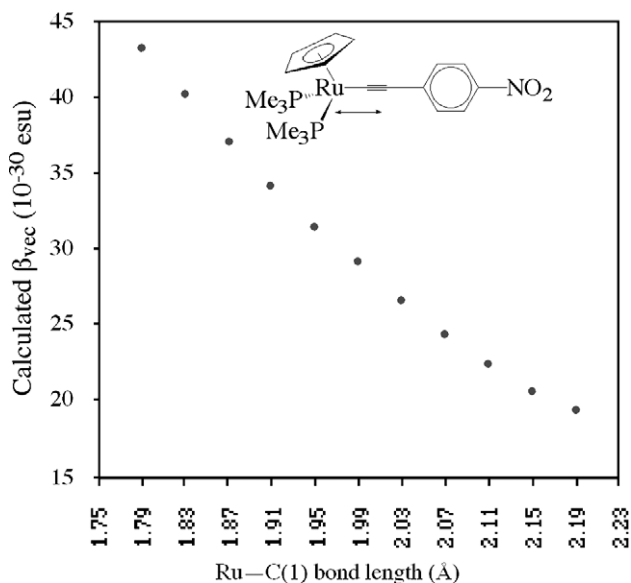


Fig. 1. The effect of varying the Ru–C bond length on the ZINDO-derived quadratic nonlinearity for [Ru(C≡CC₆H₄-4-NO₂)(PMe₃)₂(η⁵-C₅H₅)]. Reprinted with permission from I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, Organometallics 14 (1995) 3978. Copyright ©1995 American Chemical Society.

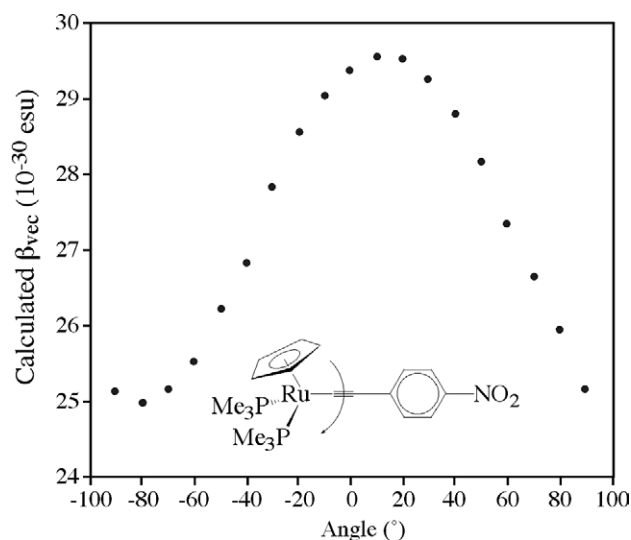


Fig. 2. The effect of nitrophenylalkynyl ligand rotation on the ZINDO-derived quadratic nonlinearity for [Ru(C≡CC₆H₄-4-NO₂)(PMe₃)₂(η⁵-C₅H₅)]. Reprinted with permission from I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, Organometallics 14 (1995) 3978. Copyright ©1995 American Chemical Society.

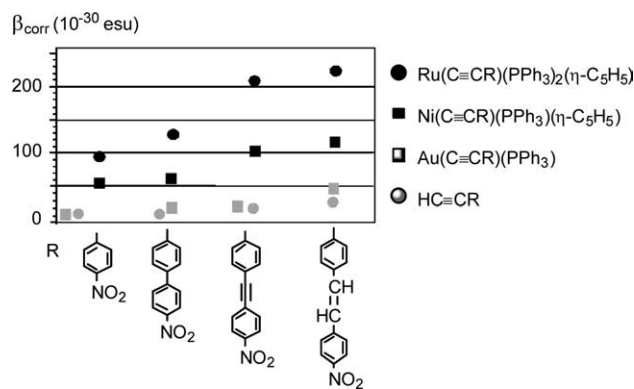


Fig. 3. The effect of varying the ligated metal upon the two-level-corrected quadratic nonlinearities for selected metal alkynyl complexes.

measure neutral dipolar compounds, but with HRS the range of accessible compounds is expanded to include charged species and octupolar compounds) [25]. The results for our series of alkynyl complexes are summarized in Fig. 3 and listed in Table 1. To compare the merit of compounds, it is desirable to obtain zero frequency nonlinearities, and thereby remove the effect of resonance enhancement. Dispersion of the quadratic nonlinearity β for linear charge-transfer molecules can be described by a two-state model. The two-level corrected β values (β_0) are available from:

$$\beta_0 = \beta(1 - (\lambda_{\max}/\lambda)^2)(1 - (2\lambda_{\max}/\lambda)^2),$$

where λ_{\max} is the optical absorption maximum and λ is the fundamental wavelength of the laser. The β_0 values for our alkynyl complexes are listed in Table 1, but these data should be treated cautiously, because the two-level model is probably not sufficient for metal alkynyl complexes (for a recent critique of the application of the two-level model to coordination complexes, see [26]). Another concern when comparing data is that different experimental techniques can sample different tensorial components of the nonlinearity (or combinations thereof). André Persoons' group examined two of the complexes in Table 1 by both HRS and EFISH, the equivalent β values (within the experimental error margins) suggesting that there is one dominant tensor component ($\beta_{\text{vec}} = \beta_{\text{EFISH}} = \beta_{\text{HRS}} = \beta_{\text{zzz}}$) (note that most data for organometallics to that time had been determined by EFISH, and the EFISH-derived $\mu \cdot \beta_{1,064}$ for both $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-(E)-CH}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ (9700×10^{-48} esu) and $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-(E)-N}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$ (5800×10^{-48} esu) were large compared to extant data for other organometallic complexes).

Perhaps not surprisingly, we found that many of the alkynyl complex structure–quadratic NLO activity trends mimicked those found for organic molecules. To understand these trends, it is helpful to note the

Table 1
Molecular quadratic NLO measurements for selected ruthenium, nickel and gold alkynyl complexes

Complex	λ_{\max} (nm)	β_0^a (10^{-30} esu)	β_0^a	Technique	Reference
$[\text{Ru}(\text{C}\equiv\text{CPh})(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$	310	89	45	HRS	[28,29]
$[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$	460	468	96	HRS	[28,30]
$[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)(\text{PMe}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$	477	248	39	HRS	[28,30]
$[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$	448	560	134	HRS	[28,29]
$[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-(E)-CH}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$	476	1455	232	HRS	[28,30]
	476	1464	234	EFISH	[28,30]
$[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$	446	865	212	HRS	[28,29]
$[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-N}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$	496	840	86	HRS	[28,30]
	496	760	78	EFISH	[28,30]
$[\text{Ni}(\text{C}\equiv\text{CPh})(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$	307	24 ^b	15	HRS	[31]
$[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$	439	221	59	HRS	[31]
$[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$	413	193	65	HRS	[31]
$[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-(E)-CH}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$	437	445	120	HRS	[31]
$[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-(Z)-CH}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$	417	145	47	HRS	[31]
$[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$	417	326	106	HRS	[31]
$[\text{Ni}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-N}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)(\eta^5\text{-C}_5\text{H}_5)]$	448	387	93	HRS	[31]
$[\text{Au}(\text{C}\equiv\text{CPh})(\text{PPh}_3)]$	296	6	4	HRS	[27,28]
$[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)]$	338	22	12	HRS	[27,28]
$[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)]$	350	39	20	HRS	[27,28]
$[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-(E)-CH}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)]$	386	120	49	HRS	[27,28]
$[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-(Z)-CH}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)]$	362	58	28	HRS	[27,28]
$[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)]$	362	59	28	HRS	[27,28]
$[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-N}=\text{CHC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)]$	392	85	34	HRS	[27,28]

^a Solutions in thf, measurements at 1.064 μm , β values have uncertainty of 10% unless otherwise noted.

^b Uncertainty of 20%.

perturbation theory-derived relationships between hyperpolarizabilities and linear optical transitions:

$$\beta \approx 3(\mu_{\text{ce}} - \mu_{\text{gg}})(\mu_{\text{ge}}^2/E_{\text{ge}}^2),$$

$$\gamma \propto -\mu_{\text{ge}}^4/E_{\text{ge}}^3 + \mu_{\text{ge}}^2\mu_{\text{ce}}^2/E_{\text{ge}}^2E_{\text{ge}'} + \mu_{\text{ge}}^2(\mu_{\text{ce}} - \mu_{\text{gg}})^2/E_{\text{ge}}^3,$$

where μ_{gg} is the ground state dipole moment, μ_{ce} is the excited state dipole moment, $\mu_{\text{ce}'}$ and μ_{ge} are transition dipole moments, and E_{ge} and $E_{\text{ge}'}$ are optical absorption energies. The former expression suggests that an intense (large μ_{ge}) charge-transfer (large $\mu_{\text{ce}} - \mu_{\text{gg}}$) transition at long wavelength (low E_{ge}) will correspond to a significant β coefficient. Not surprisingly, organic molecules containing conjugated π systems with unsymmetrical charge distribution (e.g., donor–acceptor substituted azo dyes, Schiff bases, and stilbenes) had been shown to exhibit large second-order NLO properties. Nonlinearities can be enhanced by either increasing the conjugation length (improving delocalization) or increasing the strength of donor and/or acceptor groups (improving electron asymmetry). The data for our ruthenium and nickel complexes are resonance enhanced by proximity of the optical absorption maxima to the second-harmonic frequency of the laser radiation, but our gold complexes all possess optical transitions in the UV and are optically transparent at the second-harmonic frequency, important because it permits a realistic evaluation of intrinsic off-resonance hyperpolarizabilities, and thereby reliable development of structure–NLO property relationships. The efficiency sequence for alkynyl ligand bridge variation $\text{C}_6\text{H}_4 < \text{C}_6\text{H}_4\text{C}_6\text{H}_4 < \text{C}_6\text{H}_4\text{C}\equiv\text{CC}_6\text{H}_4 < E\text{-C}_6\text{H}_4\text{CH}=\text{CHC}_6\text{H}_4$ can be rationalized from π -bridge lengthening, torsion effects at the phenyl–phenyl linkage (of the biphenyl compound), and orbital energy mismatch of p orbitals of sp-hybridized acetylenic carbons with orbitals of sp² hybridized phenyl carbons (for the diphenylacetylene compound) [27]. Bridge stereochemistry affects quadratic nonlinearities as $\beta(Z \text{ isomer}) < \beta(E \text{ isomer})$, which can be explained from a combination of greater dipole moment and more intense optical transition for the latter [27]. This series of data also gave us the opportunity to compare the efficiency of the varying ligated metal centres. The nonlinearity increases upon increasing valence electron count (14 valence electron (triphenylphosphine)gold alkynyl compounds < 18 valence electron (cyclopentadienyl)(triphenylphosphine)nickel and (cyclopentadienyl)bis(triphenylphosphine)ruthenium alkynyl compounds) and increasing ease of oxidation (less easily oxidizable (cyclopentadienyl)(triphenylphosphine)nickel alkynyl complexes < more easily oxidizable (cyclopentadienyl)bis(triphenylphosphine)ruthenium alkynyl complexes).

Ian Whittall's suite of complexes was expanded by Raina Naulty, Andrew McDonagh, and Stephanie

Hurst, which permitted further structure–NLO activity relationships to be developed. We prepared azo-linked analogues of the ene- and imino-linked examples above, finding that $[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-(E)-N}=\text{NC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)]$ was our most efficient gold complex ($\lambda_{\text{max}} = 398 \text{ nm}$, $\beta_{1.064} = 180 \times 10^{-30} \text{ esu}$, $\beta_0 = 68 \times 10^{-30} \text{ esu}$) [32]; the efficiency of this ligand had been predicted (before its synthesis) in our earlier semi-empirical ZINDO studies [30]. The ease of electron delocalization in these alkynyl ligands should be enhanced upon replacing phenyl rings with heterocycles (because the latter have lower aromatic stabilization energy, and therefore pay a lower energetic price on proceeding to the non-aromatic charge-separated excited state), so intuitively one expects nonlinearities to increase with this structural modification; however, studies with the pyridylalkynyl complexes revealed that nonlinearities do not consistently increase on replacing phenyl by pyridyl [33,34]. We also prepared complexes with indoanilinoalkynyl ligands, such as $[\text{Ru}\{\text{C}\equiv\text{CC}_6\text{H}_4\text{N}=\text{CCH}=\text{CBu}^t\text{C}(\text{O})\text{C}(\text{Bu}^t)=\text{CH}\}(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$, because in the charge-transfer excited state the ring closer to the metal center becomes quinoidal, but the ring remote from the metal center becomes aromatic (Fig. 4), eliminating loss of aromatic stabilization energy and thereby potentially enhancing nonlinearities; this idea had been exploited with organic compounds by Marder et al. [35,36]. While the quadratic nonlinearity for this complex is large ($\lambda_{\text{max}} = 645 \text{ nm}$, $\beta_{1.064} = 417 \times 10^{-30} \text{ esu}$, $\beta_0 = 124 \times 10^{-30} \text{ esu}$) [37], it is not as large as the similarly sized two-ring azo- ($\lambda_{\text{max}} = 565 \text{ nm}$, $\beta_{1.064} = 1627 \times 10^{-30} \text{ esu}$, $\beta_0 = 149 \times 10^{-30} \text{ esu}$) or ene-linked complexes above [32]. We prepared complexes allowing us to confirm the expected dependence of nonlinearity on acceptor strength, finding that quadratic nonlinearities increase on phenylalkynyl ligand acceptor modification as $\beta(\text{H}) < \beta(\text{CHO}) < \beta(\text{NO}_2)$, and confirming that the acceptor group is more efficient when conjugated with the metal alkynyl group, nonlinearities increasing for phenylalkynyl substitution site $\beta(3\text{-CHO}) < \beta(4\text{-CHO})$ [38]. We also prepared complexes permitting assessment of the effect of bridge lengthening, noting an increase in β and β_0 values for *trans*- $[\text{Ru}(\text{C}\equiv\text{C}(\text{C}_6\text{H}_4\text{-4-C}\equiv\text{C})_n\text{C}_6\text{H}_4\text{-4-NO}_2)\text{Cl}(\text{dppm})_2]$ on increasing n from 0 to 2, although the β value for $n=0$ and 1 are the same within the error margins (Table 2).

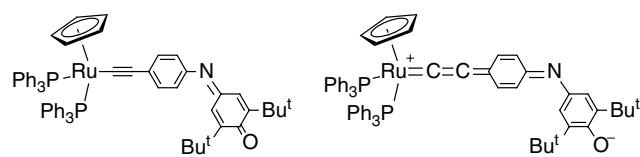


Fig. 4. Ground state (left) and charge-transfer excited state (right) representations of an indoanilinoalkynylruthenium complex.

Table 2
Molecular quadratic NLO measurements for selected ruthenium alkynyl complexes^a

Complex	λ_{\max} (nm)	β^b (10^{-30} esu)	β_0^b (10^{-30} esu)
<i>trans</i> -[Ru(C≡CC ₆ H ₄ -4-NO ₂)Cl(dppm) ₂]	473	767	129
<i>trans</i> -[Ru(C≡CC ₆ H ₄ -4-C≡CC ₆ H ₄ -4-NO ₂)Cl(dppm) ₂]	464	833	161
<i>trans</i> -[Ru(C≡CC ₆ H ₄ -4-C≡CC ₆ H ₄ -4-C≡CC ₆ H ₄ -4-NO ₂)Cl(dppm) ₂]	439	1379	365

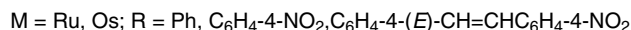
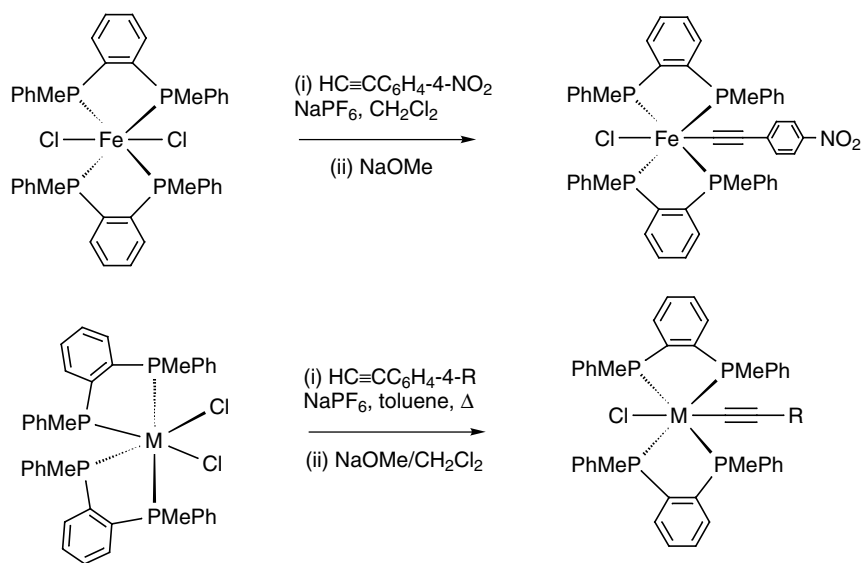
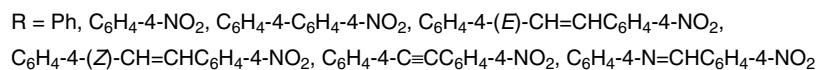
^a Ref. [39].

^b Solutions in thf, HRS measurements at 1.064 μm .

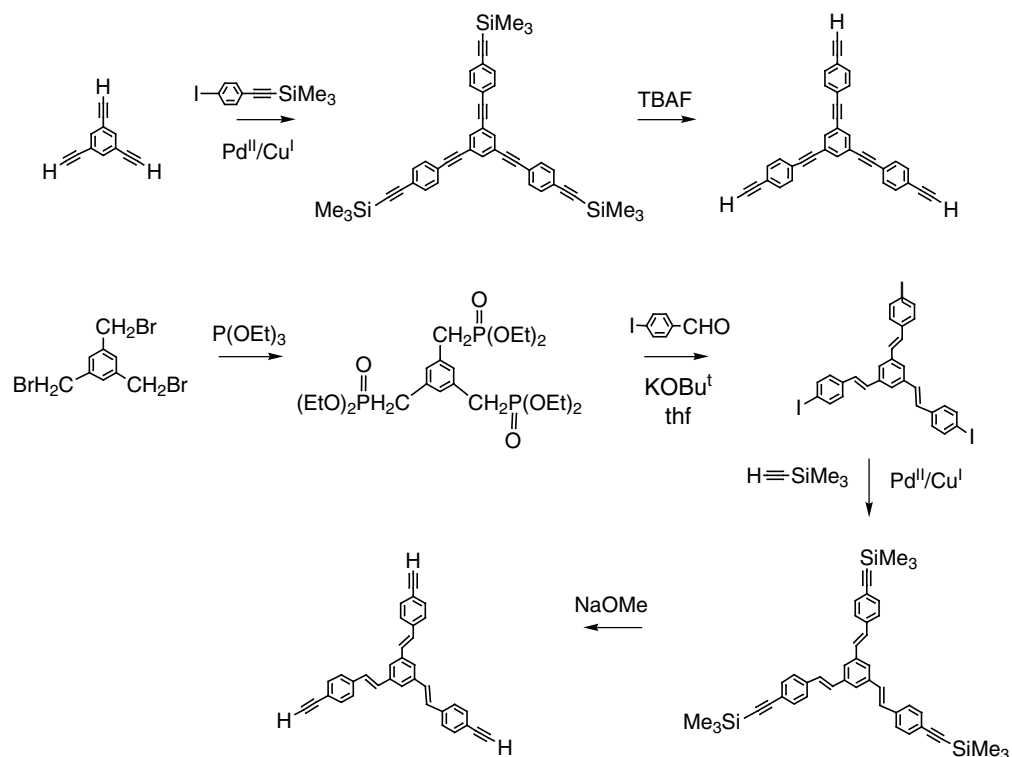
One advantage of organometallic complexes over organic compounds is the possibility of tuning NLO response by co-ligand modification. We prepared [Ru(C≡CC₆H₄-4-NO₂)(PR₃)₂(η^5 -C₅H₅)] (R = Ph, Me), finding that the quadratic nonlinearity for the triphenylphosphine complex is greater than that of the trimethylphosphine complex, suggesting that the greater delocalization possibilities of the former ligand are more important for quadratic NLO merit than the greater basicity of the latter ligand [28,30]. We also synthesized [M(C≡CC₆H₄-4-NO₂)(L₂)(η -C₅H₅)] (L₂ = 2CO, dppe), finding that replacing two CO ligands by dppe results in the expected significant increase in nonlinearity [40], while subtle variations in similar compounds (replacing

dppe by dpmm or two PPh₃ ligands) had no effect within the error margins. The series [M(C≡CC₆H₄-4-NO₂)(dppe)(η -C₅H₅)] (M = Fe, Ru, Os) was also prepared, and we found that β (iron complex) \leq β (ruthenium complex) \leq β (osmium complex) [40], although a collaboration with Maria-Helena Garcia et al. [41] suggested that β (iron complex) $>$ β (ruthenium complex) for similar complexes.

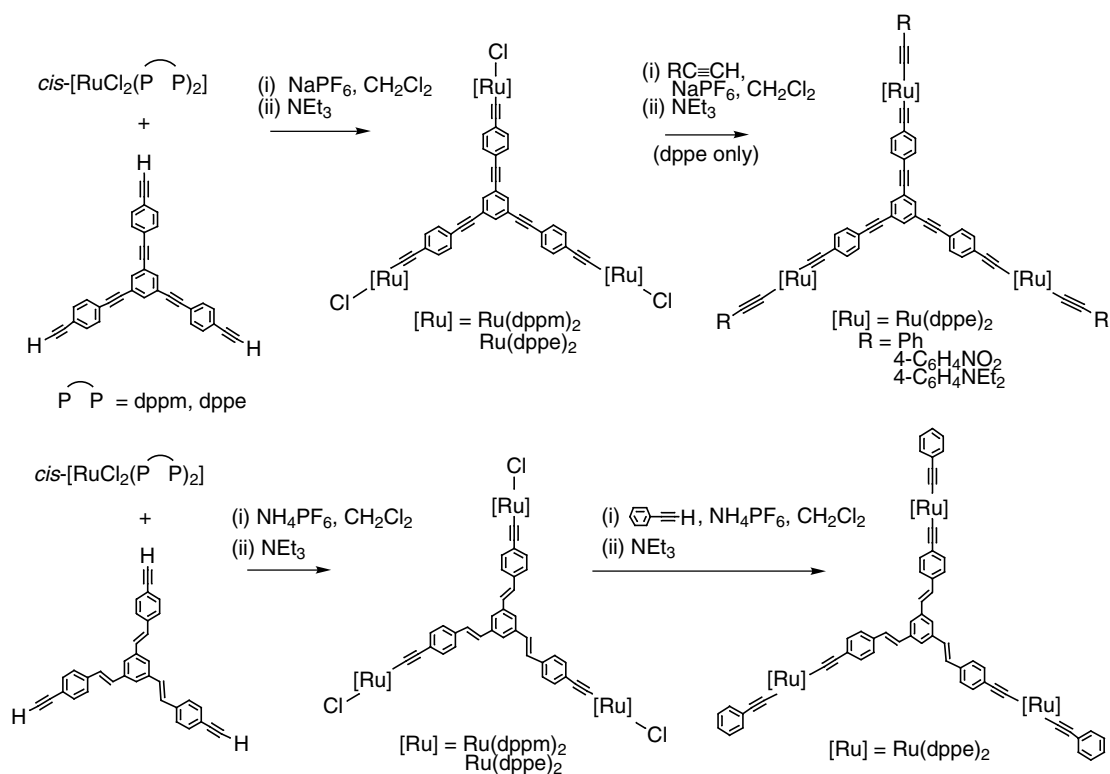
The results summarized above in most instances mirrored observations with dipolar organic compounds – crucially, NLO chromophore improvements are correlated with a red-shift in the important linear optical absorption band, which reduces optical transparency. Joseph Zyss had noted that octupolar organic molecules



Scheme 2. Synthesis of chiral phosphine-containing alkynyl iron, ruthenium, osmium and gold complexes.



Scheme 3. Synthesis of octupolar arylalkynes.

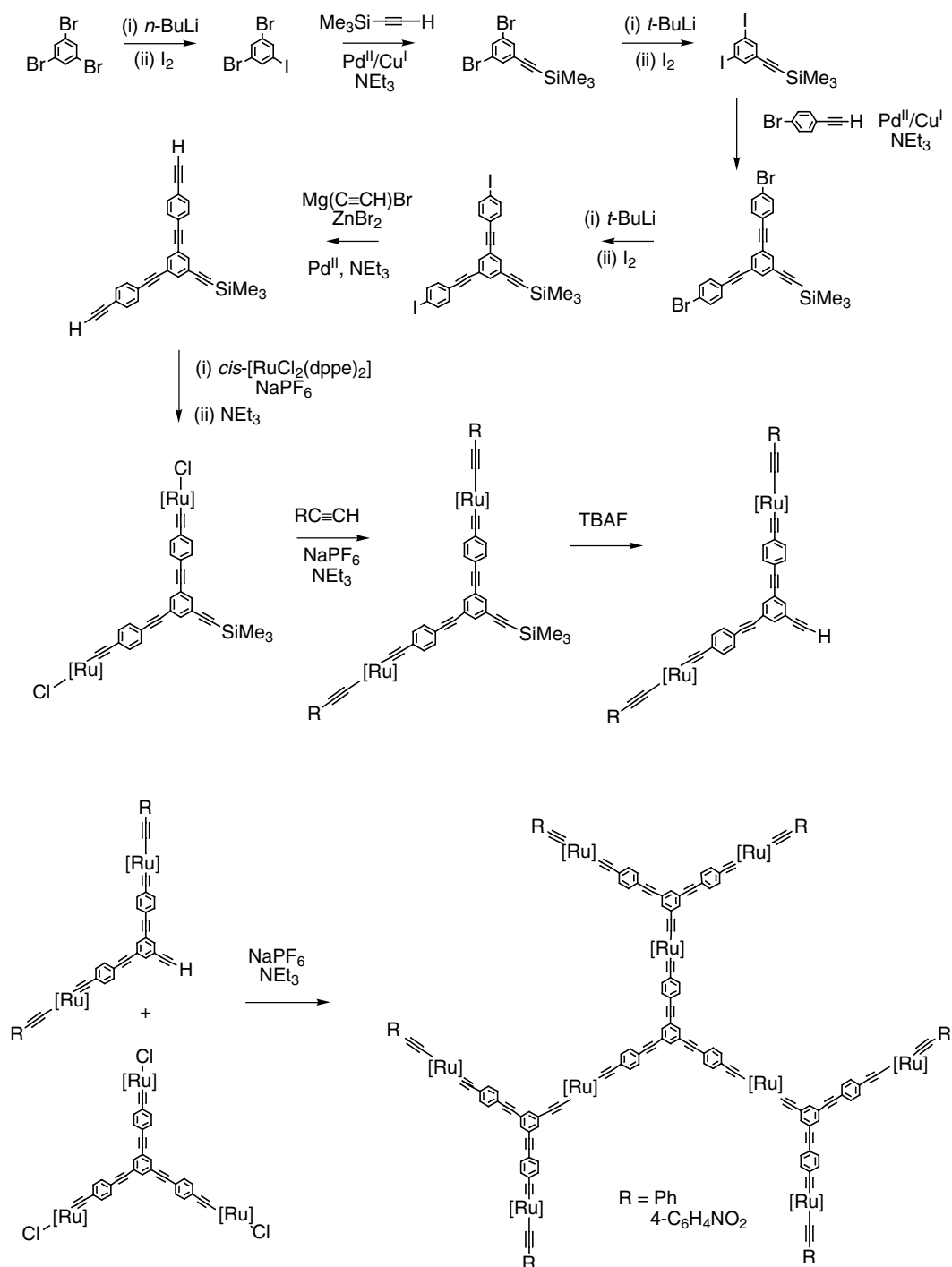


Scheme 4. Synthesis of octupolar alkynylruthenium complexes.

had the potential to overcome this NLO efficiency/optical transparency trade off – the lack of a molecular dipole in such compounds also improves the prospects of noncentrosymmetric crystal packing, required to manifest bulk susceptibility [42]. Following this lead, we prepared several octupolar alkynyl complexes (Scheme 3); their quadratic nonlinearities are modest [43–45], but none of our complexes thus far incorporate

acceptor groups at the core, introduction of which is expected to enhance nonlinearity significantly.

The discussion thus far is somewhat removed from its historical context, in that second-order bulk susceptibilities $\chi^{(2)}$ of organometallics assessed by the Kurtz and Perry [46] powder technique were the subject of most early reports of organometallics for nonlinear optics (because of the ease of this experimental technique). In



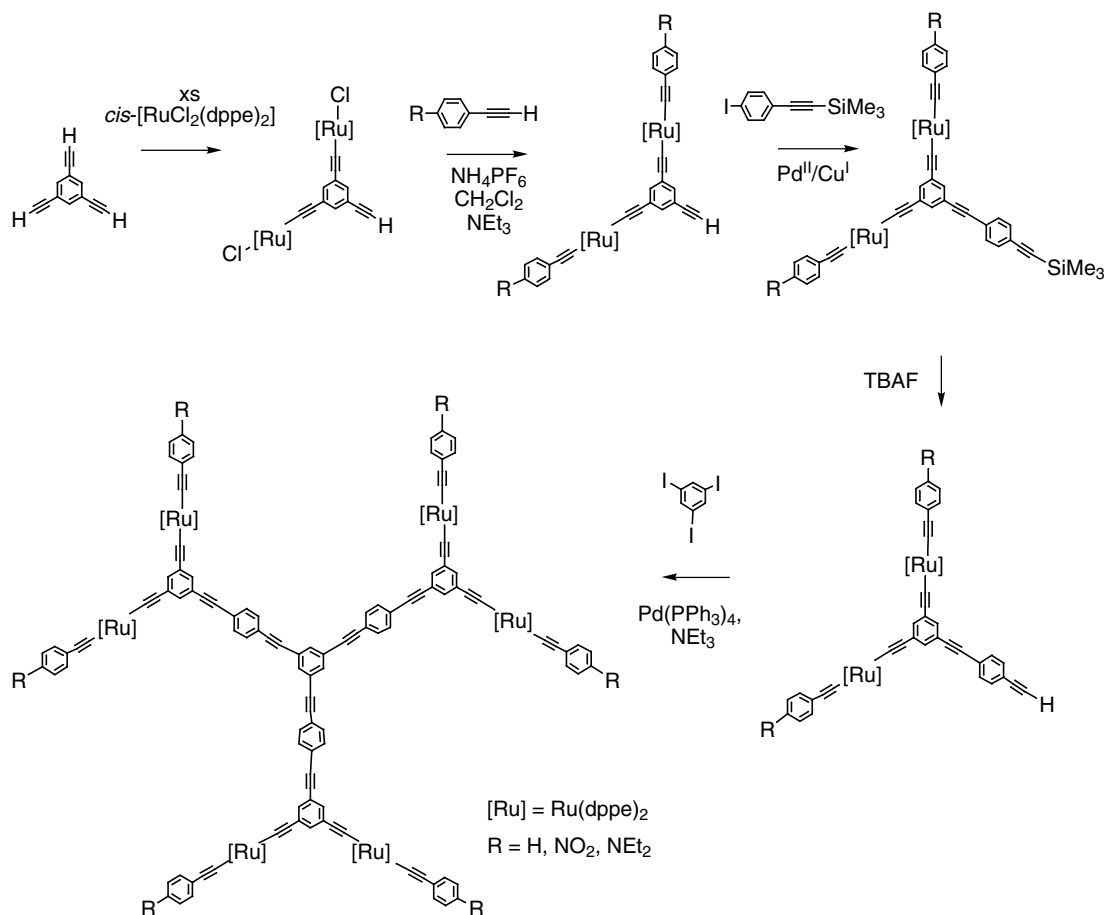
Scheme 5. Synthesis of dendritic alkynylruthenium complexes.

collaboration with Marek Samoc at the ANU, we measured $\chi^{(2)}$ values for several alkynyl complexes by the Kurtz method. Strategies to engineer sizable $\chi^{(2)}$ values had already been reported, procedures for organizing favourable lattice alignment including formation of guest–host inclusion complexes and incorporation of chiral ligands. Ian Whittall [47] and Andrew McDonagh [48] pursued the latter approach, preparing alkynyl complexes with chiral phosphine or diphosphine ligands (Scheme 2) – the bulk susceptibilities for these complexes are modest ($\leq 2 \times$ urea) in comparison with literature-extant data for ferrocenyl complexes, despite the fact that molecular quadratic nonlinearities for the most efficient alkynyl complexes are significantly larger than those for the most efficient ferrocenyl complexes (e.g., *trans*-[Ru(C≡CC₆H₄-4-(*E*)-CH=CHC₆H₄-4-NO₂)Cl-(*R,R*-diph)₂], diph = 1,2-bis(methylphenylphosphino) benzene, $\lambda_{\text{max}} = 481$ nm, $\beta_{1.064} = 2795 \times 10^{-30}$ esu, $\beta_0 = 406 \times 10^{-30}$ esu). The iron-containing complex has the largest Kurtz powder SHG efficiency across the series *trans*-[M(C≡CC₆H₄-4-NO₂)Cl{(*R,R*)-diph}₂] (M = Fe, Ru, Os), but its molecular nonlinearity is the lowest of the three complexes [48], emphasizing that the usefulness of the Kurtz technique is to rapidly identify SHG activ-

ity; molecular structure–NLO property correlations are not justified because of the aforementioned dependence of $\chi^{(2)}$ on molecular orientation in the crystal lattice. The most SHG-efficient alkynyl complex that we identified, [Ni(C≡C-2-C₅H₃N-5-NO₂)(PPh₃)(η^5 -C₅H₅)], was shown to pack in a non-centrosymmetric crystal lattice, as expected, in a complementary X-ray diffraction study [33], but more importantly the alkynyl complex chromophores were shown to not align in the most favorable arrangement. Crystal engineering to convert large molecular nonlinearities into significant bulk nonlinearities remains a major challenge.

3. Structure–cubic NLO studies

Cubic nonlinearities for our complexes have been measured at the ANU by Marek Samoc and Barry Luther-Davies, as part of a fruitful ongoing collaboration. Most of our early third-order NLO studies were carried out by the *Z*-scan technique [49] using a Ti–sapphire laser producing 100 fs pulses at 800 nm. *Z*-scan is advantageous in that it rapidly affords both the real (refractive) and imaginary (absorptive) components of



Scheme 6. Rapid synthesis of alkynylruthenium dendrimers based on steric control.

the cubic nonlinearity, but its disadvantage is that it reveals nothing about the temporal nature of the NLO response. To remedy this deficiency, one complex, namely $[\text{Ru}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-NO}_2)(\text{PPh}_3)_2(\eta^5\text{-C}_5\text{H}_5)]$, was examined by both Z-scan and degenerate four-wave mixing (DFWM). Although DFWM is experimentally more complex, it does reveal information about the time domain of the NLO response. The DFWM study revealed an equivalent γ value to the Z-scan-derived response (within the error margins), confirming an electronic origin for cubic NLO response in these molecules [50].

While less is known of molecular structure–NLO activity relationships for third-order properties than for second-order properties, it has been established with organic compounds that increase in π -delocalization possibilities (e.g., progressing from small molecules to π -conjugated polymers), the introduction of strong donor and acceptor functional groups, controlling chain orientation, packing density, and conformation, and increasing dimensionality can all result in increased cubic nonlinearity. Where applicable, similar trends are seen with our metal alkynyl complexes, although in many instances error margins are large. Negative real components of the nonlinearities (γ_{real}) were observed for many of our ruthenium [50] and nickel alkynyl complexes [31], and significant imaginary components (γ_{imag}) were seen for almost all of these complexes, consistent with two-photon effects contributing to the observed molecular nonlinearities; these two-photon states become important for an 800 nm irradiating wavelength when complexes contain $\lambda_{\text{max}} > 400$ nm [31]. The γ_{real} values for the nickel complexes are the same (within the error margins) as those of their ruthenium analogues, ease of oxidation and greater delocalization possibilities with the additional triphenylphosphine ligand making no significant difference to cubic NLO merit (in contrast to the situation with quadratic optical nonlinearities). Cubic nonlinearities for many of our 14 electron gold complexes are larger than those of their 18 electron ruthenium analogues, the opposite trend to that observed with β [51]. Replacing PMe_3 by PPh_3 and extending the π -system of the alkynyl ligand both increase π -delocalization possibilities and both resulted in an increase in $|\gamma|$ values. Introduction of polarizing nitro substituent had a similar effect.

The most important determinant of cubic NLO merit with organic molecules is the size of the π -system. To construct appropriate molecules to test these ideas, we desired access to bis-alkynyl complexes. At the time, Pierre Dixneuf had recently reported the facile stepwise synthesis of mono- and bis-alkynyl bis(bidentate diphosphine)ruthenium complexes for small alkynyl ligands [52], and Andrew McDonagh, Stephanie Hurst, and Joseph Morrall extended this methodology to the synthesis of alkynylruthenium dendrimers (Schemes 3–5) [43–45,53,54].

Table 3
Molecular cubic NLO measurements of selected alkynylruthenium complexes (Z-scan, 0.80 μm)

Complex	λ_{max} (nm)	γ_{real} (10^{-36} esu)	γ_{imag} (10^{-36} esu)	γ (10^{-36} esu)	Solvent	Reference
$1,3,5\text{-}\{\text{trans-}[\text{RuCl}(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{C})]\}_3\text{C}_6\text{H}_3$	414	-330 ± 100	2200 ± 500	2200 ± 600	thf	[43]
$1,3,5\text{-}\{\text{trans-}[\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})_2(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{C})]\}_3\text{C}_6\text{H}_3$	411	-600 ± 200	2900 ± 500	3000 ± 600	thf	[43]
$1,3,5\text{-C}_6\text{H}_3\text{-}\{\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{C-trans-}[\text{Ru}(\text{dppe})_2]\text{C}\equiv\text{C-3,5-C}_6\text{H}_3\text{-}\{\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{C-trans-}[\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})_2]\}_3$	402	-5050 ± 500	$20,100 \pm 2000$	$20,700 \pm 2000$	thf	[53]
$\text{trans-}[\text{Ru}(\text{C}\equiv\text{CPh})(\text{C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{CPh})(\text{dppe})_2]$	383	-670 ± 300	1300 ± 300	1500 ± 500	CH_2Cl_2	[43]
$\text{trans-}[\text{Ru}\{\text{C}\equiv\text{CPh}\}_2(\text{dppe})_2]$	319	-170 ± 40	71 ± 20	200 ± 50	CH_2Cl_2	[43]
$\text{trans-}[\text{Ru}\{\text{C}\equiv\text{CC}_6\text{H}_4\text{-}(E)\text{-4-CH=CHPh}\}_2(\text{dppe})_2]$	397	-600 ± 400	700 ± 400	920 ± 600	thf	[44,45]
$\text{trans-}[\text{Ru}\{\text{C}\equiv\text{CC}_6\text{H}_4\text{-}(E)\text{-4-CH=CHPh}\}_2(\text{dppe})_2]$	404	300 ± 400	300 ± 100	420 ± 350	thf	[44,45]
$1,3,5\text{-}\{\text{trans-}[\text{RuCl}(\text{dppe})_2]\}_4\text{-C}\equiv\text{CC}_6\text{H}_4\text{-}(E)\text{-4-CH=CH}\}_3\text{C}_6\text{H}_3$	415	-640 ± 500	2000 ± 500	2100 ± 600	thf	[44,45]
$1,3,5\text{-}\{\text{trans-}[\text{RuCl}(\text{dppe})_2]\}_3\text{C}\equiv\text{CC}_6\text{H}_4\text{-}(E)\text{-4-CH=CH}\}_3\text{C}_6\text{H}_3$	426	-4600 ± 2000	4200 ± 800	6200 ± 2000	thf	[44,45]
$1,3,5\text{-}\{\text{trans-}[\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})_2]\}_3\text{C}\equiv\text{CC}_6\text{H}_4\text{-}(E)\text{-4-CH=CH}\}_3\text{C}_6\text{H}_3$	421	$-11,200 \pm 3000$	8600 ± 2000	$14,000 \pm 4000$	thf	[44,45]
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-}(E)\text{-CH=CHC}_6\text{H}_4\text{-4-C}\equiv\text{CRuCl}(\text{dppe})_2)_2]$	396	-3000 ± 1200	2300 ± 800	3800 ± 1400	thf	[57]
$[\text{Fe}(\eta^5\text{-C}_5\text{H}_4\text{-}(E)\text{-CH=CHC}_6\text{H}_4\text{-4-C}\equiv\text{CRuCl}(\text{dppe})_2)_2]$	388	-7100 ± 3000	$10,600 \pm 2000$	$13,000 \pm 3000$	thf	[57]
$\text{trans,trans-}[\text{RuCl}(\text{dppe})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{C})\text{RuCl}(\text{dppe})_2]$	354	-3200 ± 500	1400 ± 300	3500 ± 600	thf	[58]
$\text{trans,trans-}[\text{RuCl}(\text{dppe})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{C})\text{RuCl}(\text{dppe})_2]$	360	-1100 ± 300	300 ± 60	1100 ± 300	thf	[58]
$\text{trans,trans-}[\text{Ru}(\text{C}\equiv\text{CPh})(\text{dppe})_2(\mu\text{-C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{CC}_6\text{H}_4\text{-4-C}\equiv\text{C})\text{-Ru}(\text{C}\equiv\text{CPh})(\text{dppe})_2]$	438	-4000 ± 1500	$12,000 \pm 2000$	$13,000 \pm 2400$	thf	[58]
$\text{trans-}[\text{Ru}(\text{C}\equiv\text{CPh})\text{Cl}(\text{dppe})_2]$	308	<120	0	<120	thf	[59,60]
$\text{trans-}[\text{Ru}(\text{C}\equiv\text{CPh})\text{Cl}(\text{dppe})_2]$	381	65 ± 40	520 ± 200	520 ± 200	thf	[59,60]

While all steps in these syntheses proceed in good to excellent yields, the long-winded route to the desired electron-rich π -delocalized dendrimers mitigates against detailed physical studies, so more recently Stephanie Hurst and Clem Powell have developed a new dendrimer synthesis, which employs “steric control” to rapidly afford the necessary dendrons (Scheme 6) [55,56].

Cubic nonlinearities for alkynylruthenium complexes increase significantly on progression from monometallic linear (“one-dimensional”) complex to bimetallic linear complex, trimetallic octupolar (“two-dimensional”) complex [43,44], and nonmetallic dendritic complex [53], without significant loss of optical transparency (Table 3). Two-photon absorption (TPA) is a third-order NLO property that is of interest for applications in multiphoton microscopy, optical limiting, and optical data storage, and for which structure–activity trends are identical with those for γ_{imag} . For these complexes, TPA increases substantially on progression to larger π -delocalizable compounds, TPA cross-sections for the dendritic examples being of the same order of magnitude as the best organic compounds.

A shortcoming of the results summarized above, and almost all other published data for organometallics, is that data were obtained at one wavelength only. To facilitate comparison, it is clearly desirable to know the

wavelength dependence of the γ_{real} and γ_{imag} coefficients for complexes. We have recently commenced wavelength-dependence studies, with initial focus on a peripherally nitro-substituted dendrimer prepared by Clem Powell and Simone Ward. Marek Samoc and Joseph Morrall employed the Z-scan technique with a recently acquired tunable laser system to afford the data summarized in Fig. 5, which we have modelled using simple dispersion formulae [56].

4. Switching nonlinearities

The possibility of reversibly modulating (“switching”) nonlinearities has recently come to the fore [61] – this is an area of research in which alkynyl complexes have considerable potential. A variety of approaches to achieve switching have been suggested, with photoisomerization, protonation/deprotonation, and oxidation/reduction the most likely candidates for modifying NLO properties. Recently, Ben Coe and André Persoons have drawn attention to the potential of inorganic complexes, demonstrating a chemical oxidation/reduction approach to quadratic NLO switching [62].

We have employed both protonation/deprotonation and redox procedures to effect NLO switching. A series

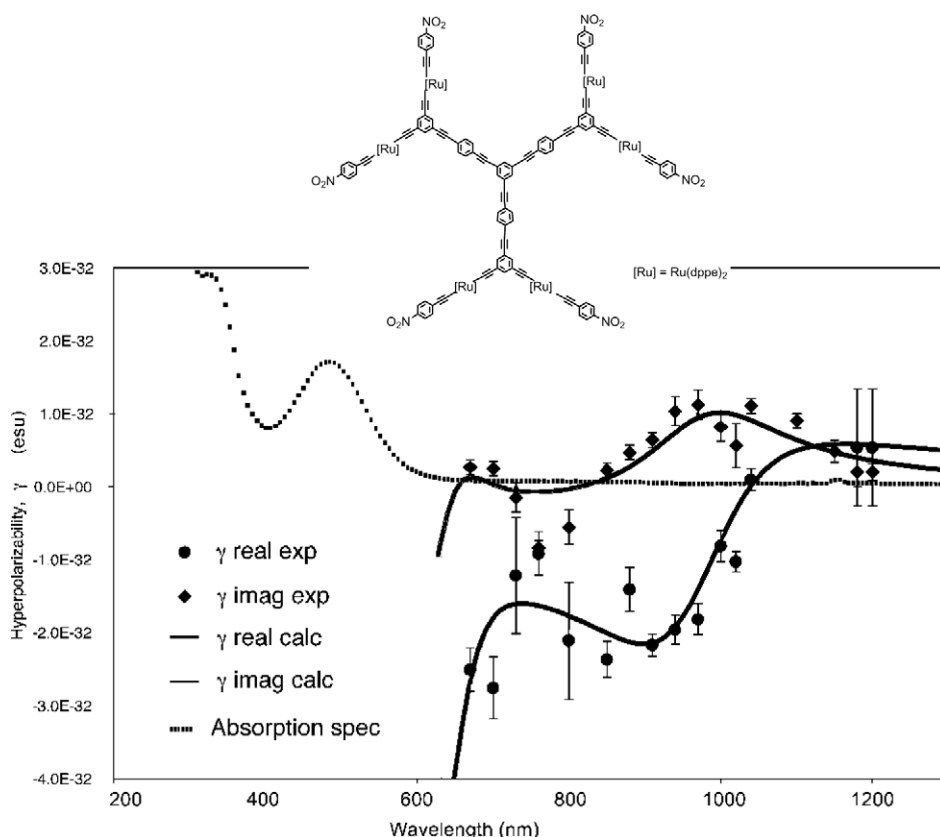


Fig. 5. Wavelength dependence of the cubic nonlinearity of an alkynylruthenium dendrimer.

of alkynyl/vinylidene complex pairs prepared by Stephanie Hurst and Joseph Morrall was used to demonstrate that quadratic NLO switching via protonation/deprotonation sequences can be effective [39], but the chemical manipulations involved in interconverting these pairs of complexes may render this of academic interest only; nevertheless, a fivefold increase in β and β_0 values is observed on deprotonating the vinylidene complex *trans*-[Ru(C=CHC₆H₄-4-(*E*)-CH=CHC₆H₄-4-NO₂)Cl(dppe)₂]PF₆ to afford the alkynyl complex *trans*-[Ru(C≡CC₆H₄-4-(*E*)-CH=CHC₆H₄-4-NO₂)Cl(dppe)₂] (Fig. 6). Chemical oxidation and reduction sequences have been assayed on iron alkynyl complexes by Claude Lapinte and Isabelle Ledoux – once again, such chemical manipulations mitigate against possible device applications. In their studies, more than two NLO “states” in a system could be accessed; they found that oxidation of [1,3,5-C₆H₃{(C≡C)Fe(dppe)(η⁵-C₅Me₅)₃} affords, in a stepwise fashion, Fe^{II}Fe^{II}Fe^{II}, Fe^{II}Fe^{II}Fe^{III}, Fe^{II}Fe^{III}Fe^{III}, and finally Fe^{III}Fe^{III}Fe^{III} complexes, with a threefold difference in β value the largest variation across these states [63].

Low nonlinearities and significant error margins frustrated most of our attempts to demonstrate cubic NLO

switching with vinylidene/alkynyl complex pairs – perhaps the most clear-cut example afforded a fivefold increase in γ value on proceeding from *trans*-[Ru(C=CHC₆H₄-4-NO₂)Cl(dppe)₂]PF₆ to *trans*-[Ru(C≡CC₆H₄-4-NO₂)Cl(dppe)₂] [23,39]. We had greater success with redox processes, and were able to demonstrate facile switching using an optically transparent thin-layer electrochemical cell [59,60], a procedure that avoids the chemical transformations remote from the optical bench employed in the studies summarized above. The three complexes that were the focus of our initial studies (*trans*-[Ru(C≡CPh)Cl(dppe)₂], *trans*-[Ru(C≡CC₆H₄-4-C≡CPh)Cl(dppe)₂], and [1,3,5-*trans*-[RuCl(dppe)₂-(C≡CC₆H₄-4-C≡C)]₃(C₆H₃)] are all transparent at wavelengths greater than 500 nm. However, following oxidation the resultant cationic complexes have (in all three cases) strong absorption bands at long wavelength which have appreciable intensity at the fundamental wavelength of a Ti-sapphire laser (800 nm). DFT calculations by Clem Powell [60] assigned these low-energy bands to chloro-to-metal charge-transfer transitions. Marek Samoc and Joseph Morrall found that the cubic nonlinearity of *trans*-[Ru(C≡CPh)Cl(dppe)₂] was too low to measure at 800 nm, and both

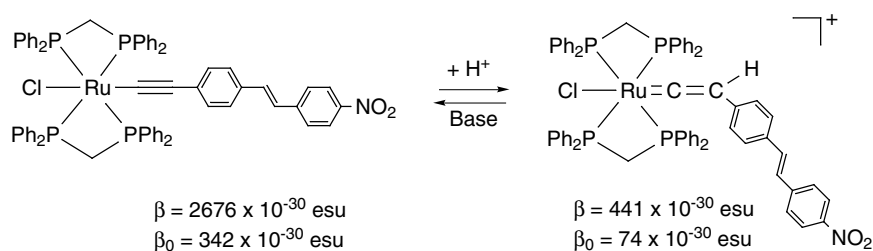


Fig. 6. Example of switching quadratic NLO response by a protonation/deprotonation sequence.

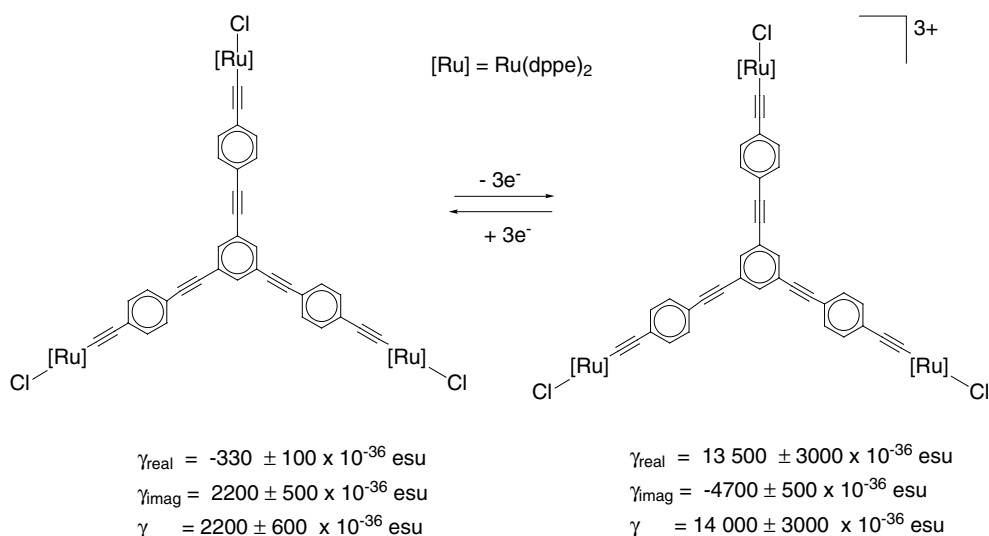


Fig. 7. Example of switching cubic NLO response by an oxidation/reduction sequence.

trans-[Ru(C≡CC₆H₄-4-C≡CPh)Cl(dppe)₂] and [1,3,5-*trans*-[RuCl(dppe)₂(C≡CC₆H₄-4-C≡C)]₃(C₆H₃)] are significant two-photon absorbers at this wavelength, but the strong one-photon absorption conditions in the oxidized form result in all three complex cations being saturable absorbers. The first-named complex therefore has third-order nonlinearity “switched on” upon oxidation, while the other two complexes have the sign and magnitude of γ_{real} and γ_{imag} changed upon oxidation (Fig. 7). This electrochemical switching in solution is diffusion controlled, the ca 5 min required for each complete oxidation or reduction process mitigating against applications. Further studies by us employing a combination of DFWM and pump–probe experiments while redox-cycling the complex [1,3,5-*trans*-[RuCl(dppe)₂(C≡CC₆H₄-4-C≡C)]₃(C₆H₃)] has revealed that picosecond timescale processes are responsible for these NLO effects [64].

5. Conclusions

Our studies of the NLO properties of alkynyl complexes have resulted in development of structure – NLO response relationships for quadratic optical nonlinearities, β values increasing with valence electron count and ease of oxidation of metal, and tunable by co-ligand modification. Alkynyl complexes can be amongst the most efficient organic or inorganic quadratic NLO molecules thus far, with β values for some small alkynyl complexes at 1.064 μm around 3000×10^{-30} esu. In contrast, low cubic nonlinearities and large error margins for many of the small alkynyl complexes have resulted in less success at developing relationships for γ . The ruthenium alkynyl dendrimers possess two-photon absorption cross-sections of the same order of magnitude as the best organic performers. Although almost all cubic NLO data thus far have been collected at one wavelength, rendering development of structure–activity relationships very difficult, progress is now starting to be made in understanding the wavelength dependence of nonlinearities by modelling the experimentally observed dependence by simplified dispersion formulae. There has also been recent progress with switching the quadratic and cubic nonlinearity of alkynyl complexes using protonation/deprotonation and, particularly, oxidation/reduction processes, and this is an area in which alkynyl complexes may well prove superior to organic molecules, and ultimately perhaps achieve a niche for organometallics in nonlinear optics.

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