Organometallic complexes for nonlinear optics☆
Part 21. Syntheses and quadratic hyperpolarizabilities of alkynyl complexes containing optically active 1,2-bis(methylphenylphosphino)benzene ligands

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Abstract

The preparation of the chloro complex *trans*-[FeCl$_2${(R,R)-diph}$_2$] (**1**) and the alkynyl complexes *trans*-[M(4-C≡CC$_6$H$_4$R)Cl{(R,R)-diph}$_2$] [M = Fe, R = NO$_2$ (**2**); M = Ru, R = H (**4**), NO$_2$ (**5**), (*E*)-CH=CH-4-C$_6$H$_4$NO$_2$ (**6**); M = Os, R = NO$_2$ (**7**)], incorporating the optically active diphosphine 1,2-bis(methylphenylphosphino)benzene (diph), are described. Oxidation potentials, as determined by cyclic voltammetry, increase as **2 < 7 < 5**. Molecular quadratic nonlinearities by hyper-Rayleigh scattering at 1064 nm increase upon introduction of an acceptor group (**4 < 5**), chain-lengthening of bridging group (**5 < 6**), and proceeding from 3d to 4d and 5d metal (**2 ≤ 5 ≤ 7**). Two-level-corrected nonlinearities reproduce the first two trends, but metal variation follows the sequence **2 < 7 < 5**. The experimental and two-level-corrected nonlinearities for **6** (2795 × 10^{-30} and 406 × 10^{-30} esu, respectively), are amongst the largest observed thus far for organometallic complexes. Crystals of complexes **2** and **7** exhibit second-harmonic generation (assessed using the Kurtz powder technique), with an efficiency for the former of twice that of urea. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

There has been much recent interest in the nonlinear optical (NLO) properties of organometallic complexes [1–4]. Most efficient NLO-active complexes have a dipolar composition, with an electron donating group linked by a π-conjugated bridge to an electron accepting group. Structure-NLO property studies have therefore focussed on systematic variation of these molecular components. Many reports describe the effect on NLO properties of variation of the organic acceptor groups, bridge modification and ligand variation about donor metal center. However, there has been little investigation thus far into the effects of variation of the metal atom in the donor fragment. The second-order nonlinearity (as determined by hyper-Rayleigh scattering), β_{HRS}, for the cationic nitrile complexes [M(4-
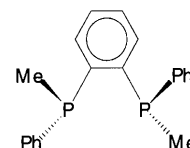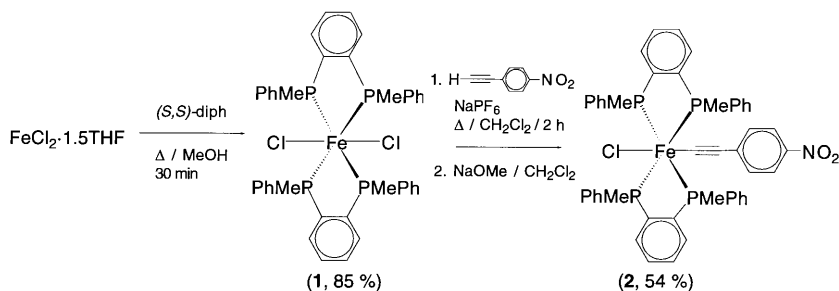

Fig. 1. (*S,S*)-1,2-Bis(methylphenylphosphino)benzene, (*S,S*)-diph.

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Scheme 1. Preparation of iron complexes **1** and **2**.

N≡CC$_6$H$_4$NO$_2$)(dppe)(η-C$_5$H$_5$)]$^{n+}$ (M = Fe, Ru, Co, Ni; n = 0, 1, 2) [5] decrease according to the sequence iron > ruthenium > nickel > cobalt, with lower N≡C stretching frequency (and hence increased back-bonding) correlating with increased β. Larger values of β are observed for the more readily oxidized ferrocenyl complexes than for the less readily oxidized ruthenocenyl examples [6–9]. We have been investigating the second-order and third-order NLO properties of systematically varied metal alkynyl complexes [10–29], but have not thus far examined the effect of variation of metals from one transition group. This paper describes the preparation of a series of Group 8 metal alkynyl complexes, and the effect of this metal variation upon electrochemical behavior and molecular second-order NLO response. The complexes reported herein have very large quadratic NLO coefficients.

Most studies of organometallic complexes have considered either molecular response or bulk material NLO properties. It is clearly of interest to assess the bulk material NLO activity of molecules with large molecular NLO coefficients, but non-zero bulk NLO activity requires noncentrosymmetric crystal packing. One method to ensure noncentrosymmetric packing is to incorporate chiral element(s) into the molecule. The optically active ligand 1,2-bis(methylphenylphosphino)benzene (diph, Fig. 1) has therefore been utilized as co-ligand in the current work, to ensure non-centrosymmetric packing in the solid state, permit assessment of the bulk material second-order NLO activity for the new complexes, and afford a comparison of bulk material NLO response with the molecular NLO properties.

2. Results and discussion

2.1. Preparation of (−)$_{589}$-trans-[FeCl$_2$[(R,R)-diph]$_2$] (1) and (−)$_{436}$-trans-[Fe(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (2)

The new iron dichloro complex (−)$_{589}$-trans-[FeCl$_2${(R,R)-diph}$_2$] (**1**) was prepared by extending the literature procedure for the synthesis of [FeCl$_2${1,2-C$_6$H$_4$(PMe$_2$)$_2$}$_2$] [30]. Stirring two equivalents of the diph ligand with [FeCl$_2$·1.5THF] in refluxing methanol affords **1** in excellent yield (Scheme 1), and avoids the racemization of the free diph ligand which occurs at a significant rate at around 80°C. The complex was characterized by ^{1}H- and ^{31}P-NMR spectroscopy, FAB mass spectrometry and optical rotation measurements. The ^{31}P-NMR spectrum contains a broad singlet at 67.7 ppm, confirming *trans* disposition of chloro ligands at the central metal atom. Optical rotation studies show a large specific rotation at 589 nm [[α]$_D$ = − 1760 (c 0.101, CH$_2$Cl$_2$)]. The UV–vis spectrum contains overlapping bands at 37 400 and 34 700 cm^{-1}, assigned to π–π* transitions in the phenyl substituents on the phosphine [24].

The alkynyl complex (−)$_{436}$-trans-[Fe(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}] (**2**) was prepared from **1** by extending the procedure described for the synthesis of trans-[Ru(C≡CPh)Cl(dppe)$_2$] [31] (Scheme 1). Stirring **1** with 4-HC≡CC$_6$H$_4$NO$_2$ and sodium hexafluorophosphate in refluxing dichloromethane for 2 h afforded the vinylidene complex cation [Fe(4-C=CHC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$]$^+$. In order to prevent the formation of the bis-alkynyl complex in subsequent reactions, the air-sensitive vinylidene complex was isolated by precipitation from the reaction mixture using petroleum spirit. The vinylidene complex was then deprotonated with sodium methoxide in dichloromethane, affording the alkynyl complex **2** in 54% yield. Complex **2** is air stable and was characterized by ^{1}H- and ^{31}P-NMR spectroscopy, IR and UV–vis spectroscopy, FAB mass spectrometry and optical rotation measurements. The IR spectrum of a dichloromethane solution shows a characteristic signal at 2043 cm^{-1} attributed to v(C≡C). The UV–vis spectrum of a tetrahydrofuran solution contains bands at 37 400 and 36 400 cm^{-1}, similar to those of the parent dichloro complex **1**. A weak band at 29 400 cm^{-1} and a more intense band at 18 400 cm^{-1} are also observed in the UV–vis spectrum of **2**, the latter assigned to a MLCT transition from the metal to the alkynyl ligand, by analogy with MLCT

assignments in related ruthenium alkynyl complexes [24]. The ^{31}P-NMR spectrum contains two sets of triplet signals (72.3 and 77.0 ppm), consistent with *trans* geometry of the chloro and alkynyl ligands at the iron. The FAB mass spectrum contains a signal due to the molecular ion, with a bandshape consistent with that predicted from the isotopic composition. Fragmentation of the molecular ion occurs through competitive loss of the chloro, alkynyl, and diphosphine ligands. Measurement of the optical rotation at the frequently used sodium 'D' line (589 nm) was precluded by a strong absorption for **2** at this wavelength. However, the weaker absorption at 436 nm affords a specific optical rotation of $[\alpha]_{436} = -3200$ (*c* 0.022, CH$_2$Cl$_2$).

2.2. Preparation of (−)$_{589}$-cis-[RuCl$_2${(R,R)-diph}$_2$] (3) and trans-[Ru(4-C≡CC$_6$H$_4$R)Cl{(R,R)-diph}$_2$] [R = H (4), NO$_2$ (5), (E)-CH=CH-4-C$_6$H$_4$NO$_2$ (6)]

The dichloro complex *cis*-[RuCl$_2${(R,R)-diph}$_2$] (**3**) was prepared following a modification to the procedure for the synthesis of *cis*-[RuCl$_2$(dppm)$_2$] [32]. Thus, reaction between *cis*-[RuCl$_2$(DMSO)$_4$] (DMSO = dimethyl-sulfoxide) and the (*S,S*)-diph ligand in refluxing methanol for 30 min afforded (−)$_{589}$-*cis*-[RuCl$_2${(R,R)-diph}$_2$] (**3**) in good yield (71%), together with a small amount of the *trans* isomer (16%); separation was achieved through fractional crystallization (Scheme 2). The ^{31}P-NMR spectrum of **3** shows two sets of triplet signals at 47.5 and 55.1 ppm, confirming the *cis*-geometry. Other spectral data have been reported previously [33].

The alkynyl complexes (−)$_{589}$-*trans*-[Ru(4-C≡CC$_6$H$_4$R)Cl{(R,R)-diph}$_2$] [R = H (**4**), NO$_2$ (**5**), (*E*)-

CH=CHC$_6$H$_4$NO$_2$ (**6**)] were prepared by extending literature procedures for the preparation of *trans*-[Ru(4-C≡CC$_6$H$_4$R)Cl(dppm)$_2$] [15,34] to the diph-containing analogues (Scheme 2). The ruthenium vinylidene complexes were formed by stirring **3** with the acetylene and sodium hexafluorophosphate in refluxing toluene for 2 h. In contrast to the iron vinylidene complex intermediate, the ruthenium vinylidene complexes are relatively air stable, allowing isolation of the precipitated compounds without the necessity of an inert atmosphere during filtration. The vinylidene complexes were then dissolved in dichloromethane and deprotonated with base to yield the air-stable alkynyl complexes **4**–**6** in good yield. A similar sequence of reactions with 4-nitrophenylacetylene and using *trans*-[RuCl$_2${(R,R)-diph}$_2$] as the precursor did not afford the desired complex, starting material being recovered from the reaction mixture after several days.

Complexes **4**–**6** were characterized by IR and UV–vis spectroscopy, ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy, FAB mass spectrometry and optical rotation measurements. The IR spectra contain characteristic signals assigned to ν(C≡C). The UV–vis spectra contain similar high energy bands to those of the *trans*-dichloro complex, together with an additional lower energy band assigned to the MLCT transition from the metal to the alkynyl ligand. The ^{31}P-NMR spectra are consistent with the assignment of a *trans* geometry, with two sets of inequivalent phosphorus centers giving rise to triplet signals. Fragmentation of the molecular ions occur by loss of the chloro, alkynyl, and diphosphine ligands. The specific optical rotations of dichloromethane solutions of **4** [[α]$_{578}$ = −261 (*c* 0.91)], **5** and **6** [[α]$_{589}$ = −504 (*c* 0.145)] and −3600 (*c* 0.022), respectively],
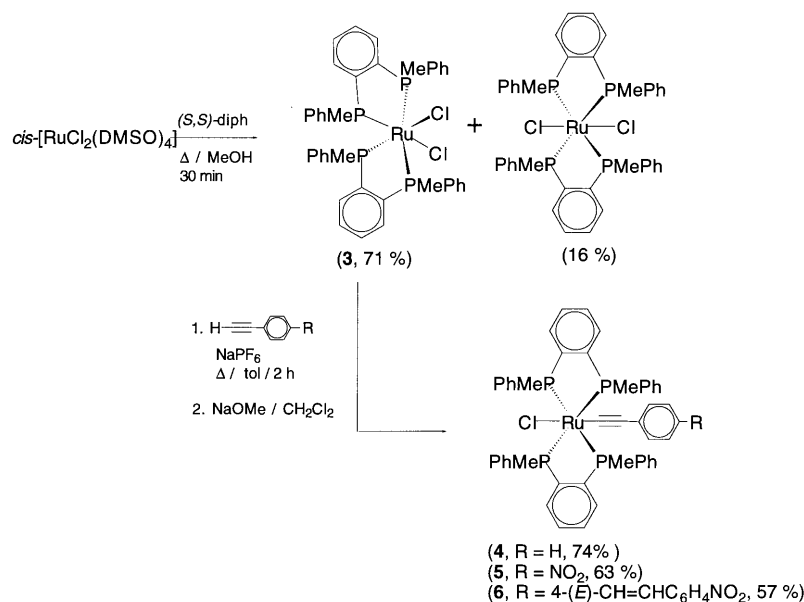
Scheme 2. Preparation of ruthenium complexes **3**–**6**.
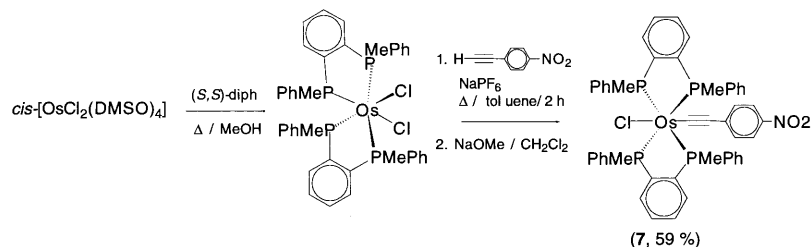
Scheme 3. Preparation of osmium complex **7**.

were measured; **4** absorbs strongly at the wavelength of the sodium 'D' line (589 nm) and was measured at the mercury line (578 nm).

2.3. Preparation of $(-)_{365}$-trans-[Os(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (7)

The preparation of $(-)_{365}$-trans-[Os(4-C≡CC$_6$H$_4$-NO$_2$)Cl{(R,R)-diph}$_2$] (**7**) followed the procedure used for its ruthenium homologue, i.e. reaction of *cis*-[OsCl$_2${(R,R)-diph}$_2$] with 4-HC≡CC$_6$H$_4$NO$_2$ and NaPF$_6$ to form the vinylidene complex cation, followed by deprotonation with base to afford **7** in 59% yield (Scheme 3). The *trans*-[OsCl$_2${(R,R)-diph}$_2$] was found to be unreactive towards the acetylene ligand in the presence of hexafluorophosphate, even under quite forcing conditions (refluxing decalin, 24 h).

The alkynyl complex **7** was characterized by a combination of ^{1}H-, ^{13}C- and ^{31}P-NMR spectroscopy, IR and UV–vis spectroscopy, FAB mass spectrometry and optical rotation measurements. The IR spectrum shows the expected peak due to v(C≡C) at 2052 cm^{-1}, the UV–vis spectrum contains a MLCT band at 20 400 cm^{-1}, the ^{31}P-NMR spectrum contains the expected two sets of triplet signals at 18.9 and 23.0 ppm and the FAB mass spectrum shows the molecular ion at 1017 mass units. Complex **5** absorbs strongly at 589 nm; however, an optical rotation measurement at 365 nm shows a specific rotation of $[\alpha]_{365} = -2730$ (*c* 0.0495, CH$_2$Cl$_2$).

2.4. Cyclic voltammetric studies

The results of cyclic voltammetric measurements of **2**, **5** and **7** are shown in Table 1. The precursor iron chloro complex **1** shows a reversible metal-centered oxidation process (Fe$^{II/III}$, $E^0 = 0.16$ V with scan rates of 100 mV s^{-1}). Replacing the chloro ligand by a 4-nitrophenylalkynyl ligand in proceeding from **1** to **2** results in an increase of 0.10 V in E^0, indicating that chloro is marginally better than 4-nitrophenylalkynyl at stabilizing the higher oxidation state.

The major interest in the current work lies in comparing the homologous metal acetylide complexes **2**, **5**

and **7**. The effect of metal variation upon E^0(M$^{II/III}$) follows the trend ruthenium > osmium > iron, the same trend as observed earlier with Group 8 metal bis-(diphosphine) complexes [30,35] and metallocenes [36]. In complexes of this type, the oxidation waves are associated with metal-centered HOMOs, and the reduction waves are associated with nitro-centered LUMOs [23]. There is almost no change in E^0(NO$_2^{0/-1}$) across these complexes. Ease of electron removal from the donor and electron addition to the acceptor may be relevant to the NLO response. The potential difference E^0(M$^{II/III}$) $-$ E^0(NO$_2^{0/-1}$) may therefore have predictive merit for NLO response [23], and for the present series of complexes this parameter follows the trend ruthenium > osmium > iron. This is also the same trend observed with the low energy bands in the UV–vis spectrum, consistent with their assignment as MLCT transitions (M^{II}–bridge–NO$_2^0$ → M^{III}–bridge–NO$_2^{-1}$). Both electrochemical and linear optical spectroscopic data suggest that β values should increase in proceeding from ruthenium to osmium, with iron complexes having the largest nonlinearities. The v(C≡C) frequencies in the IR spectra of **2**, **5** and **7** follow the trend iron < osmium < ruthenium, suggestive of greater electron back-donation from the metal to the alkynyl ligand for the

Table 1
Cyclic voltammetric data for *trans*-[M(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] [M = Fe (**2**), Ru (**5**), Os (**7**)] [a]

Compound	$E^0_{\mathrm{M^{II/III}}}$ (V) $[i_{pc}/i_{pa}]$	$E^0_{\mathrm{NO_2^{0/-1}}}$ (V) $[i_{pa}/i_{pc}]$
$(-)_{436}$-*trans*-[Fe(4-C≡CC$_6$H$_4$NO$_2$)-Cl{(R,R)-diph}$_2$] (**2**)	0.26 [1.0]	-1.15 [b]
$(-)_{589}$-*trans*-[Ru(4-C≡CC$_6$H$_4$NO$_2$)-Cl{(R,R)-diph}$_2$] (**5**)	0.74 [0.9]	-1.13 [1.0]
$(-)_{365}$-*trans*-[Os(4-C≡CC$_6$H$_4$NO$_2$)-Cl{(R,R)-diph}$_2$] (**7**)	0.52 [0.6]	-1.15 [b]

[a] Glassy carbon disc working, Pt auxiliary and Ag–AgCl reference electrodes. Scan rates were 100 mV s^{-1}. Solutions in CH$_2$Cl$_2$ with 0.1 M [NBu$_4^n$]PF$_6$ electrolyte. Referenced to internal ferrocene (E^0 at 0.56 V).

[b] $E_{pc\ \mathrm{NO_2^{0/-1}}}$ (V) for non-reversible process.

Table 2
Linear optical and quadratic nonlinear optical response parameters [a]

Compound	λ_{max} (nm) [ε (10^4 M^{-1} cm^{-1})]	β [b] (10^{-30} esu)	β_0 [c] (10^{-30} esu)
$(-)_{589}$-trans-[FeCl$_2${(R,R)-diph}$_2$] (**1**)	379 [0.13]	[d]	[d]
$(-)_{436}$-trans-[Fe(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (**2**)	543 [1.7]	440	-14
$(-)_{589}$-cis-[RuCl$_2${(R,R)-diph}$_2$] (**3**)	386 [0.11]	10	4
$(-)_{578}$-trans-[Ru(4-C≡CPh)Cl{(R,R)-diph}$_2$] (**4**)	292 [1.8]	[d]	[d]
$(-)_{589}$-trans-[Ru(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (**5**)	467 [2.1]	530	97
$(-)_{589}$-trans-[Ru(4-C≡CC$_6$H$_4$-(E)-CH=CH-4-C$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (**6**)	481 [2.6]	2795	406
$(-)_{365}$-trans-[Os(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (**7**)	490 [1.8]	620	74

[a] All compounds are optically transparent at the fundamental frequency 1064 nm.

[b] HRS at 1064 nm; values $\pm 10\%$, using p-nitroaniline ($\beta = 21.4 \times 10^{-30}$ esu) as a reference.

[c] Data corrected for resonance enhancement at 532 nm using the two-level model with $\beta_0 = \beta[1-(2\lambda_{max}/1064)^2][1-(\lambda_{max}/1064)^2]$; damping factors not included.

[d] Response too low to measure.

iron complex than for the heavier homologues. If π-backbonding is correlated to NLO merit, one should also expect β values to increase as ruthenium < osmium < iron for these complexes.

2.5. Nonlinear optical investigations

2.5.1. Molecular quadratic nonlinear optical measurements by hyper-Rayleigh scattering

The results of hyper-Rayleigh scattering (HRS) experiments are presented in Table 2. The experimental first hyperpolarizabilities (β_{HRS}) are shown together with static first hyperpolarizabilities (β_0) calculated from the experimental values using the two-level approximation [the shortcomings of the two-level model have been discussed elsewhere (e.g. reference [2]). This model was developed for a restricted class of organic compounds where structural modifications are directed at the charge-transfer band thought to contribute to the hyperpolarizability, and may not be useful where there are several dominant optical transitions close to 2ω].

The chloro complexes **1** and **3** and the phenylalkynyl complex **4** have low nonlinearities. Introduction of nitro substituent in proceeding from **4** to **5** results in a large increase in nonlinearity, a trend observed with other alkynyl complexes [12,13,18,21,23,24]. π-System lengthening in proceeding from **5** to **6** leads to a further substantial increase in quadratic nonlinearity, with β_{HRS} and β_0 values for the latter amongst the largest thus far for an organometallic complex [2].

A comparison of the β_{HRS} values for the cognate metal acetylide complexes **2**, **5** and **7** indicates that the iron-containing complex has the lowest response. This is in contrast to the trend reported for donor-acceptor nitrile [5] and metallocenyl complexes [6–9], and also in contrast to predictions based on possible correlations with linear optical and electrochemical data for the present set of complexes. In the current work, the iron complex **2** has an absorption band closer to the second-

harmonic wavelength of 532 nm than **5** or **7**, suggesting that the β_{HRS} value for **2** contains a larger resonance contribution than the β_{HRS} values for **5** and **7**. The β_{HRS} value for the osmium complex **7** is greater than that for the ruthenium-containing analogue **5**. The absorption band for the osmium complex is closer to the second-harmonic than is that of the ruthenium homologue, and the ruthenium complex has the higher calculated static value. The two-level model may have limited applicability with organometallic complexes of this type (see above). Nevertheless, the β_{HRS} and β_0 values from the present work are consistent with the relative merit: iron < ruthenium $\cong$ osmium for these alkynyl complexes.

2.5.2. Second-harmonic generation in bulk samples

Experiments to detect a bulk second-order response were performed on selected samples using the Kurtz powder technique [37], with the intensity of the measured second-harmonic generation being compared to that of urea; the results are presented in Table 3.

The non-zero responses for the iron- and osmium-containing complexes confirm the ability of the diph ligand to force non-centrosymmetric packing and permit a bulk second-order NLO response. The bulk sec-

Table 3
Second-order nonlinear optical response parameters measured by the Kurtz powder technique.

Compound	SHG (urea = 1)
$(-)_{436}$-trans-[Fe(4-C≡CC$_6$H$_4$NO$_2$)Cl-{(R,R)-diph}$_2$] (**2**)	~ 2
$(-)_{589}$-trans-[Ru(4-C≡CC$_6$H$_4$NO$_2$)Cl-{(R,R)-diph}$_2$] (**5**)	None detected
$(-)_{365}$-trans-[Os(4-C≡CC$_6$H$_4$NO$_2$)Cl-{(R,R)-diph}$_2$] (**7**)	$\ll 1$

Fig. 2. NMR numbering scheme.

referenced to residual solvent (^{1}H, ^{13}C) or external 85% H_3PO_4 (^{31}P). NMR assignments follow the numbering scheme shown in Fig. 2. Optical rotations in dichloromethane were measured at 20°C on a Perkin-Elmer model 241 polarimeter. Electrochemical measurements were recorded using a MacLab 400 interface and MacLab potentiostat from AD Instruments (using a glassy carbon disc working, Pt auxiliary and Ag–AgCl reference mini-electrodes from Cypress Systems). Scan rates were typically 100 mV s^{-1}. Electrochemical solutions contained 0.1 M [NBu^n$_4$]PF$_6$ and ca. 10^{-3} M complex in dichloromethane. Solutions were purged and maintained under an atmosphere of nitrogen. All values are referenced to an internal sample of ferrocene (E^0 at 0.56 V).
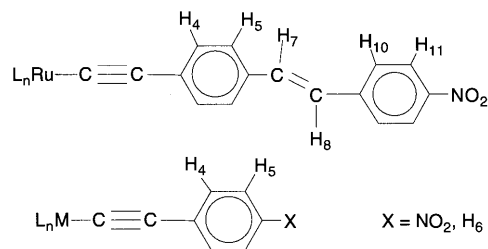
ond-order data are quite modest, though, compared to literature-extant data [38]. In particular, the data from the present series of complexes and other alkynyl complexes [20,23] are smaller than those of many ferrocenyl complexes, although the molecular NLO responses for alkynyl complexes exceed those of ferrocenyl compounds. Thus, while the alkynyl complex molecular composition has been demonstrated in many studies (including the present work) to have very large molecular NLO coefficients, it has yet to be shown how to translate this molecular efficiency to the bulk material.

3. Experimental

3.1. General

All reactions were performed under a nitrogen atmosphere with the use of Schlenk techniques unless otherwise stated. Dichloromethane was dried by distilling over CaH$_2$, methanol was dried by distilling over Mg/I$_2$, toluene was dried by distilling over sodium–benzophenone, and other solvents were used as received. 'Pet. spirit' refers to a fraction of petroleum ether of boiling range 60–80°C. 4-HC≡CC$_6$H$_4$NO$_2$ [39], *cis*-[RuCl$_2$(DMSO)$_4$] [40], (NH$_4$)$_2$[OsCl$_6$] [41], (S,S)-bis-(methylphenylphosphino)benzene (diph) [33] and FeCl$_2$·1.5THF [42] were prepared according to published methods. Sodium hexafluorophosphate (Aldrich) was recrystallized from acetonitrile before use. Sodium methoxide solutions were prepared by the slow addition of sodium to dry methanol.

Mass spectra and microanalyses were carried out at the Research School of Chemistry, Australian National University. Mass spectra were recorded using a VG ZAB 2SEQ instrument (30 kV Cs$^+$ ions, current 1 mA, accelerating potential 8 kV, 3-nitrobenzyl alcohol matrix); peaks are reported as m/z (assignment, relative intensity). Infrared spectra were recorded as dichloromethane solutions using a Perkin-Elmer System 2000 FT-IR. UV–vis spectra were recorded using a Cary 5 spectrophotometer as solutions in tetrahydrofuran in 1 cm cells. ^{1}H- (300 MHz), ^{13}C- (75 MHz) and ^{31}P- (121 MHz) NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer and are

3.2. Synthesis

3.2.1. (−)$_{589}$-trans-[FeCl$_2${(R,R)-diph}$_2$] (**1**)

A mixture of FeCl$_2$·1.5THF (145 mg, 0.62 mmol) and (S,S)-diph (400 mg, 1.24 mmol) was stirred in methanol (10 ml) for 45 min at reflux. A lime green precipitate formed. The mixture was allowed to cool to room temperature (r.t.) and then cooled in an ice bath for 15 min. The precipitate was collected by filtration in air and washed with pet. spirit (2 × 30 ml). The green solid was dissolved in dichloromethane and passed through a plug of Celite to remove any residual iron(0). Pet. spirit (30 ml) was added to the filtrate and the solvent was removed on a rotary evaporator to afford a lime green powder identified as **1** (405 mg, 85%). Anal. Calc. for C$_{40}$H$_{40}$Cl$_2$FeP$_4$: C 62.28, H 5.23. Found: C 61.89, H 5.18%. MS: 770 ([M]$^+$, 20), 735 ([M − Cl]$^+$, 20), 700 ([Fe(diph)$_2$]$^+$, 5), 413 ([FeCl(diph)]$^+$, 50), 322 (diph$^+$, 45). UV–vis (λ_{max}, nm [ε, 10^4 M^{-1} cm^{-1}]): 379 [1.3], 288 [sh, 1.1], 268 [2.3]. ^{1}H-NMR: δ 1.24 [s(br), 12H, Me], 7.27–7.46 (m, 28H, Ph). ^{31}P-NMR: δ 67.7 [s (br)]. [α]$_D$: − 1760 (c 0.101).

3.2.2. (−)$_{436}$-trans-[Fe(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (**2**)

A mixture of **1** (50 mg, 0.065 mmol), 4-HC≡CC$_6$H$_4$NO$_2$ (20 mg, 0.14 mmol) and sodium hexafluorophosphate (20 mg, 0.12 mmol) was stirred in dichloromethane (5 ml) for 2 h at reflux. The mixture was allowed to cool to r.t. and 12 ml of pet. spirit added to afford a brown precipitate. The solvent and excess acetylene were removed by filter-tipped cannula under nitrogen. The remaining solid was dissolved in dichloromethane and sodium methoxide solution (1 ml, 0.3 M solution in methanol) was added with stirring. The mixture immediately turned a deep purple in color. The solvent was removed in vacuo and the residue extracted into diethyl ether and passed through an alumina (basic, ungraded) plug, eluting with diethyl

ether. The solvent was removed on a rotary evaporator to give a purple powder identified as **2** (31 mg, 54%). Anal. Calc. for $C_{48}H_{44}ClNO_2P_4Ru$: C 65.36, H 5.03, N 1.59. Found: C 64.41, H 5.39, N 1.78%. MS: 881 ([M]$^+$, 100), 846 ([M − Cl]$^+$, 15), 735 ([FeCl(diph)$_2$]$^+$, 20), 700 ([Fe(diph)$_2$]$^+$, 5), 559 ([M − diph]$^+$, 35), 413 ([FeCl(diph)]$^+$, 50). UV–vis (λ_{max}, nm [ε, 10^4 M^{-1} cm^{-1}]): 543 [1.7], 340 [1.1], 275 [2.3], 268 [2.4]. IR (cm^{-1}): 2043 (w) v(C≡C). ^{1}H-NMR: δ 1.52 (t, J_{HH} = 4 Hz, 6H, Me), 1.59 (t, J_{HH} = 4 Hz, 6H, Me), 6.23 (d, J_{HH} = 9 Hz, 2H, H$_4$), 7.23 to 7.53 (m, 28H, Ph), 7.78 (d, J_{HH} = 9 Hz, 2H, H$_5$). ^{31}P-NMR: δ 72.3 (t, J_{PP} = 43 Hz, 2P), 77.0 (t, J_{PP} = 43 Hz, 2P). [α]$_{436}$ = − 3200 (c 0.022).

3.2.3. (−)$_{589}$-cis-[RuCl$_2${(R,R)-diph}$_2$] (3)

A mixture of [RuCl$_2$(DMSO)$_4$] (375 mg, 0.77 mmol) and (S,S)-diph (500 mg, 1.56 mmol) was stirred in methanol (15 ml) for 30 min at reflux. The mixture was allowed to cool to r.t. to afford a yellow precipitate which was removed by filtration. The filtrate was reduced to a viscous oil on a rotary evaporator and water (5 ml) added. A yellow precipitate formed and was collected by filtration, dissolved in dichloromethane and dried over anhydrous magnesium sulfate. This mixture was filtered and the yellow solution reduced to dryness on a rotary evaporator to give a yellow powder. Both samples of yellow solid contained *cis* and *trans* isomers and so they were combined to give 572 mg (90%). The *cis/trans* isomers were cleanly separated by fractional crystallization in dichloromethane (10 ml) with the slow addition of pet. spirit (65 ml). Lemon yellow crystals were formed on standing which were identified as **3** (450 mg, 71%). MS: 816 ([M]$^+$, 60), 781 ([M − Cl]$^+$, 100), 745 ([Ru(diph)$_2$]$^+$, 25), 423 ([Ru(diph)]$^+$, 27). ^{1}H-NMR: δ 1.63 (m, 6H, Me), 2.31 (m, 6H, Me), 6.55 to 7.68 (28H, Ph). ^{31}P-NMR: δ 55.1 (t, J_{PP} = 22 Hz, 2P), 47.5 (t, J_{PP} = 22 Hz, 2P). [α]$_D$ = − 26 (c 0.42).

The volume of the filtrate was reduced to ∼ 10 ml and left standing to afford golden yellow microcrystals identified as the *trans* isomer of **3** (100 mg, 16%). ^{1}H-NMR: δ 1.55 (br s, 12H, Me), 6.60 to 7.49 (28H, Ph). ^{31}P-NMR: δ 52.0 (s).

3.2.4. (−)$_{578}$-trans-[Ru(4-C≡CPh)Cl{(R,R)-diph}$_2$] (4)

A mixture of (−)$_{589}$-cis-[RuCl$_2${(R,R)-diph}$_2$] (220 mg, 0.27 mmol), phenylacetylene (160 μl, 1.5 mmol) and sodium hexafluorophosphate (95 mg, 0.56 mmol) was refluxed in toluene (20 ml) for 4 h. The resulting pink precipitate was collected and dissolved in a minimum of dichloromethane. Triethylamine was added dropwise to the stirred solution until no pink color remained. The yellow solution was then passed through a short alumina column, eluting with dichloromethane. The solvent was removed on a rotary evaporator to afford a yellow solid identified as **4** (175 mg, 74%).

Anal. Calc. for $C_{48}H_{45}ClP_4Ru$: C 65.34, H 5.14. Found: C 65.69, H 5.00%. MS: 882 ([M]$^+$, 85), 847 ([M − Cl]$^+$, 14), 783 ([M − C≡CPh]$^+$, 14), 745 ([Ru(diph)$_2$]$^+$, 16), 423 ([Ru(diph)]$^+$, 12). IR (KBr, cm^{-1}): 2077 (m) v(C≡C). UV–vis (λ_{max}, nm [ε, 10^4 M^{-1} cm^{-1}]): 292 [1.8]. ^{1}H-NMR: δ 1.62 (m, 12H, Me), 6.56 (d, J_{HH} = 7 Hz, 2H, H$_4$), 6.84 (t, J_{HH} = 7 Hz, 1H, H$_6$), 6.98 (t, J_{HH} = 7 Hz, 2H, H$_5$), 7.23 to 7.55 (m, 28H, Ph). ^{31}P-NMR: δ 52.2 (t, J_{PP} = 26 Hz, 2P), 54.1 (t, J_{PP} = 26 Hz, 2P). [α]$_{578(Hg)}$ = − 261 (c 0.91).

3.2.5. (−)$_{589}$-trans-[Ru(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (5)

A mixture of **3** (50 mg, 0.061 mmol), 4-HC≡CC$_6$H$_4$NO$_2$ (20 mg, 0. 14 mmol) and sodium hexafluorophosphate (25 mg, 0.15 mmol) in toluene (5 ml) was stirred at reflux for 2 h to afford a light brown precipitate which was collected by filtration in air and then dissolved in dichloromethane. Sodium methoxide (1 ml, 0.2 M solution in methanol) was added with stirring. The solvent was then removed on a rotary evaporator and the residue extracted into dichloromethane (∼ 10 ml). The mixture was filtered, pet. spirit (about 5 ml) was added and the solution taken to dryness to give a red powder identified as **5** (36 mg, 63%). Anal. Calc. for $C_{48}H_{44}ClNO_2P_4Ru$: C 62.17, H 4.78, N 1.51. Found: C 61.97, H 4.89, N 1.37%. MS: 927 ([M]$^+$, 100), 892 ([M − Cl]$^+$, 20), 745 ([Ru(diph)$_2$]$^+$, 28), 423 ([Ru(diph)]$^+$, 26). IR (cm^{-1}): 2057 (m) v(C≡C). UV–vis (λ_{max}, nm [ε, 10^4 M^{-1} cm^{-1}]: 467 [2.1], 251 [4.0], 243 [sh, 4.8]. ^{1}H-NMR: δ 1.62 (d of t, J_{HP} = 15 and 3 Hz, 12H, Me), 6.41 (d, J_{HH} = 9 Hz, 2H, H$_4$), 7.24 to 7.53 (in, 28H, Ph), 7.82 (d, J_{HH} = 9 Hz, 2H, H$_5$). ^{31}P-NMR: δ 50.4 (t, J_{PP} = 22 Hz, 2P), 54.4 (t, J_{PP} = 22 Hz, 2P). ^{13}C-NMR: δ 12.4 (t, J_{CP} = 16 Hz, Me), 14.9 (t, J_{CP} = 16 Hz, Me), 111.6 (C$_2$), 123.4 to 147.4 (Ph). [α]$_D$ = − 504 (c 0.145).

3.2.6. (−)$_{365}$-trans-[Ru(4-C≡CC$_6$H$_4$-(E)-CH=CH-4-C$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (6)

A mixture of **3** (50 mg, 0.061 mmol), 4-HC≡CC$_6$H$_4$-(E)-CH=CH-4-C$_6$H$_4$NO$_2$ (31 mg, 0.12 mmol) and sodium hexafluorophosphate (20 mg, 0.12 mmol) in toluene (5 ml) was stirred at reflux for 2 h. On cooling, the red solution was decanted and the remaining solid was washed twice with toluene (5 ml). Addition of dichloromethane (5 ml) and sodium methoxide (1 ml, 0.2 M solution in methanol) afforded a dark purple solution which was taken to dryness in vacuo. Dichloromethane (5 ml) was added, and the mixture was filtered to remove the excess sodium hexafluorophosphate. Addition of pet. spirit (10 ml) and reduction of the solvent volume afforded a purple solid which was collected and washed with pet. spirit to afford **6** (36 mg, 57%). Anal. Calc. for $C_{56}H_{50}ClNO_2P_4Ru$: C 65.34, H 4.90, N 1.36. Found: C

64.67, H 5.40, N 1.52%. MS: 1029 ($[M]^+$, 100), 745 ($[Ru(diph)_2]^+$, 50), 423 ($[Ru(diph)]^+$, 40). IR (cm^{-1}): 2062 (m) $\nu(C\equiv C)$. UV–vis (λ_{max}, nm [ε, 10^4 M^{-1} cm^{-1}]): 481 [2.6]. ^{1}H-NMR: δ 1.63 (m, 12H, Me), 6.51 (d, $J_{HH} = 9$ Hz, 2H, H$_{10}$), 6.93 to 7.54 (m, 34H, Ph + H$_{4,5,7,8}$), 8.15 (d, $J_{HH} = 9$ Hz, 2H, H$_{11}$). ^{31}P-NMR: δ 51.6 (t, $J_{PP} = 22$ Hz, 2P), 54.1 (t, $J_{PP} = 22$ Hz, 2P). $[\alpha]_D = -3600$ (c 0.022).

3.2.7. ($-$)$_{365}$-trans-[Os(4-C≡CC$_6$H$_4$NO$_2$)Cl{(R,R)-diph}$_2$] (7)

A mixture of ($+$)$_{589}$-cis-[OsCl$_2${(R,R)-diph}$_2$] (50 mg, 0.055 mmol), 4-HC≡CC$_6$H$_4$NO$_2$ (20 mg, 0.14 mmol) and sodium hexafluorophosphate (20 mg, 0.12 mmol) was stirred in toluene (5 ml) for 2 h at reflux. The mixture was allowed to cool to r.t. and the brown precipitate that formed was collected by filtration in air and washed with pet. spirit. It was then dissolved in dichloromethane and 1 ml of sodium methoxide solution (0.3 M in methanol) was added with stirring. The mixture immediately turned deep red in color. The solvent was removed in vacuo, the residue extracted into dichloromethane and filtered. Pet. spirit was added to the filtrate and the solvent removed on a rotary evaporator, to give a dark red powder identified as **5** (33 mg, 59%). Anal. Calc. for C$_{48}$H$_{44}$ClNO$_2$OsP$_4$: C 56.72, H 4.36, N 1.38. Found: C 57.31, H 4.80, N 1.65%. MS: 1017 ($[M]^+$, 100). IR (cm^{-1}): 2052 (w) $\nu(C\equiv C)$. UV–vis (λ_{max}, nm [ε, 10^4 M^{-1} cm^{-1}]): 490 [1.8]. ^{1}H-NMR: δ 1.67 (d of t, $J_{HP} = 27$ and 4 Hz, 12H, Me), 6.38 (d, $J_{HH} = 9$ Hz, 2H, H$_4$), 7.22 to 7.48 (m, 28H, Ph), 7.82 (d, $J_{HH} = 9$ Hz, 2H, H$_5$). ^{31}P-NMR: δ 18.9 (t, $J_{PP} = 13$ Hz, 2P), 23.0 (t, $J_{PP} = 13$ Hz, 2P). ^{13}C-NMR: δ 10.7 (t, $J_{CP} = 20$ Hz, Me), 13.7 (t, $J_{CP} = 20$ Hz, Me), 109.7 (C$_2$), 123.4 to 147.4 (Ph). $[\alpha]_{365} = -2730$ (c 0.0495).

3.3. Nonlinear optical measurements

3.3.1. Hyper-Rayleigh scattering

An injection-seeded Nd:YAG laser (Q-switched Nd:YAG Quanta Ray GCR5, 1064 nm, 8 ns pulses, 10 Hz) was focussed into a cylindrical cell (7 ml) containing the sample. The intensity of the incident beam was varied by rotation of a half-wave plate placed between crossed polarizers. Part of the laser pulse was sampled by a photodiode to measure the vertically polarized incident light intensity. The frequency doubled light was collected by an efficient condenser system and detected by a photomultiplier. The harmonic scattering and linear scattering were distinguished by appropriate filters; gated integrators were used to obtain intensities of the incident and harmonic scattered light. All measurements were performed in tetrahydrofuran using p-nitroaniline ($\beta = 21.4 \times 10^{-30}$ esu) [43] as a reference. Further details of the experimental procedure have been reported in the literature [44,45].

3.3.2. Powder SHG measurements

Samples were ungraded powders placed in the circular cavity (10 mm diameter × 0.5 mm depth) of a microscope slide with a cover slip. Powder SHG efficiencies were measured using the Kurtz technique [37]. The fundamental output of a Q-switched Quanta-Ray GC-130 Nd:YAG laser was directed onto the sample (spot size ∼ 5 mm; energy per pulse: up to 20 mJ). A collecting lens (orthogonally placed with respect to the fundamental beam) focussed the backscattered second harmonic light through an infrared absorbing filter and a 532 nm interference filter onto a photodiode detector, which was connected to a HP 54510A digital oscilloscope. Measurements thus made were compared with a urea powder sample.

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