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Design of ruthenium-alkynyl complexes as nonlinear optical chromophores

J-L FILLAUT

Institut des Sciences Chimiques de Rennes, UMR 6226 CNRS - Université de Rennes 1, Campus de Beaulieu, 35042 Rennes Cedex, France

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This review paper focuses on the design and non linear optical properties of *trans*-Ru(dppe)$_2$ (dppe = 1,2-bis(diphenylphosphino)ethane) alkynyl complexes and their derivatives. These systems constitute remarkable second and third-order non linear optical active chromophores. Furthermore, modifying the environment around the ruthenium affords the possibility of tuning their non linear optical performances and accessing facile non linear optical switching. The coverage is focused on quadratic (second-order) and cubic (third-order) non linear optical properties measured at molecular level from solution studies as well as on non linear optical properties of bulk materials.

Keywords: Organometallic complexes, Alkynyl-ruthenium complexes, Dendrimers, Second-order nonlinear optics, Third-order nonlinear optics

1. INTRODUCTION

Photonics, an analog to electronics, where control and utilization of photons in place of electrons allows the generation, transmission, modulation, switching of signals associated with the manipulation of light, has become a rapidly expanding area of science and technology with major technological and economic impact. Nonlinear optics is expected to play a pivotal role in this field, as nonlinear media have the ability to modify the frequency, polarization, amplitude or direction of the incident light.[1] The design of highly efficient

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*Corresponding author: jean-luc.fillaut@univ-rennes1.fr

nonlinear optical (NLO) molecules and materials suitable for information processing, optical switching, optical frequency conversion and optical limiting is thus very crucial. Intensive fundamental research over the past thirty years has positioned organic and transition metal based-NLO materials to make a technological impact in a variety of photonic applications. Further advantage of organometallics is their potential to combine the advantages of organics, such as low cost, high flexibility in terms of molecular structure, high optical damage threshold and short response time to optical excitation with the benefits that may result from incorporation of a metal center such as variable oxidation state, ligand design and coordination geometry.

This review focuses on the design of ruthenium alkynyl derivatives and on their second- and third-order NLO properties, at molecular level from solution studies, as well as on properties of bulk materials. We develop a chemist's point of view of this field: after briefly introducing the main techniques and methods used to measure second-order or third-order NLO activity of these complexes, we consider in more detail the widely investigated family of ruthenium alkynyl derivatives, of general form *trans*-RuX(C≡C-R)(dppe)$_2$, from structure-properties relationships to NLO-active molecular materials.

2. PRINCIPLE AND ORIGIN OF NONLINEAR OPTICS

Nonlinear optical effects arise from the polarization response of matter submitted to external electromagnetic fields to produce new fields altered in phase, frequency, amplitude or other propagation characteristics relative to the incident optical fields[1, 2]. When a material is subjected to very high intensity electric fields, the material can become sufficiently polarized that its polarizability can be driven beyond the linear regime: the response of medium is no longer linear.

Second-order NLO effects are essentially related with a three wave mixing process where the optical waves interact with one another through the intercession of the nonlinear medium. Second harmonic generation (SHG) can be explained as a frequency-doubling process: two waves, each of frequency ω, simultaneously superimpose constructively [$\omega + \omega = 2\omega$]. Sum frequency generation spectroscopy was rapidly applied to deduce the composition, orientation distributions, and some structural information of molecules at gas–solid, gas–liquid and liquid–solid interfaces[3].

Third order optical nonlinearity is the lowest order non-vanishing nonlinearity found in any material regardless of its spatial symmetry. Third-order nonlinear processes include a vast variety of four-wave mixing processes, which are extensively used for frequency conversion of laser radiation and as powerful methods of nonlinear spectroscopy. These nonlinear optical phenomena have attracted increasing attention from basic research to photonic applications for telecommunications (optical signal processing, transmission of optical signals), lasers (pulse compression and generation of super continuum), sensing (temperature sensors, spectroscopy, and imaging), multiphoton processes (3D- biomedical imaging and photodynamic therapy, 3D microfabrication)[4-6].

For chemists, the general approach to improve the 2nd-order NLO activity of materials is to modify their structure at the molecular level. The starting point for the development of effective 2nd-order NLO materials is the design, synthesis and characterization of highly active chromophore molecules which have a large molecular hyperpolarizability, β. At the molecular level, the molecule must possess (a) excited states close in energy to the ground state, (b) large oscillator strength for electronic transitions from ground to excited state and (c) a large difference between ground and excited state dipole moments[7]. The largest β values were obtained for push–pull dipolar π-conjugated molecules (D–π–A molecules). The magnitude of β can be correlated with the electron-donating or/and -withdrawing strength of the substituents D and A, and can be enhanced by increasing the path of conjugation between these substituents (-π-). At the macroscopic level, the material must be non-centrosymmetric by nature, SHG being an even (second) order tensorial effect (even-ordered electric dipole coefficients are zero for centrosymmetric systems, and as a result, molecular structures and materials must be non-centrosymmetric for them to exhibit second-order nonlinear optical properties) [1].

Similarly to 2nd-order NLO-phores, highly active 3rd-order NLO-chromophores need to have polarizable π-electrons and low-energy intramolecular charge transfer, but they differ in the nature of their multi-polar charge distributions. Some structure–property relationships were determined: (i) a general dependence of γ on conjugation length (polymeric structures), (ii) higher γ-values for electron-deficient unsaturated bridge and (iii) a relation between γ and the charge-transfer nature of these one-dimensional chromophores. The second type of structure concerns quadrupolar systems on the base of two acceptor or donor units linked by an unsaturated π-delocalized bridge, with possible intercalation of a electron-deficient group between two electron-rich termini (and vice versa). Here again, structure–property relationships determined for these molecules include the following: (i) the second hyperpolarizability γ increases rapidly with increased conjugation length for quasi-one-dimensional molecules, (ii) the incorporation of heteroatoms into the π-electron system can be beneficial to γ, (iii) π-electron delocalization in two dimensions enhances γ without reducing optical transparency. The third type of cubic NLO-active compounds consists in those possessing octupolar geometries (T_d, D_{3h}).

The introduction of a metal center into a conjugated organic system, where the metal may act variously as a donor or acceptor group, may introduce a range of properties (that is, redox, magnetic, optical, and electronic properties) that differ from those of conventional organic chromophores. Finally, favoring the interaction of transition metal d-orbitals with the conjugated π-orbitals of the organic moiety has been shown to enhance optical nonlinearities [8].

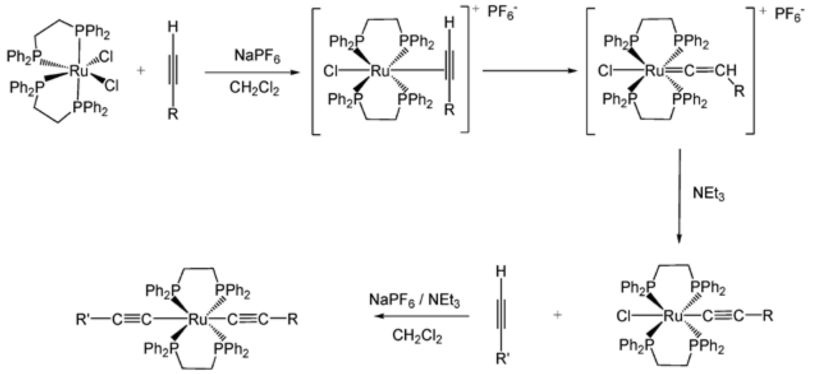
2. RUTHENIUM-ALKYNYL COMPLEXES AS NLO-PHORES

Amongst coordination and organometallic complexes with second-order or third-order NLO activity[9], ruthenium σ-alkynyl complexes constitute a remarkable family of NLO-phores. These compounds, in which the metal center is directly incorporated into the plane of the chromophore π-system, allowing the metal and carbon orbitals to overlap[10], are more NLO-active than fully organic alternatives of similar size[11]. This is related to the existence of strongly allowed metal-to-ligand charge-transfer (MLCT) transitions, which improve optical nonlinearities with respect to those of organic analogues. Furthermore, ruthenium σ-alkynyl complexes are very attractive, due to high-yield syntheses, easy construction of multimetallic dendrimers[11, 12], reversible redox properties which afford the possibility of accessing facile NLO switching[13].

2.1. Synthesis and chemistry of (bis(diphenyphosphino)ethane)-ruthenium s-alkynyl complexes

Excellent review articles[10, 14] feature the synthesis and chemistry of metal alkynyl complexes, their properties and their application in materials science and we were selective in our coverage by concentrating on the specific class of *trans*-$RuCl(C{\equiv}C\text{-}R)(dppe)_2$ monoacetylide and *trans*-$Ru(C{\equiv}C\text{-}R^1)(C{\equiv}C\text{-}R^2)(dppe)_2]$ bis-acetylide derivatives [dppe (1,2-bis(diphenyphosphino)ethane); $R^1 = R^2$ or $R^1 \neq R^2$]. dppe (1,2-bis(diphenyphosphino)ethane) is an excellent ligand to stabilize these carbon rich species, for steric and electronic reasons[15]. Comparative studies with other series of ruthenium σ-alkynyl complexes also showed that the bis-(1,2-bis(diphenyphosphino)ethane) ruthenium σ-alkynyl complexes are also very attractive for nonlinear optical properties[16].

For a long time, preparations of *trans*-$Ru(C{\equiv}CR)_2(dppe)_2$ complexes from the precursor *trans*-$RuCl_2(dppe)_2$ were restricted to transmetalation strategies using trimethyltin alkynes and CuI catalysts[10]. The main limitation of these routes is the use of sensitive reagents and low yields of desired products. Dixneuf and co-workers developed an efficient, stepwise route to mono- and unsymmetrical bis-alkynyl ruthenium compounds, provided by a vinylidene formation (Scheme 1) [17]. These authors indicated that *cis*-$[RuCl_2(dppe)_2]$ readily activates terminal alkynes, in presence of a non-coordinating salt (usually $NaPF_6$), to produce stable and isolable vinylidene complexes in excellent yields. The vinylidene species are then deprotonated by the addition



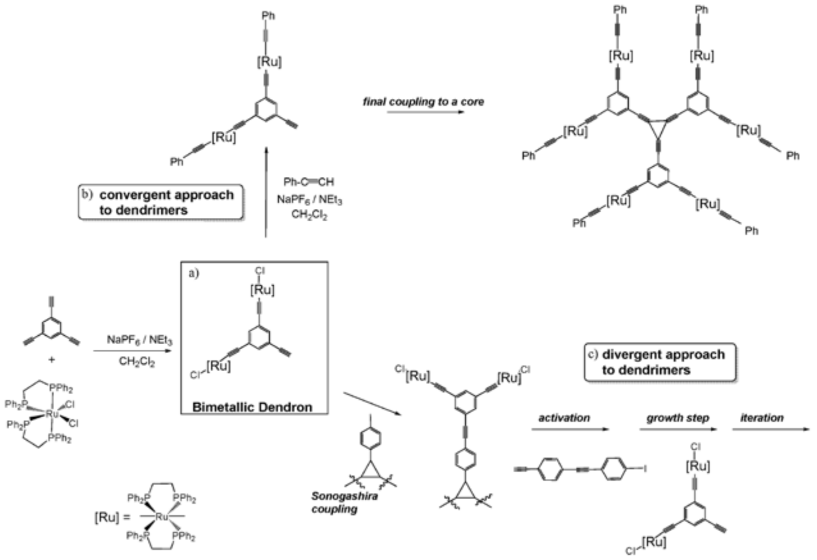
SCHEME 1
Preparation of *trans*-Ru-Cl(C≡CR)(dppe)$_2$ from *cis*-RuCl$_2$(dppe)$_2$, and a *trans*-Ru(C≡CR)(C≡CR′)(dppe)$_2$ Complex via Intermediate Vinylidene Complexes [RuCl(C=CHR)(dppe)$_2$]PF$_6$

of a soft base, usually 1 equiv NEt$_3$ or DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) in CH$_2$Cl$_2$. Both reactions are carried out at room temperature and give the *trans*-[Cl(dppe)$_2$Ru-C≡C-R] monoacetylide derivatives in good to excellent yields. The *trans*-position of the chloro and acetylide ligands is indicated by the equivalence of the phosphorus nuclei in the ^{31}P NMR spectrum as singlets near 49 ppm.

Symmetrical ($R^1 = R^2$) and unsymmetrical ($R^1 \neq R^2$) bis-alkynyl complexes *trans*- [(dppe)$_2$Ru(-C≡C-R^1)(-C≡C-R^2)] can be prepared in two steps via intermediate monoacetylide *trans*-RuCl(C≡CR^1)(dppe)$_2$ or vinylidene [RuCl(C=CHR^1)(dppe)$_2$]$^+$ complexes (Scheme 1) [15, 18-32]. The ^{31}P NMR spectra of these bis-alkynyl derivatives show resonances near 54 ppm, as singlets indicative of the *trans*-position of the acetylide ligands. These features reflect the π-donor/weak π-acceptor character of the alkynyl ligand.

Crystallographic studies indicate that the mono- and bis-alkynyl complexes adopt an approximately octahedral environment at the Ru center, with small distortions due to the constrained bite angle of the dppe ligands[10, 14, 17, 25]. The bis(alkynyl) complexes generally present a linear rod-like structure with angles along the –C≡C–Ru–C≡C– fragment close to 180°.

Humphrey and co-workers prepared ruthenium alkynyl based dendrimers up to second generation following both convergent and divergent approaches, affording access to nanometer-sized π-delocalized quadrupolar and octopolar complexes. The zero- and first-generation dendrimers that they first reported were prepared by convergent procedures using 1,3,5-triethynylbenzene as a precursor for the preparation of dendrons. Treating 1,3,5-triethynylbenzene with an excess of *cis*-RuCl$_2$(dppe)$_2$ affords a dimetallated dendron, due to the steric bulk of the dppe ligands that precludes trimetallation of the 1,3,5-triethynylbenzene unit (Scheme 2). This “steric control” methodology was exploited to rapidly afford a number of ruthenium-alkynyl dendrimers with



SCHEME 2
a) Steric Control affording the Preparation of the Dimetallated Dendron from 1,3,5-triethynylbenzene via Intermediate Vinylidene Complexes $[RuCl(C{=}CHR)(dppe)_2]PF_6$ b) Convergent route c) Divergent route

various cores and branching units[12, 29, 33-36]. Humphrey and co-workers also reported the syntheses of zero-, first-, and second-generation dendrimers by a divergent way. The second-generation, a 21-metallic system , actually the largest ruthenium alkynyl dendrimer thus far, was obtained in a procedure that exploits both the formation of unsymmetrical Ru bis-alkynyl complexes via intermediate vinylidene complexes and palladium-catalyzed Sonogashira coupling of preformed organometallic dendrons and cores[37].

2.2. Photophysical and electrochemical properties

The optical and electronic properties of the Ru^{II} mono- and bis-alkynyl complexes are mainly due to the efficient mixing of the organic alkynyl π-electron system with the central metal d-orbitals, which gives rise to highly delocalized electronic structures. A number of studies have focused on potential applications in the fields of molecular wires and junctions[19, 38-42], molecular switches[40, 43, 44], molecular magnetism and ferroelectricity[31, 45, 46], hydrogen bonded systems[26, 47], colorimetric sensors[20, 23, 48] and dye sensitizers for solar cells[49].

The electrochemical properties of Ru^{II} mono- and bis-alkynyl complexes are important indicators of the π-conjugation in the molecular backbone. A reversible oxidation process can be observed in almost every *trans*-$RuX(C{\equiv}CR)(dppe)_2$ ($X = Cl, C{\equiv}CR$) complex, that can be assigned to the $Ru^{II/III}$ couple. $E_{1/2}$ recorded for *trans*-$RuCl(C{\equiv}CR)(dppe)_2$ mono-alkynyl complexes generally

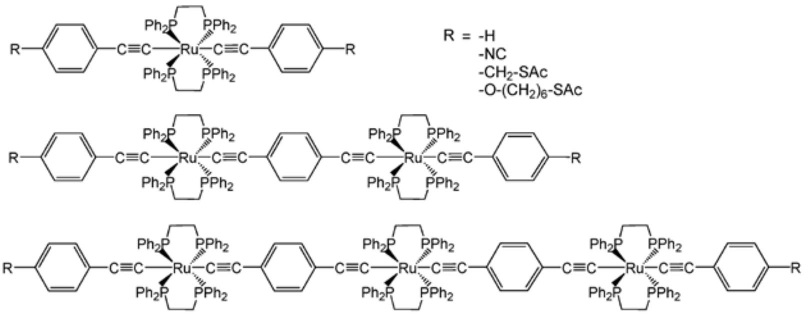


FIGURE 1
Mono- to tri-metallic s-alkynyl ruthenium redox-active conjugated molecular wires

range from 500 mV to over 700 mV, the higher potentials being characteristic of complexes with an arylalkynyl ligand containing an electron-withdrawing substituent[50]. In comparison to mono-alkynyl complexes, few variations were found in the electrochemical properties of the bis-alkynyl complexes, for which the observed values are consistent with the oxidation potential of $Ru^{II/III}$ couple [51]. As an extension of these studies, *trans*-$RuX(C{\equiv}CR)(dppe)_2$ units were incorporated as active redox parts of rigid-wire-like systems, of the general model [M]–C≡C–R–C≡C–[M], that allow direct connection of a π-conjugated bridge with these redox-active metal centers. In this context, Rigaut and co-workers demonstrated the exceptional ability of ruthenium to operate as a connector allowing electron flow to occur between different elements in extensively π-conjugated systems (Figure 1) [19, 39, 52].

These bi- and tri-metallic complexes display two and three redox processes, respectively, at low potential. The observed first and second oxidation potentials are consistent with the oxidation potential of the parent $Ru(dppe)_2(–C{\equiv}C–Ph)_2$ complex. A large separation can be observed between the first two or three processes for both compounds ($\Delta E° \approx 300$ mV, $K_c = \exp(\Delta E°F/RT) = 1.5 \times 10^5$) that is significant of the overall electronic delocalization in the system[19, 38, 41, 42, 52].

Such molecular wires with a good charge transport performance are of primary interest to the development of molecular transport junctions. Rigaut and co-workers reported the electrical transport behavior of a series of ruthenium redox-active conjugated molecular wires with anchoring moieties (Figure 1, $R \neq H$), as a function of length and temperature using conducting probe atomic force microscopy. A hopping mechanism was observed in junctions incorporating the longest systems (n = 2, 3 where n is the number of Ru atoms) while direct tunneling appeared to be the dominant transport mechanism in shortest junctions (n = 1) [41, 53].

Chemical tailoring of functional molecules with multi-addressable properties is an area of intensive research because of promising applications of multi-modulable molecular devices in the fabrication of computing nanocircuits. In this context, Rigaut and Chen designed ruthenium-alkynyl based systems functionalized with dithienylethene (DTE) units bearing fragments in which the addressable and stepwise optical and/or electrochemical control of molecular isomerization of the dithienylethene units can be repeatedly and reversibly applied to reach the controllable switching of conductivity between two distinct states. These authors have taken advantage of the accurate combination in the same molecule of the electronic and optical properties of both the DTE photochromic unit that undergoes reversible interconversion between a non-conjugated open form and a π-conjugated closed form,[54] and the *trans*-$RuX(C{\equiv}CR)(dppe)_2$ redox active units.[43] These photo-/electro-cooperative nanodevices can be applied as electronic logic gates, such as a two-input OR and a three-input AND-OR.[40, 42] This approach was also developed by Humphrey in a system that responds orthogonally to protic (alkynyl ligand $\rightleftarrows$ vinylidene ligand), electrochemical ($Ru^{II/III}$), and photochemical (DTE ring-opening $\rightleftarrows$ ring-closing) stimuli. The resulting six states are interconverted along seven pathways, all of which result in distinct changes to cubic nonlinearity[55].

2.3. NONLINEAR OPTICAL PROPERTIES

Several techniques have been used to measure the second- and third-order NLO responses of ruthenium alkynyl complexes including the Kurtz powder technique, electric field-induced second-harmonic generation (EFISH), hyper-Rayleigh scattering (HRS), degenerate four-wave mixing (DFWM), and Z-scan (For description of these experimental techniques, see ref [16]). It is important to be very cautious in comparing results obtained using these different techniques. On the other side, β-value being dependent on the incident wavelength, measurement over a range of wavelengths is necessary to ascertain the relevant β-value for a specific device operating wavelength. Finally, if high β_{HRS} values have been obtained but it is worth pointing out that the HRS measurements have been usually carried out at 1064 nm where some resonance couldn't be excluded.

2.3.1. Second-order nonlinearities

Second-order NLO studies, mainly developed by M. Humphrey et al., first focused on rigid-rod ruthenium(II) alkynyl push-pull derivatives with a range of acceptor substituents on the alkynyl ligands[16]. The 18 electron ruthenium(II) centers in these complexes being efficient donors, the nitro group has been the most widely used acceptor, resulting in large NLO coefficients (Replacement of the nitro group with other acceptors generally results in a decrease in nonlinearity) : *trans*-$[Ru(C{\equiv}CPh)Cl(dppe)_2]$ λ_{max} (nm) = 319, β (10^{-30}esu) = 6, β_0 (10^{-30}esu) = 3; *trans*-$[Ru(C{\equiv}C\text{-}C_6H_4\text{-}4\text{-}NO_2)Cl(dppe)_2]$

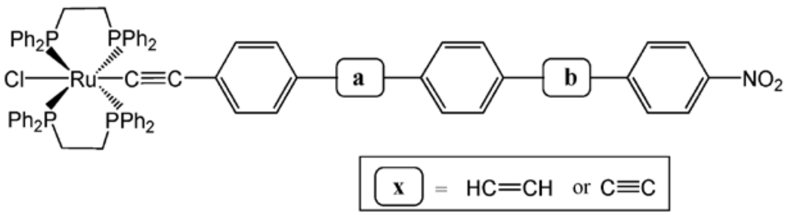


FIGURE 2
Complexes establishing the effect of replacing ethynyl linkages by alkenyl groups in positions **a** ("**a**" linkage) or **b** ("**b**" linkage)

λ_{max} (nm) = 477, β (10^{-30}esu) = 351, β_0 (10^{-30}esu) = 55 [HRS; THF; β values have uncertainty of 10% unless otherwise noted][56]. β_0 is the static quadratic hyperpolarizability that can be extrapolated using the so-called "two-level" model[57]. The smallest second-order nonlinearities are found with complexes bearing the shorter alkynyl ligands between the ruthenium centre and this 4-nitrophenyl group. Increasing the length of the alkynyl ligand by formal sequential insertion of two phenylene-ethynylene units results in an increase in both β and β_0 values (*trans*-$\mathrm{[Ru(C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}C\text{-}C_6H_4NO_2)Cl(dppe)_2]}$ λ_{max} (nm) = 468, β (10^{-30}esu) = 1240 ± 110, β_0 (10^{-30}esu) = 225 ± 20)[58].

The effect of replacing one or two ethynyl linkages by alkenyl groups in alkynyl complexes depicted in Figure 2 has been studied by Humphrey and co-workers[59]. The replacement of the yne adjacent to the metal-bound phenylethynyl unit ("**a**" linkage) by an *E*-ene linkage leads to a significant increase in the β value (*trans*-$\mathrm{[Ru(4,4',4''\text{-}C{\equiv}CC_6H_4C{\equiv}CC_6H_4C{\equiv}CC_6H_4NO_2)\ Cl(dppe)_2]}$ λ_{max} (nm) = 429, β(10^{-30}esu) = 1327 ± 110, β_0(10^{-30}esu) = 388 ± 32; trans-$\mathrm{[Ru((\mathit{E})\text{-}4,4',4''\text{-}C{\equiv}CC_6H_4CH{=}CHC_6H_4C{\equiv}CC_6H_4NO_2)Cl\ (dppe)_2]}$ λ_{max} (nm) = 459, β (10^{-30}esu) = 2800 ± 280, β_0 (10^{-30}esu) = 580. In contrast, replacement of the yne unit by an *E*-ene linking unit at the "**b**" linkage, more remote from the metal centre, results in a much less significant increase in the second-order NLO response (*trans*-$\mathrm{[Ru((\mathit{E})\text{-}4,4',4''\text{-}C{\equiv}CC_6H_4C{\equiv}CC_6H_4CH{=}CHC_6H_4NO_2)\ Cl\ (dppe)_2]}$ λ_{max} (nm) = 448, β(10^{-30} esu) = 1800 ± 180, β_0(10^{-30} esu) = 430). For complexes with two *E*-alkenyl linkages, the β values fall between the values of complexes incorporating only one *E*-alkenyl linkage (*i.e.* at one of the two possible sites).

The ability of ruthenium to operate as a connector allowing electron flow to occur between different elements in trans-ditopic architectures was assessed by De Angelis, Biagini and co-workers (Figure 3)[60]. Interestingly, the complexes **C** and **D** are characterized by the largest values of $\mu\beta_{1.907\ \mathrm{EFISH}}$ ever reported for alkynyl metal complexes. **C**: $\mu\beta_{1.907\ \mathrm{EFISH}}$ (-1550×10^{-48} esu); **D**: (-1700×10^{-48} esu). This work can be related with a previous paper from these authors[61], where a benzothiadiazole moiety acts as an acceptor flanked on either side by 2,5-thienyl units, in diruthenium σ-acetylide sys-

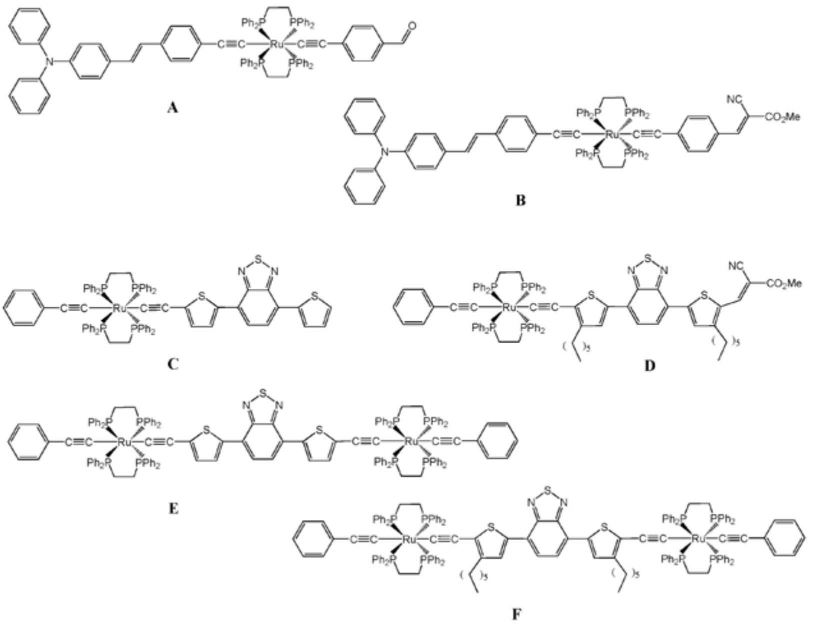


FIGURE 3
Dipolar π-delocalized Ru^{II} dialkynyl complexes investigated by the electric-field-induced second harmonic generation (EFISH) technique

tems **E**, **F**. These complexes are characterized by good to excellent $\mu\beta_{EFISH}$ values (−520/−1370 × 10^{-48} esu). These complexes were used as building blocks of active polymeric films characterized by an excellent second-order NLO response, the signal remaining even after two months. This particularly long-term high stability was attributed by these authors to the relatively large size of the NLO chromophore which would hinder its mobility[61].

Ruthenium σ-acetylide based dendrimers developed by Humphrey constitute an important class of organometallic NLO-phores[11]. Even if extending the delocalized π-system through the metal (progressing from **B** to **C**, Figure 4) does not increase β, an average 50% gain in β values is found on progressing from the three-metal-centre zero-generation dendrimers **C** and **D** to the nine-metal-centre first-generation dendrimers **E** and **F**, the β value at 1064 nm for the latter (1880 × 10^{-30} esu) being particularly large for a formally octupolar molecule. No loss in transparency is seen on progressing on dendrimer generation.

2.3.2. Third-order nonlinearities

First attempts to optimize γ and $\chi^{(3)}$ have focused on the use of one-dimensional push-pull ruthenium(II) acetylides designed for enhanced quadratic response. Even if comments on the effect of structural varia-

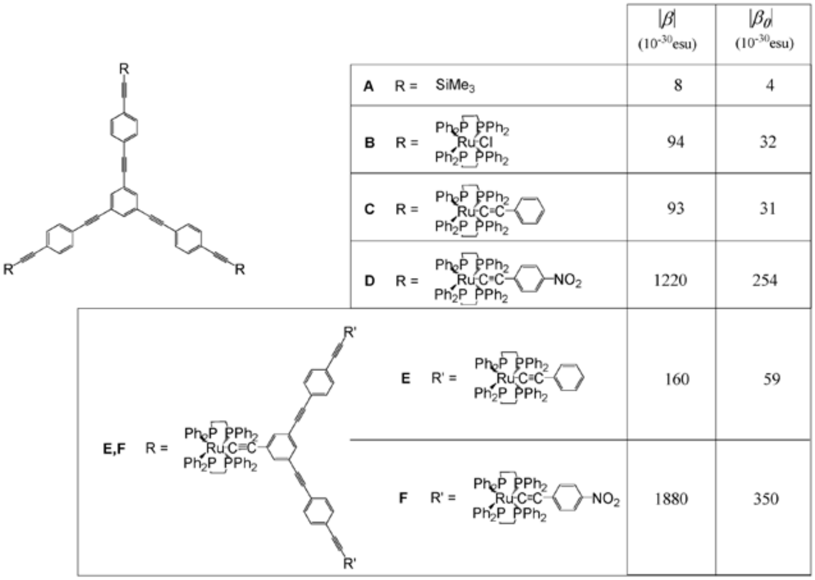


FIGURE 4
Ruthenium σ-acetylide based dendrimers as organometallic NLO-phores

tion on the magnitude of γ are cautious in light of the error margins, the well-established dependence of the NLO response as a function of the p-bridge length was verified in series of push-pull complexes by Sahraoui and Fillaut. Extending the p-system through the metal center, in proceeding from **A** to **D** (Table 1), and replacing yne- with ene- linkage, in proceeding from **D** to **E**, result in significant increases in $|\gamma|_{800}$ values. Negative real components of the nonlinearities (γ_{real}) are observed in many instances and significant imaginary components (γ_{imag}) are seen for almost all complexes, consistent with two-photon effects contributing to the observed molecular nonlinearities. The effect of the introduction of electron-acceptor end groups (CHO, NO_2) is not obvious, nonlinearities of the alkynyl complexes **B**, **C** and **F** being characterized by large error margins, rendering extraction of structure–property relationships difficult.

Degenerate four-wave mixing studies at 532 nm of the (poly)thiophene-5 bridged complexes $\mathbf{A}_{\text{a-d}}$ and $\mathbf{B}_{\text{a-d}}$ (Figure 5) by Sahraoui and Fillaut [21, 62] have confirmed the dependence of the cubic NLO response as a function of the π-bridge length, while barbiturate-terminated complexes were found to be less active, at this wavelength, than aldehyde–terminated analogues, even if the latter are less efficient electron-withdrawing groups. An electronic origin for cubic nonlinearities in these metal acetylide complexes has been demonstrated and nonlinearities for the present series of compounds are, therefore, likely to be electronic in origin.

	Complex	lmax (nm)	γ_{real} (10^{-36} esu)	γ_{imag} (10^{-36} esu)	γ (10^{-36} esu)	Technique	Solvent	Ref
A	*trans*-$[Ru(C{\equiv}CPh)Cl(dppe)_2]$	319	-170 ± 40	71 ± 20	200 ± 50	Z-scan	CH_2Cl_2	[64]
B	*trans*-$[Ru(C{\equiv}C\text{-}C_6H_4\text{-}CHO)Cl(dppe)_2]$	413	-300 ± 500	< 200	-300 ± 500	Z-scan	THF	[56]
C	*trans*-$[Ru(C{\equiv}C\text{-}C_6H_4\text{-}NO_2)Cl(dppe)_2]$	477	-320 ± 55	< 50	-320 ± 55	Z-scan	THF	[56]
D	*trans*-$[Ru(C{\equiv}CPh)(C{\equiv}C\text{-}C_6H_4\text{-}C{\equiv}CPh)(dppe)_2]$ $C{\equiv}CPh)$ $(dppe)_2]C{\equiv}CPh)(dppe)_2]$	383	-670 ± 300	1300 ± 300	1500 ± 500	Z-scan	THF	[78]
E	*trans*-$[Ru(C{\equiv}CC_6H_4\text{-}$(*E*)-$4\text{-}CH{=}CHPh)Cl(dppe)_2]$	404	300 ± 400	300 ± 100	420 ± 350	Z-scan	THF	[78]
F	*trans*-$[Ru(C{\equiv}CC_6H_4\text{-}$(*E*)-$4\text{-}CH{=}CH\text{-}C_6H_4NO_2)Cl(dppe)_2])$	489	40 ± 200	< 100	40 ± 200	Z-scan	THF	[56]
G	*trans*,*trans*-$[Ru(C{\equiv}CPh)(dppe)_2(C{\equiv}CC_6H_4\text{-}4\text{-}C{\equiv}C\text{-})]_2$	438	-4000 ±1500	12000 ±2000	13000 ± 2400	Z-scan	THF	[63]
H	1,3,5-(*trans*-$[(dppe)_2ClRu(C{\equiv}CC_6H_4\text{-}C{\equiv}C])_3C_6H_3$	414	-330 ± 100	2200 ± 500	2200 ± 600	Z-scan	THF	[78]
I	1,3,5-(*trans*-$[(dppe)_2(C{\equiv}CPh)Ru(C{\equiv}CC_6H_4\text{-}C{\equiv}C\text{-}C_6H_4\text{-}$	411	-600 ± 200	2900 ± 500	3000 ± 600	Z-scan	THF	[78]
J	1,3,5-(*trans*-$[(dppe)_2ClRu(C{\equiv}CC_6H_4\text{-}$(*E*)-4-$CH{=}CH])_3C_6H_3$	426	-4600 ± 2000	4600 ± 800	6200 ± 2000	Z-scan	THF	[79]
K	1,3,5-(*trans*-$[(dppe)_2(C{\equiv}CPh)Ru(C{\equiv}CC_6H_4\text{-}$(*E*)-4-$CH{=}CH])_3C_6H_3$	421	-11200 ±3000	8600 ±2000	14000 ± 4000	Z-scan	THF	[79]

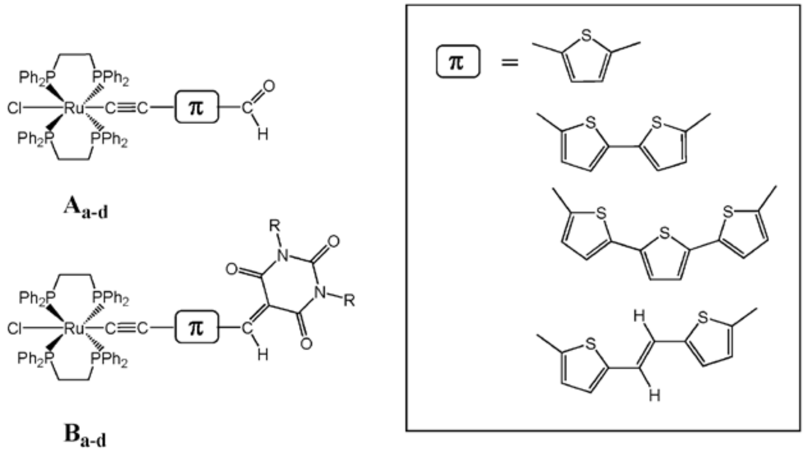


FIGURE 5
Thiophene-containing complexes $\mathbf{A}_{\text{a-d}}$ and $\mathbf{B}_{\text{a-d}}$ measured at single wavelengths by DFWM and Z-scan

The 3rd-order NLO characteristics of complexes with a D–π–D composition, determined by *Z*-scan at 800 nm, were first reported in 2002 by Samoc and Humphrey [63]. The quadrupolar D–π–D composition results in significant increases in $|\gamma|$, the presence of the second electron-rich metal center being more efficient than electron-withdrawing groups (dipolar composition) in enhancing cubic NLO merit. Complex **G** (Table 1) has a very large γ_{imag} component. Evaluating the TPA cross-section σ_2 for **G** (2910×10^{-50} cm^4 s) revealed that its σ_2/MWt (1.3×10^{-50} cm^4 s mol g^{-1}) value was the largest thus far for an organometallic complex[63]. $|\gamma|$ values for complexes **D** and **H-K** (Table 1) reveal a drastic increase in this parameter upon progressing from linear to octupolar complexes. Extending the π-system through the metal center (in proceeding from **G** to **H**) and replacing yne- with ene- linkage, in proceeding from **H** to **J** or from **I** to **K**, also result in significant increases in $|\gamma|_{800}$, an observation that prompted Humphrey and co-workers to study the third-order NLO properties of Ru^{II} alkynyl dendrimeric species (Figure 6). Proceeding from 1,3,5-C_6H_3(4-C≡CC_6H_4C≡C-*trans*-[Ru(dppe)$_2$]C≡CPh)$_3$ to dendrimers resulted in (i) no loss of optical transparency, (ii) an increase in the second hyperpolarizability, γ, which is proportionately greater than either the increase in the number of phenylethynyl units, and (iii) a dramatic enhancement of two-photon absorption[64, 65].

Both the peripheral units, the branching units and the core are of importance in designing these dendrimeric systems: Z-scan studies at 800 nm of a selection of alkynylruthenium dendrimers functionalized by acceptor nitro groups on their periphery revealed the most efficient system in this series to be 1,3,5-(3,5-(*trans*-[(dppe)$_2$($O_2NC_6H_4$-4-C≡C)Ru(C≡C)])(1-C_6H_3-C≡CC_6H_4-4-C≡C)$_3C_6H_3$, at that wavelength[56]. On the other side, femtosecond Z-scan

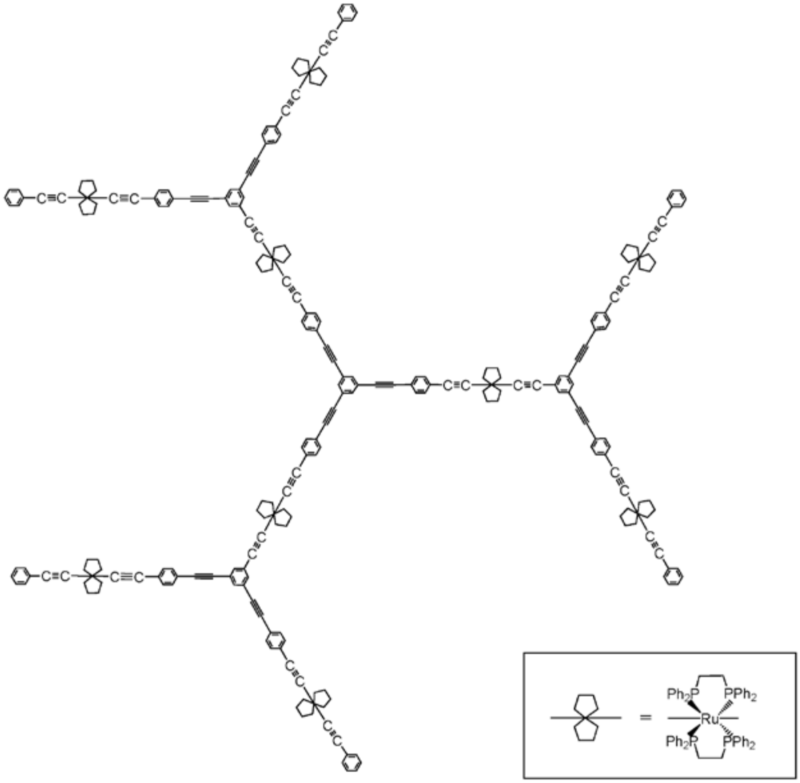


FIGURE 6
A nonaruthenium dendrimer obtained by the convergent strategy

studies at 800 nm of first-generation phenyleneethynylene-based dendrimers revealed a *ca.* fourfold increase in cubic nonlinearity in proceeding from peripheral Ru_6 metallation ($|\gamma| = 1600 \pm 2400 \times 10^{-36}$ esu) to peripheral Ru_6/internal Pt_3 metallation ($|\gamma| = 7200 \pm 2900 \times 10^{-36}$ esu) [36]. The cubic optical nonlinearity of this dendrimer is lower than that of the nonaruthenium dendrimer depicted in Figure 6, suggesting that a search for organometallic dendrimers with larger NLO coefficients should focus on those with electron-rich (18 valence electron) metal centers[29].

Although the 3rd-order NLO properties of these systems have been the subject of many investigations, most reports only provide γ values at a fixed wavelength, whereas wavelength dependence studies of nonlinear properties are crucial for determining the spectral regions in which the nonlinear absorption is the strongest. Humphrey and co-workers studied the wavelength dependence of γ of alkynylruthenium dendrimers and interpreted the dispersion of γ_{imag} in terms of competition between two-photon absorption and saturable absorption processes in these organometallic dendrimers. In particular, they observed the wavelength dependence of nonlinear absorption and nonlinear refraction of a peripherally nitrophenylethynyl-functionalized first-generation arylethynylruthenium dendrimer in the range 625–1500 nm by employing fs pulses. This compound acts as a strong two-photon absorber in the range 600–800 nm and as an exceptional three-photon absorber in the range 1100–1200 nm[66].

Spectral dependence studies of *N*-cored analogues developed by Marder and Humphrey, in which the planarity at the sp^2-hybridized nitrogen was expected to improve π-delocalisation and optical nonlinearity, revealed 2PA behavior at wavelengths below 1000 nm, the maximal values being consistent with a dendritic effect in nonlinearity upon increasing generation, while at wavelengths above 1000 nm, the data are consistent with 3PA-induced photochemistry[33]. The 2PA cross-sections of these organometallic dendrimers were found to be much larger than those of comparable *N*-cored organic dendrimers, and this increased performance is maintained even if the cross-sections are scaled by "effective number of (delocalizable) electrons", molecular weight, molecular volume[67].

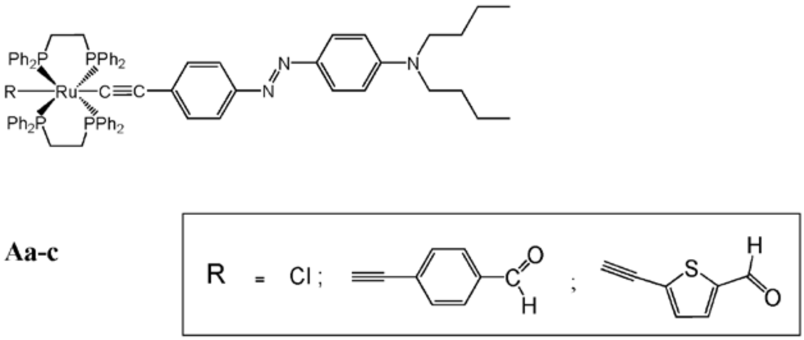
2.3.3. Switches and Materials

Group 8 metal alkynyl complexes have also attracted significant interest, because of the accessibility to molecular systems and materials for which one can reversibly modulate ("switch") the linear and nonlinear optical properties, by chemical, photochemical or electrochemical means. In particular, redox switching of the NLO properties of metal alkynyl complexes has been of considerable interest over the past decade, because the reversible redox processes, so redox-facilitated NLO switching, they offer. The reader is referred to [68] and [13] for recent accounts of these aspects.

Materials development exploiting NLO properties of organometallics remains rather slow, reflecting the fact that the focus is still on assessment of molecular nonlinearities for establishing structure-property relationships rather than bulk material properties.

SHG values as large as 1.94 pm/V at 980 nm following optical poling were reported for doped polymer made from complexes **Aa-d** (Figure 5) in the presence of an acoustic signal (80 Hz–1.1 MHz), the latter is required to obtain an SHG signal from these samples containing randomly oriented NLO-active complexes[69, 70]. The maximal susceptibility is observed at 5–6% of the chromophores in a poly(methylmethacrylate) (PMMA) matrice. Note that the resulting $\chi^{(2)}$ value is not stable and decreases over time (by *ca.* 76% after 600 min of laser treatment)[21].

The azobenzene-containing ruthenium(II) acetylides **Aa-c** (Figure 7) designed by Fillaut showed satisfactory processability and were spin-coated from 2–10 wt% concentration CH_2Cl_2 solutions. This procedure afforded films with good optical quality having a thickness ranging from 100 to 300 nm ± 10 nm. Oriented organometallic thin films were also obtained from these compounds by corona poling at 120 C over 5 min, the best $\chi^{(2)}$ values of *ca.* 1 pm/V at 1064 nm being seen for **45b**[71]. The



Aa-c

FIGURE 7
Photoisomerizable azobenzene-containing ruthenium(II) acetylides

$\chi_{elec}^{(3)}$ values for the films have been measured using the Maker fringes technique at 1064 nm using 15 ps pulses[72] and revealed a ca. 50% increase in $\chi^{(3)}$ values on proceeding from **Aa** to **Ab** and **Ac** (Figure 7), which is consistent with both the lengthening of the p-system and the introduction of a push-pull character for the latter complexes involving the *trans*-disposed alkynyl ligands.

Spin coated thin films of pure compounds **Aa**-**c** were also studied in the context of all-optical single step surface patterning[73-75]. Ultrafast formation of photoinduced surface relief gratings was observed. Interestingly, long term stability of the SRGs was also observed, recording of the films being maintained even after several months, at room temperature, without protecting them from ambient air. Comparative studies involving PMMA doped polymers with the complexes **Aa**-**c** in comparison with the DR1-PMMA model also revealed the specific efficiency of the investigated organometallic complexes. These studies indicate that azobenzene-containing ruthenium(II) acetylides containing materials exhibit significant macroscopic mass transport under inhomogeneous irradiation, and could be engineered to optimize SRG formation and surface patterning for a variety of optical material applications[76, 77].

3. CONCLUDING REMARKS

In this review, the chemical and opto-electronic properties of a series of ruthenium alkynyl derivatives are discussed. More specifically, the capability of ruthenium alkynyl derivatives of the form *trans*-RuX(C≡C-R)(dppe)$_2$ to generate second- and third-order NLO responses, either as quadrupolar, octupolar or as push–pull systems, has been described, at molecular level from solution studies, as well as on properties of bulk materials.

trans-RuX(C≡C-R)(dppe)$_2$ derivatives are very attractive, due to high-yield syntheses which led to the formation of a wide range of symmetric and unsymmetric Ru^{II} mono- and bis-alkynyl mono- and poly-metallic complexes, as for instance the construction of multimetallic dendrimers. Regarding the NLO properties, at molecular level, *trans*-RuX(C≡C-R)(dppe)$_2$ complexes, in which the metal center is directly incorporated into the plane of the alkynyl π-system, allowing the metal and carbon orbitals to overlap, are more NLO-active than fully organic alternatives of similar size. Of course, the presence of the metal is thus crucial to the NLO properties of these systems, but their molecular quadratic β and cubic γ hyperpolarisability values are strongly influenced by the symmetry of the complexes, the nature of the ligands, and in the case of dendrimeric systems, the location and nature of the metallic centers, which can be exploited to tune the nonlinear response. The introduction of electron-acceptor remote groups, the extension of the p-system through (or not) the metal center, the replacement of yne- with ene- linkage in this p-system are good strategies to enhance the nonlinear optical responses of the *trans*-RuX(C≡C-R)(dppe)$_2$ derivatives. On the other hand, the ease with which other functionalities, photochromism, reversible redox properties can be incorporated into these systems has led to molecular systems which afford the possibility of accessing facile NLO switching.

Finally, *trans*-RuX(C≡C-R)(dppe)$_2$, either as quadrupolar, octupolar or as push–pull systems, can be seen as advantageous building blocks of functional materials. Meanwhile, examples of materials exploiting the NLO properties of these organometallics remains rather rare. These studies indicate that materials containing *trans*-RuX(C≡C-R)(dppe)$_2$ complexes as molecular building blocks exhibit satisfactory optical linear and non linear properties, long-term stability of the signal and processability, to achieve relevant technological goals, including potential applications in image storage and proceeding. No doubt that the versatile synthesis and the ease with which molecular functionalities can be incorporated into these systems will lead to innovative materials with more than one property coming from the same molecular building-block. Specifically, the evolution towards applications in molecular electronics and photonics and other related areas, together with the trend towards nanoscale materials, are foreseen for this multidisciplinary field.

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