

Organometallic complexes for non-linear optics VII¹. Cubic optical non-linearities of octahedral *trans*-bis(bis(diphenylphosphino)methane)ruthenium acetylide complexes; X-ray crystal structure of *trans*-[Ru(C≡CPh)(4-C≡CC₆H₄NO₂)(dppm)₂]

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Received 9 April 1996

Abstract

Cubic molecular optical non-linearities of a systematically varied series of octahedral bis(bis(diphenylphosphino)methane)ruthenium σ -acetylide complexes have been determined by the Z-scan technique: the influence on the non-linear response of sequential replacement of chloro by acetylide ligand in *trans*-[RuCl₂(dppm)₂] and acetylide chain length in proceeding from 4-nitrophenyl- to 4-nitrobiphenyl- and 4-nitro-(*E*)-stilbenylacetylide has been studied. The first X-ray structural study of an unsymmetrical bis(acetylide) complex of this type, *trans*-[Ru(C≡CPh)(4-C≡CC₆H₄NO₂)(dppm)₂], is reported and confirms the *trans*-disposed stereochemistry of the alkynyl ligands.

Keywords: Ruthenium; Acetylide; Alkynyl; Non-linear optics; Cubic hyperpolarizabilities; Crystal structure

1. Introduction

New materials with large non-linear optical (NLO) responses are required for applications in photonics. Attention has recently turned to organometallic compounds, but the vast majority of such studies have been concerned with quadratic optical non-linearities – third-order responses are little investigated [2,3]. We have commenced a detailed investigation of the NLO behaviour of organometallic compounds [1,4–8], and have recently reported the third-order molecular hyperpolarizabilities of systematically-varied (cyclopentadienyl)bis(phosphine)ruthenium acetylide complexes [6];

for these complexes, the presence of acetylide ligands incorporating the strong acceptor group NO₂ gave rise to enhanced third-order responses. The extended conjugation present in octahedral *trans*-bis(acetylide)-ruthenium complexes could contribute to heightened third-order non-linear optical response. With this in mind, we have now extended our investigations of cubic molecular optical non-linearities to include octahedral bis(diphosphine)ruthenium σ -acetylide complexes of general formula *trans*-[Ru(4-C≡CC₆H₄R)X-(dppm)₂] (X = Cl, R = NO₂, 4-C₆H₄NO₂, (*E*)-4-CH=CHC₆H₄NO₂; X = 4-C≡CC₆H₄R, R = NO₂, 4-C₆H₄NO₂, (*E*)-4-CH=CHC₆H₄NO₂). The results of these studies are detailed below, together with the first structural determination of an unsymmetrical bis(acetylide) complex of this type, *trans*-[Ru(C≡CPh)(4-C≡CC₆H₄NO₂)(dppm)₂].

¹ For Part VI, see Ref. [1].

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2. Results and discussion

2.1. Syntheses of octahedral bis(dppm)ruthenium acetylide complexes and X-ray structural study of *trans*-[Ru(C≡CPh)(4-C≡CC₆H₄NO₂)(dppm)₂] (8)

The complexes studied are of general formula *trans*-[Ru(4-C≡CC₆H₄R)X(dppm)₂] (X = Cl, R = NO₂ (2), 4-C₆H₄NO₂ (3), (*E*)-4-CH=CHC₆H₄NO₂ (4); X = 4-C≡CC₆H₄R, R = NO₂ (5), 4-C₆H₄NO₂ (6), (*E*)-4-CH=CHC₆H₄NO₂ (7); X = C≡CPh, R = NO₂ (8)) and were synthesized by literature procedures (Scheme 1).

Complex 8 is the first unsymmetrical bis(acetylide) complex with one alkynyl ligand bearing the prototypical organic acceptor 4-C₆H₄NO₂, and is of interest as a model donor-acceptor complex for quadratic optical non-linearities. Computational estimations of its second-order performance have been reported [1], but at the time of this earlier report no structural study was available, a deficiency which the current work has now remedied. The solid state structure of 8 is shown in Fig. 1, atomic coordinates are listed in Table 1 and selected bond lengths and angles are given in Table 2. The structural study confirms the octahedral geometry at ruthenium and *trans*-disposed acetylide ligands. The ruthenium atom sits on a crystallographic inversion centre; the acetylide ligands are consequently disordered. The elongation of the acetylide ligand thermal ellipsoids along the C(1)–Ru–C(1) axis is possibly consistent with a subtle difference in Ru–C(1) parameter on replacing arylacetylide 4-H by the electron-withdrawing nitro substituent, but any further discussion of intraacetylide bond lengths and angles is not warranted. The Ru–P distances [2.339(3), 2.333(3) Å] and ∠P(1)–Ru(1)–P(2) at chelating dppm [70.59(9)°] are not unusual, being similar to values for the previously

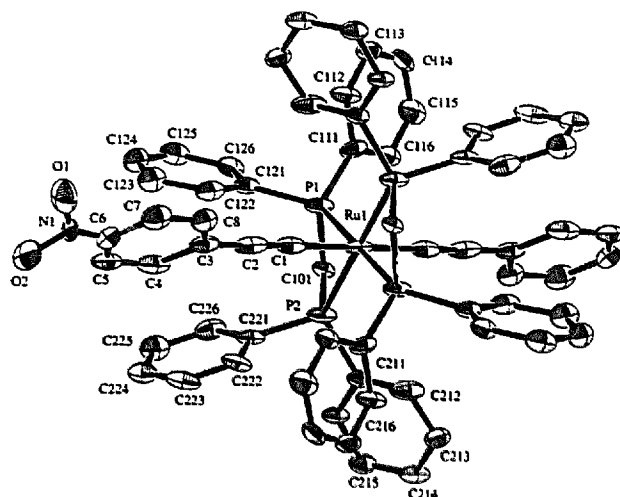
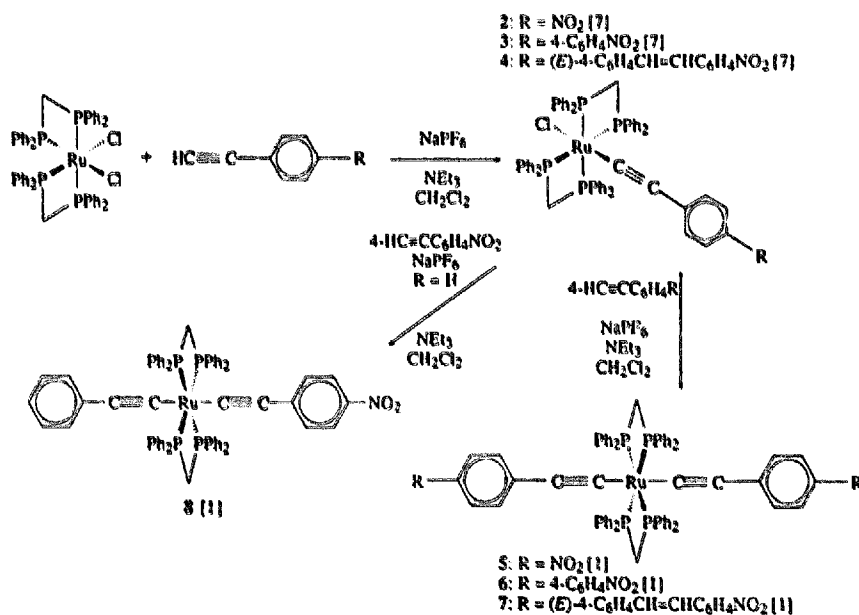


Fig. 1. Molecular geometry and atomic labelling scheme for *trans*-[Ru(C≡CPh)(4-C≡CC₆H₄NO₂)(dppm)₂] (8). 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.

reported *trans*-[Ru(4,4'-C≡CC₆H₄C₆H₄NO₂)Cl(dppm)₂] (3) [2.350(1), 2.361(1), 2.330(1), 2.358(1) Å; 71.63(5), 71.85(5)°] [7]. While the focus of our investigations is molecular optical non-linearities, crystal packing in these complexes is of interest as an indicator of bulk material quadratic response; for 8, though, the crystallographic disorder has removed the possibility of examining molecular orientation in the crystal lattice.

2.2. Cubic optical non-linearities by Z-scan measurements

The third-order non-linearities were evaluated by the Z-scan technique [9]. We have previously utilized Z-scan



Scheme 1.

Table 1

Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in *trans*-[Ru(C≡CPh)(4-C≡CC₆H₄NO₂)(dppm)₂] (8)

Atom	x	y	z	B _{eq}
Ru(1)	1.0000	0.0000	1.0000	5.25(2)
P(1)	0.7438(2)	0.0437(2)	1.1055(2)	5.25(5)
P(2)	0.8890(2)	-0.1221(2)	0.9586(2)	5.19(5)
O(1) *	1.354(2)	-0.451(1)	1.575(1)	10.4(5)
O(2) *	1.262(3)	-0.572(2)	1.543(2)	15.1(8)
N(1) *	1.297(3)	-0.484(2)	1.524(2)	11.7(7)
C(1)	1.0813(8)	-0.1177(8)	1.1182(8)	5.4(2)
C(2)	1.1315(8)	-0.1883(9)	1.1883(9)	5.8(2)
C(3)	1.1817(9)	-0.2676(8)	1.2678(8)	6.1(2)
C(4)	1.119(1)	-0.3614(9)	1.3201(9)	7.5(3)
C(5)	1.163(1)	-0.4371(9)	1.4038(10)	8.3(3)
C(6)	1.273(2)	-0.428(1)	1.442(1)	8.9(4)
C(7)	1.339(1)	-0.3382(10)	1.3952(9)	7.9(3)
C(8)	1.2940(9)	-0.2587(9)	1.3088(8)	6.7(3)
C(101)	0.6974(7)	-0.0235(5)	1.0071(6)	4.2(1)
C(111)	0.6268(8)	0.1930(7)	1.1177(7)	5.7(2)
C(112)	0.6242(9)	0.2502(7)	1.2065(7)	6.7(2)
C(113)	0.535(1)	0.3597(9)	1.2221(9)	8.1(3)
C(114)	0.455(1)	0.4180(7)	1.148(1)	8.1(3)
C(115)	0.4610(10)	0.3640(7)	1.0622(9)	7.6(2)
C(116)	0.5473(9)	0.2547(7)	1.0464(8)	5.6(2)
C(121)	0.6546(8)	-0.0245(7)	1.2463(7)	5.3(1)
C(122)	0.7361(9)	-0.1031(8)	1.3045(8)	6.0(2)
C(123)	0.667(1)	-0.1646(8)	1.4107(8)	7.3(2)
C(124)	0.509(1)	-0.1321(9)	1.4513(8)	7.4(3)
C(125)	0.4277(9)	-0.0500(9)	1.3922(9)	7.2(3)
C(126)	0.4971(8)	0.0071(7)	1.2867(8)	6.6(2)
C(211)	0.9168(7)	-0.1521(6)	0.8120(7)	4.8(1)
C(212)	1.0104(9)	-0.1101(8)	0.7227(7)	7.0(2)
C(213)	1.0309(10)	-0.1292(7)	0.6095(7)	6.7(2)
C(214)	0.9586(9)	-0.1982(8)	0.5928(8)	6.6(2)
C(215)	0.8656(9)	-0.2478(7)	0.6861(7)	5.9(2)
C(216)	0.8437(8)	-0.2213(6)	0.7961(7)	5.3(2)
C(221)	0.8820(8)	-0.2583(6)	1.0448(7)	5.4(1)
C(222)	1.0186(8)	-0.3398(7)	1.0417(8)	6.2(2)
C(223)	1.0222(10)	-0.4457(8)	1.1055(9)	6.9(2)
C(224)	0.893(1)	-0.4726(8)	1.1725(8)	6.7(2)
C(225)	0.755(1)	-0.3940(9)	1.1771(9)	7.7(3)
C(226)	0.7521(8)	-0.2836(8)	1.1120(7)	6.4(2)

* Population 0.5.

$$B_{eq} = (8/3)\pi^2(U_{11}(aa^*)^2 + U_{22}(bb^*)^2 + U_{33}(cc^*)^2 + 2U_{12}aa^*bb^*\cos\gamma + 2U_{13}aa^*c^*\cos\beta + 2U_{23}bb^*c^*\cos\alpha).$$

and degenerate four-wave mixing (DFWM) to evaluate non-linearities of (cyclopentadienyl)bis(phosphine)ruthenium acetylide complexes [6]; Z-scan has a significant advantage over the more widely used DFWM in that the signs of the NLO susceptibility components (both real and imaginary) are accessible without the need to carry out measurements on many solutions with a wide range of concentrations. Its shortcoming is in not providing information about the temporal behaviour of the NLO response. Our previous studies with ruthenium acetylide complexes revealed femtosecond responses, consistent with the observed signals being electronic rather than thermal in origin. A good agreement be-

tween the Z-scan and DFWM results indicated that the same phenomena are observed by both techniques.

Results of measurements for 1–7 are given in Table 3, together with previously reported data for (cyclopentadienyl)bis(phosphine)ruthenium acetylide complexes Ru(4-C≡CC₆H₄R)(PR'₃)₂(η-C₅H₅) (R' = Me, R = NO₂ (12); R' = Ph, R = H (9), Br (10), NO₂ (11), (E)-4-CH=CHC₆H₄NO₂ (13), 4-C≡CC₆H₄NO₂ (14)) [6]. A number of observations from these data can be made. Imaginary components of non-linearities for complexes from the octahedral bis(diphosphine)-ruthenium acetylide system are very large; complex 3 is the only example reported herein with a larger real component than imaginary component of its cubic optical non-linearity. The imprecision resulting from these large imaginary non-linearities has rendered extraction of values for real components of 1, 6 and 7 impossible; from the accuracy of the numerical fits for the Z-scan shapes, one can deduce that these missing data are less than one third of the corresponding imaginary values. We have previously noted that observed responses of the acetylide complexes are not simply the sums of values for the corresponding chloro complex and acetylene; γ for 12 is much larger than that of RuCl(PMe₃)₂(η-C₅H₅) (≤ 80 × 10⁻³⁶ esu) and 4-nitrophenylethyne (20 × 10⁻³⁶ esu), indicating that electronic communication between the ligated metal and acetylide fragments is important [6]. A similar conclusion is reached in the present work, with γ for 2 substantially greater than the sum of those for 1 and 4-nitrophenylethyne. The present studies extend this concept to assess communication through the metal, although the results are unclear; adding a second 4-nitrophenylacetylide ligand in proceeding from 2 to 5 leads to a doubling of response, whereas the effect of the introduction of a second 4-nitrobiphenylacetylide (in proceeding from 3 to 6) or 4-nitro-(E)-stilbenylacetylide (in proceeding from 4 to 7) ligand is rendered uncertain by the large imaginary components for 6 and 7. It is perhaps significant that extinction coefficients for λ_{max} in the mono(acetylide) complexes 2, 3 and 4 are significantly larger than those for the bis(acetylide)

Table 2

Selected bond lengths (Å) and angles (°) for *trans*-[Ru(C≡CPh)(4-C≡CC₆H₄NO₂)(dppm)₂] (8)

Ru(1)–P(1)	2.339(3)	Ru(1)–P(2)	2.333(3)
Ru(1)–C(1)	2.04(2)	P(1)–C(101)	1.854(9)
P(1)–C(111)	1.82(1)	P(1)–C(121)	1.82(1)
P(2)–C(101)	1.854(9)	P(2)–C(211)	1.84(1)
P(2)–C(221)	1.81(1)	C(1)–C(2)	1.22(2)
C(2)–C(3)	1.36(2)		
P(1)–Ru(1)–P(2)	70.59(9)	P(1)–Ru(1)–C(1)	98.9(3)
P(2)–Ru(1)–C(1)	94.2(3)	Ru(1)–P(1)–C(101)	93.0(3)
Ru(1)–P(2)–C(101)	93.2(3)	Ru–C(1)–C(2)	178(1)
C(1)–C(2)–C(3)	177(1)		

Table 3
Cubic hyperpolarizabilities of complexes from Z-scan measurements

Complex	λ_{\max} (nm) ^a	ϵ (l mol ⁻¹ cm ⁻¹)	γ (10 ⁻³⁶ esu) ^b	
			Real part	Imaginary part
1			≤ 30	100 ± 20
2	466	16200	170 ± 34	230 ± 46
3	448	17500	140 ± 28	64 ± 13
4	471	25730	200 ± 40	1100 ± 220
5	474	3310	300 ± 60	490 ± 98
6	453	8310	≤ 800	2500 ± 500
7	367	10700	≤ 1100	3400 ± 680
9 ^{c,d}			≤ 150	
10 ^{c,e}			≤ 150	
11 ^{c,f}			-210 ± 50	≤ 10
12 ^{c,g}			-230 ± 70	74 ± 30
13 ^{c,h}			-450 ± 100	210 ± 100
14 ^{c,i}			-450 ± 100	≤ 20

^a All as MeCN solutions.

^b Measurements at 800 nm (all complexes are optically transparent at this wavelength) for dichloromethane solutions.

^c Ref. [6].

^d Ru(C≡CPh)(PPh₃)₂(η-C₅H₅).

^e Ru(4-C≡CC₆H₄Br)(PPh₃)₂(η-C₅H₅).

^f Ru(4-C≡CC₆H₄NO₂)(PPh₃)₂(η-C₅H₅).

^g Ru(4-C≡CC₆H₄NO₂)(PMe₃)₂(η-C₅H₅).

^h Ru((E)-4,4'-C≡CC₆H₄CH=CHC₆H₄NO₂)(PPh₃)₂(η-C₅H₅).

ⁱ Ru(4,4'-C≡CC₆H₄C≡CC₆H₄NO₂)(PPh₃)₂(η-C₅H₅).

complexes 5, 6 and 7 (in fact, no band with $\lambda_{\max} > 400$ nm was found for 7). The observed responses seem to be electronic resonance enhanced, with the imaginary component resulting from non-linear absorption. Weak oscillator strengths for MLCT optical transitions in the bis(acetylide) complexes are consistent with comparatively little resonance enhancement of cubic non-linearities. Strong MLCT bands in the corresponding mono(acetylide) complexes give rise to substantially more resonance enhancement. This suggests that the relation between the hyperpolarizabilities of bis(acetylide) and mono(acetylide) complexes may be quantitatively different off-resonance from that measured at 800 nm, but studies remote from absorption bands are required to confirm this. The present results for 2 and 5 do indicate an increase in non-linearity upon introduction of a second *trans*-disposed acetylide ligand, and suggest that it is possible that the effect of acetylide ligands on cubic optical non-linearity in *trans*-bis(diphosphine)ruthenium acetylide complexes is additive. Previous studies with (cyclopentadienyl)ruthenium acetylide complexes had suggested that extension from a one-ring chromophore 11 to an extended chain two-ring chromophore 13 and 14 leads to a large increase in γ . The present studies are equivocal. Replacement of the 4-nitrophenylacetylide by 4-nitro-(*E*)-stilbenylacetylide in proceeding from 2 to 4 leads to a small increase, but introduction of 4-nitrobiphenylacetylide in proceeding to 3 leads to a decrease; given the size of the experimental uncertainties, further data are required.

Complexes 11–14 incorporating a strong donor-acceptor interaction have the first negative γ reported for organometallic complexes [6]; thermal lensing and bond-length alternation effects were rejected as the cause, and two-photon dispersion deemed likely, but a negative static hyperpolarizability could not be ruled out. The present series of acetylide complexes is similar in that they have strong MLCT bands with $\lambda_{\max} > 400$ nm and cubic non-linearities which are almost certainly resonance enhanced, but differ in displaying positive γ . Further studies using systematically varied organometallic molecules to elucidate structure-property relationships for molecular optical non-linearities are currently underway.

3. Experimental details

3.1. Starting materials

The following were prepared by literature methods: *trans*-[RuCl₂(dppm)₂] [10], *trans*-[Ru(4-C≡CC₆H₄R)Cl(dppm)₂] (R = NO₂, 4-C₆H₄NO₂, (*E*)-4-CH=CHC₆H₄NO₂) [7], *trans*-[Ru(4-C≡CC₆H₄R)₂(dppm)₂] (R = NO₂, 4-C₆H₄NO₂, (*E*)-4-CH=CHC₆H₄NO₂) [1], *trans*-[Ru(C≡CPh)(4-C≡CC₆H₄NO₂)(dppm)₂] [1].

3.2. Instruments

UV-visible spectra were recorded using a Cary 5 spectrophotometer as solutions in distilled acetonitrile in 1 cm cells.

3.3. Z-scan measurements

Measurements were performed at 800 nm using a system consisting of a Coherent Mira Ar-pumped Ti-sapphire laser generating a mode-locked train of approximately 100 fs pulses and a home-built Ti-sapphire regenerative amplifier pumped with a frequency-doubled Q-switched pulsed YAG laser (Spectra Physics GCR) at 30 Hz and employing chirped pulse amplification. Dichloromethane solutions were examined in a 0.1 cm path-length cell. The Z-scans were recorded at a few concentrations of each compound, and the real and imaginary parts of the non-linear phase change determined by numerical fitting using equations given in Ref. [9]. The real and imaginary parts of the hyperpolarizability of the solute were then calculated by linear regression from the concentration dependencies. The non-linearities and light intensities were calibrated using measurements of a 1 mm thick silica plate for which a non-linear refractive index $n_2 = 3 \times 10^{-16}$ cm² W⁻¹ was assumed.

3.4. X-ray structure determination

3.4.1. General conditions

After we made numerous unsuccessful attempts to obtain crystalline samples, a specimen of fairly poor crystal quality was obtained from slow diffusion of methanol into a dichloromethane solution; data collected on this crystal displayed broad, split peaks which, coupled with the inherent disorder, resulted in fairly high final residual values. A unique low-temperature diffractometer data set ($T \approx 213$ K; monochromatic Cu K α radiation ($\lambda = 1.54178$ Å; ω - 2θ scan mode, $2\theta_{\max} = 120.9^\circ$) was obtained, yielding 3990 independent reflections, 2301 of these with $I \geq 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after application of an empirical absorption correction based on azimuthal scans. 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 , R_w on $|F|$ at convergence were 0.063, 0.096, the weighting function $w = 4F_o^2/\sigma^2(F_o^2)$ where $\sigma^2(F_o^2) = [\sigma^2(C + 4B) + (pF_o^2)^2]/Lp^2$ (with σ the scan rate, C the peak count, B the background count and $p = 0.001$ determined experimentally from standard reflections) being employed. Computation used the teXsan package [11]. Pertinent results are given in the figures and tables. Tables of hydrogen atom 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.

3.4.2. Crystal data

$C_{66}H_{32}NO_2P_4Ru$, $M = 1116.11$. Triclinic, space group $P1$ (No. 2), $a = 9.879(5)$, $b = 12.261(6)$, $c = 12.454(9)$ Å, $\alpha = 78.68(5)^\circ$, $\beta = 69.12(4)^\circ$, $\gamma = 71.73(4)^\circ$, $V = 1332(1)$ Å³, ($Z = 1$) $D_c = 1.391$ g cm⁻³;

$F(000) = 575$, $\mu_{Cu} = 38.90$ cm⁻¹; specimen $0.20 \times 0.06 \times 0.08$ mm³; $T_{\text{min,max}} = 0.85, 1.00$.

Acknowledgements

We thank the Australian Research Council, Telstra (Australia) and the Harry Triguboff AM Syndicate for support of this work, and Johnson-Matthey Technology Centre for a generous loan of ruthenium salts. IRW is the recipient of an Australian Postgraduate Research Award (Industry), MGH holds an ARC Australian Research Fellowship, and MPC holds an ARC Australian Postdoctoral Research Fellowship.

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