Organometallic complexes for nonlinear optics. 14 [1]. Syntheses and second-order nonlinear optical properties of ruthenium, nickel and gold σ-acetylides of 1,3,5-triethynylbenzene: X-ray crystal structures of $1\text{-}(HC \equiv C)\text{-}3,5\text{-}C_6H_3(\textit{trans-}C \equiv CRuCl(dppm)_2)_2$ and $1,3,5\text{-}C_6H_3(C \equiv CAu(PPh_3))_3$

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Abstract

The complexes $1\text{-}(HC \equiv C)\text{-}3,5\text{-}C_6H_3[M]_2$ ([M] = $\textit{trans-}C \equiv CRuCl(dppm)_2$ (1), $C \equiv CNi(PPh_3)(\eta^5\text{-}C_5H_5)$ (2)) and $1,3,5\text{-}C_6H_3(C \equiv CAu(PPh_3))_3$ (3) have been prepared by extensions of well-established σ-acetylide synthetic methodologies, and 1 and 3 have been structurally characterized. Steric restrictions preclude coordination of three $\textit{trans-}RuCl(dppm)_2$ or $Ni(PPh_3)(\eta^5\text{-}C_5H_5)$ moieties about the central 1,3,5-triethynylbenzene unit, a problem which the smaller $Au(PPh_3)$ group does not experience. The quadratic optical nonlinearities at 1.06 μm have been investigated by hyper-Rayleigh scattering with the C_{2v} symmetry complexes 1 and 2 having significantly larger β_{HRS} than their monometallic [M]C ≡ CPh ([M] = $\textit{trans-}RuCl(dppm)_2$ (4) and $Ni(PPh_3)(\eta^5\text{-}C_5H_5)$ (5)) counterparts. The D_{3h} symmetry octopolar complex 3 has a similar nonlinearity to its dipolar monometallic analogue $Au(C \equiv CPh)(PPh_3)$ (6). Complexes 1, 2 and 3 have λ_{max} similar to 4, 5 and 6 (i.e., no loss of optical transparency is observed), but have significantly larger oscillator strengths for the important optical transitions. © 1997 Elsevier Science S.A.

Keywords: Acetylide; Alkynyl; Susceptibility; Ruthenium; Nickel; Gold; Nonlinear optics

1. Introduction

The classical second-order nonlinear optical (NLO) material design has involved a donor–bridge–acceptor composition. However, attention has recently turned to molecules with three-fold rotation symmetry which can exhibit non-zero β despite being nonpolar [2–5] (it has been shown by an irreducible tensor decomposition that β is composed of both a vector part and an octopolar component). Octopolar molecules with, for example, D_{3h} or T_d symmetry are therefore of interest for their

potential in NLO applications. The major advantages of octopolar compounds are (i) greater likelihood of producing crystals with noncentrosymmetric packing (donor–acceptor molecules have a propensity to align in an antiparallel fashion which opposes dipoles), and (ii) improved nonlinearity/transparency trade-off (due to a decreased conjugation pathway). Examples of octopolar molecules that have been examined for their quadratic NLO response include 1,3,5-triamino-2,4,6-trinitrobenzene, with a Kurtz powder efficiency of 3 × urea which was assumed to be derived from the off-diagonal component β_{zyy} [6,7], subphthalocyanines with $< \beta^2 >^{1/2}$ up to 2000×10^{-30} esu and tetrahedral tin complexes, one example being $Sn(C_6H_4N=NC_6H_4NMe_2)_4$ ($\beta_{xyz} = 159 \times 10^{-30}$ esu) [8].

We have been investigating the NLO properties of ruthenium, gold and nickel σ-acetylide complexes [1,9–21] but have thus far focused on dipolar complexes with a donor–bridge–acceptor composition. We report herein syntheses, X-ray structural studies and molecular quadratic NLO measurements of ruthenium, gold and nickel σ-acetylide complexes derived from 1,3,5-triethynylbenzene, tris-substitution of which will afford octopolar acetylide complexes.

2. Results and discussion

2.1. Syntheses of σ-acetylide complexes

The new σ-acetylide complexes were prepared by extension of previously-established procedures. Thus, reaction of cis-RuCl$_2$(dppm)$_2$ with 1,3,5-triethynylbenzene in the presence of NaPF$_6$ and deprotonation of the intermediate vinylidene complex afforded 1-(HC $\equiv$ C)-3,5-C$_6$H$_3$(trans-C $\equiv$ CRuCl(dppm)$_2$)$_2$ (1) in 57% yield (Scheme 1). Attempts to effect tris-substitution by employing more than three equivalents of cis-RuCl$_2$(dppm)$_2$ per equivalent of 1,3,5-triethynylbenzene, and refluxing toluene rather than dichloromethane solvent were unsuccessful. Similarly, reaction of NiCl(PPh$_3$)(η^5-C$_5$H$_5$) with 1,3,5-triethynylbenzene in the presence of CuI afforded the bis-product 1-(HC $\equiv$ C)-3,5-C$_6$H$_3$(C $\equiv$ CNi(PPh$_3$)(η^5-C$_5$H$_5$))$_2$ (2) in 75% yield with no evidence for the tris-product being formed (Scheme 1). Conversely, reaction of AuCl(PPh$_3$) with 1,3,5-triethynylbenzene in sodium methoxide in methanol solution gave the tris-product 1,3,5-C$_6$H$_3$(C $\equiv$ CAu(PPh$_3$))$_3$ (3) in 79% yield, with no bis-product isolated (Scheme 2). Complexes 1–3 were identified by IR, ^{1}H, ^{31}P NMR, and UV–vis spectroscopy, mass spectrometry, and satisfactory microanalyses, with all spectral data for 1–3 very similar to those of their mononuclear σ-phenylacetylide analogues [12,15,18]. Significantly, 1,3-bis- or 1,3,5-tris-complexation of the 1,3,5-triethynylbenzene leads to a more extensive π-system without extended conjugation and concomitant decrease in energy of λ_{max}; λ_{max} for 1–3 are similar to those of the corresponding phenylacetylide complexes but with an increase in intensity (1: 323 nm (ϵ = 34 000
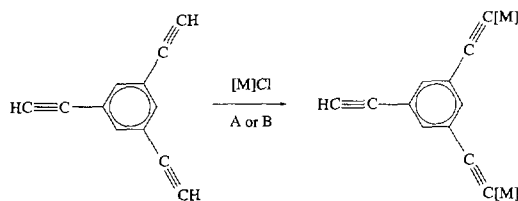
Scheme 1. Syntheses of 1-(HC $\equiv$ C)-3,5-C$_6$H$_3$(C $\equiv$ C[M])$_2$: (A) [M] = cis-RuCl(dppm)$_2$; (i) NaPF$_6$, CH$_2$Cl$_2$, reflux, 2 h, (ii) NEt$_3$; (B) [M] = Ni(PPh$_3$)(η^5-C$_5$H$_5$); CuI, NEt$_3$, 16 h.
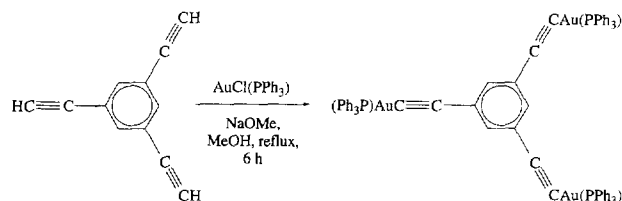
Scheme 2. Synthesis of 1,3,5-C$_6$H$_3$(C $\equiv$ CAu(PPh$_3$))$_3$.

M^{-1} cm^{-1}) c.f. trans-Ru(C $\equiv$ CPh)Cl(dppm)$_2$ (4): 308 nm (ϵ = 17 000 M^{-1} cm^{-1}) [22]; 2: 316 nm (ϵ = 38 000 M^{-1} cm^{-1}) c.f. Ni(C $\equiv$ CPh)(PPh$_3$)(η^5-C$_5$H$_5$) (5): 307 nm (ϵ = 25 000 M^{-1} cm^{-1}) [18]; 3: 298 nm (ϵ = 69 000 M^{-1} cm^{-1}) c.f. Au(C $\equiv$ CPh)(PPh$_3$) (6): 296 nm (ϵ = 13 000 M^{-1} cm^{-1}) [15]). The identities of 1 and 3 were confirmed by single crystal X-ray diffraction studies.

2.2. X-ray structural studies

We have completed X-ray diffraction studies on complexes 1 and 3. Crystallographic data are collected in Table 1 and important geometric parameters are shown in Table 2 (1) and Table 3 (3). ORTEP plots are displayed in Fig. 1 (1) and Fig. 2 (3). We have previously tabulated important structural data for (phosphine)gold and octahedral trans-bis(diphosphine)ruthenium σ-acetylide complexes [12,13,15]. For 1, Ru–P distances [2.305(4)–2.359(4) Å] fall within the range of those previously observed in (diphosphine)ruthenium complexes and all intraphosphine bond lengths and angles are not unusual. Ru–Cl vectors [2.475(3),

Table 1
Crystallographic data for complexes 1 and 3

	1	3
Empirical formula	C$_{117.5}$H$_{92}$Cl$_2$O$_{0.5}$P$_8$Ru$_2$	C$_{66}$H$_{48}$Au$_3$P$_3$
Molecular weight	2032.9	1524.9
Crystal colour, habit	yellow, block	colourless, block
Crystal dim. (mm^3)	0.20 × 0.04 × 0.03	0.4 × 0.3 × 0.2
Space group	$P\bar{1}$ (#2)	$P2_12_12_1$ (#19)
a (Å)	11.315(2)	10.741(7)
b (Å)	20.801(3)	17.621(9)
c (Å)	23.484(4)	30.045(4)
α (°)	73.20(1)	–
β (°)	82.69(1)	–
γ (°)	74.42(1)	–
V (Å^3)	5089(1)	5687(3)
Z	2	4
D_{calc} (g cm^{-3})	1.33	1.78
Trans. factors	0.94–1.00	0.41–1.00
μ (Cu-$K\alpha$) cm^{-1}	44.56	78.71
N	12788	3508
N_o ($I > 3.00\sigma(I)$)	5870	1764
No. variables	1153	319
R	0.047	0.048
R_w	0.052	0.039

Table 2
Selected geometric parameters for complex 1 (Å, °)

Ru(1)–P(1)	2.359(4)	C(10)–C(11)	1.19(1)
Ru(1)–P(2)	2.356(4)	C(20)–C(21)	1.17(1)
Ru(1)–P(3)	2.305(4)	C(30)–C(31)	1.150(9)
Ru(1)–P(4)	2.344(4)	C(11)–C(101)	1.47(1)
Ru(2)–P(5)	2.354(4)	C(21)–C(103)	1.43(1)
Ru(2)–P(6)	2.349(3)	C(31)–C(105)	1.47(2)
Ru(2)–P(7)	2.324(4)	C(101)–C(102)	1.39(1)
Ru(2)–P(8)	2.366(3)	C(102)–C(103)	1.40(1)
Ru(1)–Cl(1)	2.475(3)	C(103)–C(104)	1.38(1)
Ru(2)–Cl(2)	2.487(3)	C(104)–C(105)	1.39(1)
Ru(1)–C(10)	2.01(1)	C(105)–C(106)	1.40(1)
Ru(2)–C(20)	2.02(1)	C(106)–C(101)	1.38(1)
Cl(1)–Ru(1)–P(1)	84.8(1)	Cl(2)–Ru(2)–P(5)	85.2(1)
Cl(1)–Ru(1)–P(2)	82.9(1)	Cl(2)–Ru(2)–P(6)	82.3(1)
Cl(1)–Ru(1)–P(3)	95.1(1)	Cl(2)–Ru(2)–P(7)	95.5(1)
Cl(1)–Ru(1)–P(4)	97.2(1)	Cl(2)–Ru(2)–P(8)	99.1(1)
Cl(1)–Ru(1)–C(10)	178.3(4)	Cl(2)–Ru(2)–C(20)	176.5(3)
P(1)–Ru(1)–P(2)	70.2(1)	P(5)–Ru(2)–P(6)	70.8(1)
P(1)–Ru(1)–P(3)	177.5(1)	P(5)–Ru(2)–P(7)	177.7(1)
P(1)–Ru(1)–P(4)	111.4(1)	P(5)–Ru(2)–P(8)	111.4(1)
P(1)–Ru(1)–C(10)	95.2(4)	P(5)–Ru(2)–C(20)	91.6(3)
P(2)–Ru(1)–P(3)	107.3(1)	P(6)–Ru(2)–P(7)	107.1(1)
P(2)–Ru(1)–P(4)	178.4(1)	P(6)–Ru(2)–P(8)	177.4(1)
P(2)–Ru(1)–C(10)	98.7(3)	P(6)–Ru(2)–C(20)	97.9(3)
P(3)–Ru(1)–P(4)	71.1(1)	P(7)–Ru(2)–P(8)	70.6(1)
P(3)–Ru(1)–C(10)	84.9(4)	P(7)–Ru(2)–C(20)	87.8(3)
P(4)–Ru(1)–C(10)	81.2(3)	P(8)–Ru(2)–C(20)	80.9(3)
Ru(1)–C(10)–C(11)	176(1)	C(20)–C(21)–C(103)	175(1)
C(10)–C(11)–C(101)	179(1)	C(30)–C(31)–C(105)	175(2)
Ru(2)–C(20)–C(21)	175(1)		

Table 3
Selected geometric parameters for complex 3 (Å, °)

Au(1c)–P(1c)	2.265(9)	P(1c)–C(131c)	1.78(2)
Au(1c)–C(1c)	1.95(4)	C(1b)–C(2b)	1.05(3)
Au(1b)–P(1b)	2.272(9)	C(1c)–C(2c)	1.16(5)
Au(1b)–C(1b)	2.02(3)	C(1a)–C(2a)	1.45(2)
Au(1a)–P(1a)	2.26(1)	C(2a)–C(3a)	1.36(3)
Au(1a)–C(1a)	1.99(2)	C(2c)–C(3c)	1.49(5)
P(1a)–C(111a)	1.84(3)	C(2b)–C(3b)	1.48(3)
P(1a)–C(121a)	1.79(3)	C(3b)–C(4)	1.45(4)
P(1a)–C(131a)	1.79(2)	C(3b)–C(5)	1.33(4)
P(1b)–C(111b)	1.86(3)	C(3c)–C(5)	1.40(4)
P(1b)–C(121b)	1.79(2)	C(3c)–C(6)	1.47(4)
P(1b)–C(131b)	1.82(3)	C(3a)–C(4)	1.35(4)
P(1c)–C(111c)	1.79(2)	C(3a)–C(6)	1.32(4)
P(1c)–C(121c)	1.77(2)		
P(1c)–Au(1c)–C(1c)	174(1)	C(1a)–C(2a)–C(3a)	176(4)
P(1b)–Au(1b)–C(1b)	173.3(9)	C(1c)–C(2c)–C(3c)	172(4)
P(1a)–Au(1a)–C(1a)	171(1)	C(1b)–C(2b)–C(3b)	163(3)
Au(1a)–P(1a)–C(111a)	109(1)	C(2b)–C(3b)–C(4)	120(3)
Au(1a)–P(1a)–C(121a)	115(1)	C(2b)–C(3b)–C(5)	126(3)
Au(1a)–P(1a)–C(131a)	114(1)	C(4)–C(3b)–C(5)	112(3)
Au(1b)–P(1b)–C(111b)	112(1)	C(2c)–C(3c)–C(5)	128(3)
Au(1b)–P(1b)–C(121b)	116(1)	C(2c)–C(3c)–C(6)	120(3)
Au(1b)–P(1b)–C(131b)	113(1)	C(5)–C(3c)–C(6)	111(3)
Au(1c)–P(1c)–C(111c)	111(1)	C(2a)–C(3a)–C(4)	114(3)
Au(1c)–P(1c)–C(121c)	114(1)	C(2a)–C(3a)–C(6)	118(3)
Au(1c)–P(1c)–C(131c)	115(1)	C(4)–C(3a)–C(6)	128(3)
Au(1b)–C(1b)–C(2b)	172(4)	C(3b)–C(4)–C(3a)	117(3)
Au(1c)–C(1c)–C(2c)	169(4)	C(3b)–C(5)–C(3c)	131(3)
Au(1a)–C(1a)–C(2a)	164(3)	C(3c)–C(6)–C(3a)	117(3)

2.487(3) Å] are similarly unremarkable. Bonds between ruthenium and the acetylide α-carbons [2.01(1), 2.02(1) Å] are normal for a *trans*-chlorobis(diphosphine)-ruthenium σ-acetylide [12]. Bonds between the alkynyl carbons [C(10)–C(11) 1.19(1) Å; C(20)–C(21) 1.17(1) Å] are 'normal' with the comparable bond in the terminal alkyne [C(30)–C(31) 1.150(9) Å] slightly shorter although differences are within 3σ. The ruthenium atoms are 0.151 Å (Ru(1)) and 0.372 Å (Ru(2)) from coplanarity with the diethynylethynebenzene ring.

For 3, the Au–P distances [2.26(1), 2.265(9), 2.272(9) Å] are similar to those in mononuclear (phosphine)gold acetylides [15]; other bond lengths and angles are not unusual, with the error factors precluding a detailed analysis. While Au(1a) and Au(1c) do not deviate significantly from coplanarity with the central triethynylbenzene ring [0.0471 Å and 0.0936 Å, respectively], Au(1b) is displaced significantly [0.9742 Å] and its phosphine even further removed from coplanarity [deviation of P(1b): 1.7416 Å], consistent with significant steric strain about the central ring. Although 1,3,5-benzenetri(ethynylplatinum) complexes been reported previously [23], complexes 1 and 3 are the first structurally characterized organometallic derivatives of 1,3,5-triethynylbenzene (several organic molecules with this structural unit have been characterized by X-ray crystallography [24–27]).
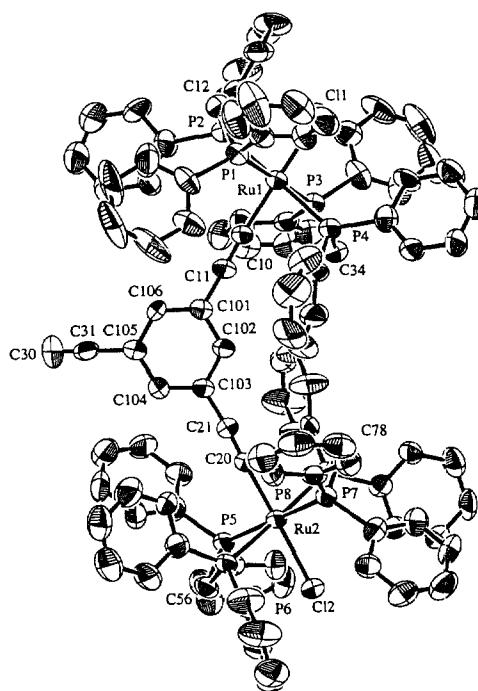

Fig. 1. Molecular structure and atomic labelling scheme of 1-(HC ≡ C)-3,5-C$_6$H$_3$(C ≡ CRuCl(dppm)$_2$)$_2$ (1). 50% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms are removed for clarity.
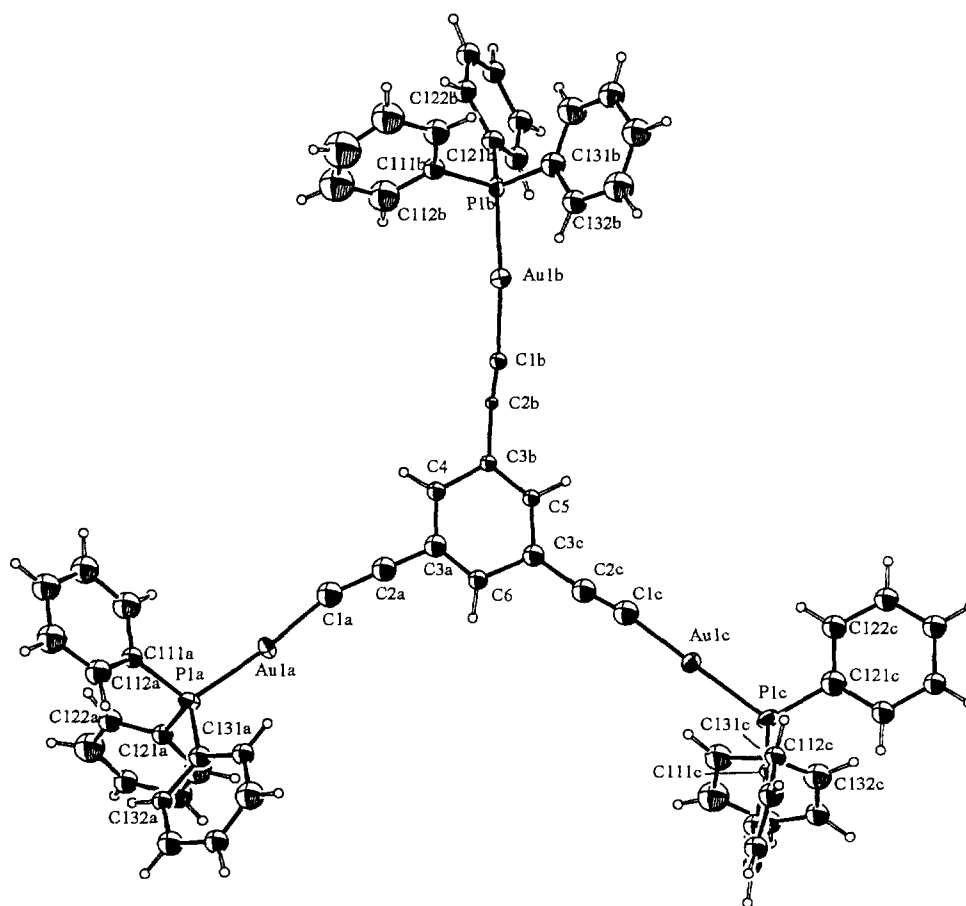
Fig. 2. Molecular structure and atomic labelling scheme of $1,3,5$-$C_6H_3(C \equiv CAu(PPh_3))_3$ (3). 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii.

2.3. Hyperpolarizabilities

The optical nonlinearities of **1–3** were measured by hyper-Rayleigh scattering; results are listed in Table 4, together with relevant data from related monometallic σ-phenylacetylide complexes. [Note: it should be emphasized that the two-state model has been utilized for calculating frequency independent values, but it may not be adequate for organometallic systems; it 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 is not useful where there are several dominant optical transitions close to 2ω. For the present

Table 4
Experimental nonlinear optical response and linear optical spectroscopic parameters [a]

Complex	λ (nm) ($\epsilon(10^4 \text{ L mol}^{-1} \text{ cm}^{-1})$)	$\beta(10^{-30} \text{ esu})$		Ref.
		exptl [b]	corr [c]	
trans-RuCl(C $\equiv$ CPh)(dppm)$_2$ (4)	308 (1.7)	20	12	[22]
1-(HC $\equiv$ C)-3,5-C_6H_3(*trans*-C $\equiv$ CRuCl(dppm)$_2$)$_2$ (1)	323 (3.4), 267 (6.6)	42 [d]	24	
Ni(C $\equiv$ CPh)(PPh$_3$)(η^5-C_5H_5) (5)	307 → (2.5)	24 [e]	15	[18]
1-(HC $\equiv$ C)-3,5-C_6H_3(C $\equiv$ CNi(PPh$_3$)(η^5-C_5H_5))$_2$ (2)	316 (3.8)	94	55	
Au(C $\equiv$ CPh)(PPh$_3$) (6)	296 (1.3), 282 (3.0), 268 (2.7)	6	4	[15]
$1,3,5$-C_6H_3(C $\equiv$ CAu(PPh$_3$))$_3$ (3)	298 (6.9), 290 (9.4), 276 (7.6), 263 (4.5), 239 (9.6)	6 [f]	4	

[a] Solutions in thf. [b] HRS at 1.06 μm; all values $\pm 10\%$ except where indicated. [c] HRS experimental data corrected for resonance enhancement 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] Upper bound only: deconvolution of SHG and fluorescence contribution could not be effected. [e] Value $\pm 20\%$. [f] Upper bound only: deconvolution of SHG and fluorescence contribution could not be effected. For a discussion regarding dipolar and octopolar molecules, see reference [2]. Value $\pm 60\%$.

case, however, λ_{max} is far removed from 2ω, charge transfer involving the phosphine or cyclopentadienyl ligands will not result in appreciable charge displacement, and the two-level correction may have some validity]. Complexes 1 and 2 both have β_{HRS} (experimental and two-level corrected) values significantly larger than those of their monometallic analogues 4 and 5. Although the data for 1 are complicated by the presence of fluorescence, there is no doubt that the nonlinearity for 2 is much larger than that for 5. This is initially a surprising result; however, organic chromophores with C_{2v} symmetry have been recently reported to have larger hyperpolarizabilities than would be predicted on the basis of their absorption maxima [28]. Significantly, it was proposed that these organic compounds possess two excited states close to each other in energy, both of which contribute to the nonlinearity; one critical piece of evidence in that case was unusually large oscillator strengths for λ_{max}. In the present case, a significantly increased oscillator strength of λ_{max} is observed in progressing from 4, 5 to 1, 2, which results in increased nonlinearity, but it is not clear if this results from more than one electronic state. Molecular orbital calculations may shed light on this. We are proceeding to synthesize 5-nitro-substituted analogues (i.e., incorporation of a strong acceptor moiety) to enable a more detailed study to be undertaken.

Complex 3 has a nonlinearity about the same as that of 6 despite lacking a molecular dipole. Unfortunately, problems with fluorescence (the stated value is an upper bound to the nonlinearity) and large experimental error preclude a more detailed analysis. Introduction of, for example, 2,4,6-trinitro substitution at the central ring may be required to establish the potential of these octopolar organometallic complexes, but it is not certain that this is sterically achievable. Even with complex 6, it should be noted that it is possible that the steric compression observed in the structural study removes the idealized molecular symmetry on the timeframe of the NLO measurement. ^{31}P NMR data (one singlet) are consistent with D_{3h} symmetry on the NMR timescale (ms), but the molecular symmetry on the NLO timescale (ns) is unknown.

Quadratic nonlinearities of organometallics have been reviewed [29]; for complexes lacking a donor–acceptor composition, the molecular first hyperpolarizability for 2 is the largest value for an organotransition metal complex thus far (both experimental and two-level corrected), and amongst the largest data for organometallics (the only larger data are for the main group compounds $Sn(4,4'-C_6H_4N=NC_6H_4NMe_2)_4$ ($\beta = 159 \times 10^{-30}$ esu, $\beta_0 = 47.5 \times 10^{-30}$ esu) and $SnPh_3(4,4'-C_6H_4N=NC_6H_4NMe_2)$ ($\beta = 181 \times 10^{-30}$ esu, $\beta_0 = 57 \times 10^{-30}$ esu) [4]. Significantly, attaching two ligated metal units to the central 1,3,5-triethynylbenzene core leads to nonlinearities up to four times that of the

monometallic analogues, but with negligible shift to low energy of λ_{max}. Furthermore, extending the π-system without extending the conjugation results in a dramatic increase in molar absorptivity for λ_{max} in 1–3 over those of their monometallic analogues. These results then may suggest a design strategy for polymetallic NLO chromophores: utilizing 1,3,(5)-substituted aryl bridges (leading to, for example, dendrimers) rather than the extensively investigated 1,4-disubstituted aryl systems (en route to linear polymers) as building blocks may circumvent the optical transparency/nonlinearity trade-off usually manifested upon 1,4-oligomerization. Our results also suggest that enlarged dendrimeric cores are required to accommodate three suitably ligated metal centres, in order to explore the full potential of octopolar organometallic species in nonlinear optics. Further studies of the optical nonlinearities of organometallic complexes are currently underway.

3. Experimental section

3.1. General

All organometallic reactions were carried out under an atmosphere of nitrogen with the use of standard Schlenk techniques; no attempt was made to exclude air during work-up of organometallic products. cis-RuCl$_2$-(dppm)$_2$ [30], AuCl(PPh$_3$) [31], and NiCl(PPh$_3$)(η^5-C$_5$H$_5$) [32] were prepared by literature methods. 1,3,5-Tribromobenzene (Aldrich) was used as received. NaPF$_6$ (Aldrich) was recrystallized from acetonitrile. 1,3,5-Triethynylbenzene was prepared from 1,3,5-tribromobenzene by adapting the preparation of 1,4-diethynylbenzene [33]. Dichloromethane was dried and distilled over calcium hydride. Petroleum ether refers to a fraction of boiling range 60–80°C. 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) at the Research School of Chemistry, Australian National University; peaks are reported as m/z (assignment, relative intensity). Microanalyses were carried out at the Research School of Chemistry, Australian National University. Infrared spectra were recorded using a Perkin-Elmer System 2000 FTIR spectrometer. UV–vis spectra were recorded using a Cary 5 spectrophotometer. ^{1}H and ^{31}P NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer and are referenced to residual CHCl$_3$ (7.24 ppm) or external 85% H$_3$PO$_4$ (0.0 ppm), respectively.

3.2. Syntheses

3.2.1. Synthesis of 1-(HC ≡ C)-3,5-C$_6$H$_3$(trans-C ≡ CRuCl(dppm)$_2$)$_2$ (1)

cis-RuCl$_2$(dppm)$_2$ (400 mg, 0.43 mmol), 1,3,5-triethynylbenzene (30 mg, 0.20 mmol) and NaPF$_6$ (150

mg, 0.90 mmol) were refluxed in CH_2Cl_2 (40 ml) for 2 h, and the solution allowed to cool to room temperature. NEt_3 (3 ml) was added and the mixture was passed through an alumina plug. The filtrate was reduced to dryness, dissolved in CH_2Cl_2/petroleum ether 40/60 (100 ml) and passed through an alumina plug. The volume was reduced to remove the CH_2Cl_2, causing the precipitation of the product **1** which was collected as a yellow powder by filtration (225 mg, 57%). Anal. calc. for $C_{112}H_{92}Cl_2P_8Ru_2$: C 68.67, H 4.74%. Found: C 68.38, H 5.20%. IR: (CH_2Cl_2) $\nu(C \equiv C)$ 2066 cm^{-1}. UV–vis: λ (nm) (ϵ (M^{-1} cm^{-1})) (thf); 323 (33 600), 267 (65 600). ^{1}H NMR: (δ, 300 MHz, CDCl$_3$); 2.87 (s, 1H, HC $\equiv$), 4.91 (m, 8H, CH$_2$), 6.93–7.45 (m, 83H, Ph); resonances for the three hydrogens on the central aromatic ring are obscured. ^{31}P NMR: (δ, 121 MHz, CDCl$_3$); -5.6. FAB MS; m/z (fragment, relative intensity): 1958 ([M]$^+$, 13), 1054 ([M–RuCl(dppm)$_2$]$^+$, 4), 905 ([RuCl(dppm)$_2$]$^+$, 24), 869 ([Ru(dppm)$_2$]$^+$, 100). Crystals of **1** suitable for diffraction analysis were grown by vapour diffusion of ether into a toluene solution at room temperature.

3.2.2. Attempted synthesis of 1,3,5-C_6H_3(trans-$C \equiv CRuCl(dppm)_2$)$_3$

Following the same procedure as for the synthesis of **1**, cis-RuCl$_2$(dppm)$_2$ (200 mg, 0.21 mmol), 1,3,5-triethynylbenzene (10 mg, 0.07 mmol) and NaPF$_6$ (150 mg, 0.90 mmol) in refluxing CH_2Cl_2 (30 ml) afforded **1** (80 mg, 58%), with no evidence for tris-substitution by ^{1}H, ^{31}P NMR or FAB MS of the crude reaction mixture. cis-RuCl$_2$(dppm)$_2$ (200 mg, 0.21 mmol), 1,3,5-triethynylbenzene (10 mg, 0.07 mmol) and NaPF$_6$ (150 mg, 0.90 mmol) in refluxing toluene (30 ml) caused decomposition without formation of the tris-substituted product.

3.2.3. Synthesis of 1-(HC $\equiv$ C)-3,5-C_6H_3($C \equiv CNi(PPh_3)(\eta^5$-$C_5H_5$))$_2$ (2)

NiCl(PPh$_3$)(η^5-C$_5$H$_5$) (170 mg, 0.40 mmol), 1,3,5-triethynylbenzene (20 mg, 0.13 mmol) and CuI (5 mg, 0.03 mmol) were stirred in NEt$_3$ (20 ml) for 16 h. The solvent was removed under reduced pressure and the residue extracted with dichloromethane (20 ml), and then filtered through a plug of silica, eluting with acetone. Petroleum ether (10 ml) was added to the eluate and the dichloromethane removed under reduced pressure, precipitating the product which was collected by filtration (90 mg, 75%). Anal. calc. for $C_{58}H_{44}Ni_2P_2$: C 71.14, H 4.54. Found: C 71.19, H 4.50%. IR: (CH_2Cl_2) $\nu(C \equiv C)$ 2089 cm^{-1}. UV–vis: λ (nm) (ϵ (M^{-1} cm^{-1})) (thf); 316 (38 000). ^{1}H NMR: (δ, 300 MHz, CDCl$_3$); 2.75 (s, 1H, HC $\equiv$), 5.20 (s, 10H, C$_5$H$_5$), 7.24–7.69 (m, 33H, Ph, C$_6$H$_3$). ^{31}P NMR: (δ, 121 MHz, CDCl$_3$); 41.4. FAB MS; m/z (fragment, relative intensity): 920 ([M]$^+$, 5), 656 ([M–PPh$_3$]$^+$, 20), 385 ([Ni(PPh$_3$)(C$_5$H$_5$)]$^+$, 100).

3.2.4. Synthesis of 1,3,5-C_6H_3($C \equiv CAu(PPh_3)$)$_3$ (3)

AuCl(PPh$_3$) (200 mg, 0.40 mmol) and 1,3,5-triethynylbenzene (20 mg, 0.13 mmol) were added to a methanol solution of sodium methoxide (10 ml, 0.5 M), and the mixture was stirred at reflux for 6 h. The methanol was removed, the residue dissolved in dichloromethane (20 ml), and then passed through an alumina column, eluting with dichloromethane (50 ml). Petroleum ether (20 ml) was added to the eluate and the volume reduced, precipitating the product which was filtered to afford a white powder of **3** (160 mg, 79%). Anal. Calc. for $C_{66}H_{48}Au_3P_3$: C 51.98, H 3.13%. Found: C 51.69, H 2.89%. IR: (CH_2Cl_2) $\nu(C \equiv C)$ 2120 (vw) cm^{-1}. UV–vis: λ (nm) (ϵ (M^{-1} cm^{-1})) (thf); 298 (69 200), 290 (93 600), 276 (76 300), 263 (47 800), 239 (96 300). ^{1}H NMR: (δ, 300 MHz, CDCl$_3$); 7.40–7.58 (m, 48H, Ph, C$_6$H$_3$). ^{31}P NMR: (δ, 121 MHz, CDCl$_3$); 43.0. FAB MS; m/z (fragment, relative intensity): 1983 ([M + Au(PPh$_3$)]$^+$, 3), 1525 ([M + H]$^+$, 13), 1067 ([M–Au(PPh$_3$)]$^+$, 21), 721 ([Au(PPh$_3$)$_2$]$^+$, 86), 459 ([Au(PPh$_3$)]$^+$, 100). Crystals of **3** suitable for diffraction analysis were grown by slow evaporation of dichloromethane from a dichloromethane/toluene solution at room temperature.

3.3. X-ray structure determinations

Unique diffractometer data sets were obtained using the $\omega - 2\theta$ scan technique (graphite monochromated CuKα radiation; 1.54178 Å; $2\theta_{max} = 50.1$; 295 K) and yielded N independent reflections, N_o of these with $I \geq 3.00\sigma(I)$ being considered 'observed' and used in full matrix least squares refinement; an empirical psi-type absorption correction was applied in each case. Anisotropic thermal parameters were refined for the non-hydrogen atoms; (x, y, z, U$_{iso}$)$_H$ were included constrained at estimated values. Conventional residuals R and R_w on $|F|$ are given; the weighting function $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [S^2(C + 4B) + (pF_o^2)^2]/Lp^2$ (S = scan rate, C = peak count, B = background count, $p = p$ factor determined experimentally from standard reflections) was employed. Computation used the teXsan package [34]. Specific data collection, solution and refinement parameters are given in Table 1. Pertinent results are given in the figures and tables. Tables of atomic coordinates and thermal parameters and complete lists of bond lengths and angles for non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.

3.4. 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 under $90°$ 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 thf using p-nitroaniline ($\beta = 21.4 \times 10^{-30}$ cm^5 esu^{-1}) [35] as a reference. Further details of the experimental procedure have been reported elsewhere [36–38].

Acknowledgements

References

[1] R.H. Naulty, M.P. Cifuentes, M.G. Humphrey, S. Houbrechts, C. Boutton, A. Persoons, G.A. Heath, D.C.R. Hockless, B. Luther-Davies, M. Samoc, J. Chem. Soc., Dalton Trans., in press.

[2] M. Joffre, D. Yaron, R.J. Silbey, J. Zyss, J. Chem. Phys. 97 (1992) 5607.

[3] T. Verbiest, K. Clays, C. Samyn, J. Wolff, D. Reinhoudt, A. Persoons, J. Am. Chem. Soc. 116 (1994) 9320.

[4] S. Stadler, C. Bräuchle, S. Brandl, R. Gompper, Chem. Mater. 8 (1996) 414.

[5] J. Zyss, I. Ledoux, Chem. Rev. 94 (1994) 77.

[6] I. Ledoux, J. Zyss, J. Seigal, J. Brienne, J.-M. Lehn, Chem. Phys. Lett. 172 (1990) 400.

[7] I.G. Voigt-Martin, G. Li, A. Yakimanski, G. Schulz, J.J. Wolff, J. Am. Chem. Soc. 118 (1996) 12830.

[8] M. Lequan, C. Branger, J. Simon, T. Thami, E. Chauchard, A. Persoons, Adv. Mater. 6 (1994) 851.

[9] I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, Organometallics 14 (1995) 3970.

[10] I.R. Whittall, M.G. Humphrey, A. Persoons, S. Houbrechts, Organometallics 15 (1996) 1935.

[11] I.R. Whittall, M.G. Humphrey, M. Samoc, J. Swiatkiewicz, B. Luther-Davies, Organometallics 14 (1995) 5493.

[12] A.M. McDonagh, I.R. Whittall, M.G. Humphrey, B.W. Skelton, A.H. White, J. Organomet. Chem. 519 (1996) 229.

[13] A.M. McDonagh, I.R. Whittall, M.G. Humphrey, D.C.R. Hockless, B.W. Skelton, A.H. White, J. Organomet. Chem. 523 (1996) 33.

[14] A.M. McDonagh, M.P. Cifuentes, I.R. Whittall, M.G. Humphrey, M. Samoc, B. Luther-Davies, D.C.R. Hockless, J. Organomet. Chem. 526 (1996) 99.

[15] I.R. Whittall, M.G. Humphrey, S. Houbrechts, A. Persoons, D.C.R. Hockless, Organometallics 15 (1996) 5738.

[16] I.R. Whittall, M.G. Humphrey, M. Samoc, B. Luther-Davies, Angew. Chem., Int. Ed. Engl. 36 (1997) 370.

[17] I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G.A. Heath, D.C.R. Hockless, J. Organomet. Chem., in press.

[18] I.R. Whittall, M.P. Cifuentes, M.G. Humphrey, B. Luther-Davies, M. Samoc, S. Houbrechts, A. Persoons, G.A. Heath, D. Bogsányi, Organometallics 16 (1997) 2631.

[19] I.R. Whittall, M.G. Humphrey, M. Samoc, B. Luther-Davies, D.C.R. Hockless, J. Organomet. Chem., in press.

[20] S. Houbrechts, K. Clays, A. Persoons, V. Cadierno, M.P. Gamasa, J. Gimeno, I.R. Whittall, M.G. Humphrey, Proc. SPIE-Int. Soc. Opt. Eng. 2852 (1996) 98.

[21] M.G. Humphrey, Chem. Aust. 63 (1996) 442.

[22] A.M. McDonagh, M.G. Humphrey, S. Houbrechts, A. Persoons, unpublished results.

[23] M.S. Khan, D.J. Schwartz, N.A. Pasha, A.K. Kakkar, B. Lin, P.R. Raithby, J. Lewis, Z. Anorg. Allg. Chem. 616 (1992) 121.

[24] R. Diercks, J.C. Armstrong, R. Boese, K.P.C. Vollhardt, Angew. Chem., Int. Ed. Engl. 25 (1986) 268.

[25] R. Boese, J.R. Green, J. Mittendorf, D.L. Mohler, K.P.C. Vollhardt, Angew. Chem., Int. Ed. Engl. 31 (1992) 1643.

[26] S.A. Bourne, M.R. Caira, L.R. Nassimbeni, M. Sakamoto, K. Tanaka, F. Toda, J. Chem. Soc., Perkin Trans. 2 (1994) 1899.

[27] J.T. Mague, H.E. Ensley, S. Mahadevan, Acta Cryst. C 51 (1995) 2595.

[28] C.R. Moylan, S. Ermer, S.M. Lovejoy, I.-H. McComb, D.S. Leung, R. Wortmann, P. Krdmer, R.J. Twieg, J. Am. Chem. Soc. 118 (1996) 12950.

[29] I.R. Whittall, A.M. McDonagh, M.G. Humphrey, M. Samoc, Adv. Organomet. Chem., (1997) in press.

[30] B. Chaudret, G. Commenges, R. Poilblanc, J. Chem. Soc., Dalton Trans., (1984) 1635.

[31] M.I. Bruce, B.K. Nicholson, O. Bin Shawkataly, Inorg. Synth. 26 (1989) 324.

[32] K.W. Barnett, J. Chem. Educ. 51 (1974) 422.

[33] S. Takahashi, Y. Kuroyama, K. Sonogashira, N. Hagihara, Synthesis, (1980) 627.

[34] teXsan: Single Crystal Structure Analysis Software, Version 1.7-3, (1995), Molecular Structure Corporation, The Woodlands, TX.

[35] M. Stähelin, D.M. Burland, J.E. Rice, Chem. Phys. Lett. 191 (1992) 245.

[36] E. Hendrickx, C. Dehu, K. Clays, J.L. Brédas, A. Persoons, Polymers for Second-Order Nonlinear Optics, G.A. Lindsay, K.D. Singer (Eds.), ACS Symp. Series 601, Washington, DC, 1995, p. 82.

[37] K. Clays, A. Persoons, Rev. Sci. Instrum. 63 (1992) 3285.

[38] S. Houbrechts, K. Clays, A. Persoons, Z. Pikramenou, J.-M. Lehn, Chem. Phys. Lett. 258 (1996) 485.