Organometallic materials for non-linear optics. Second harmonic generation by (aryldiazovinylidene)ruthenium complexes; X-ray structure of $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4] \cdot CH_2Cl_2$

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Abstract

A series of (aryldiazovinylidene)ruthenium complex salts of general formula $[Ru(C{=}CPhN{=}NAr)(PPh_3)_2(\eta\text{-}C_5H_5)][X]$ has been synthesized. The Kurtz method was used to investigate their effectiveness in second harmonic generation, and revealed efficiencies up to that of a urea reference standard. An X-ray structural study of the complex exhibiting the strongest response, $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4] \cdot CH_2Cl_2$ revealed that the material packs centrosymmetrically, suggesting that the observed moderate bulk $\chi^{(2)}$ responses arise from large molecular β responses and some crystal mispacking.

Key words: Ruthenium; Second harmonic generation; Solvochromatic properties; Cyclopentadienyl

1. Introduction

The non-linear optical (NLO) properties of materials are of current interest because of their potential applications in photonic devices [1–5]. Most NLO research on molecular materials thus far has been concerned with second harmonic generation (SHG). A great deal of work has been done with organic molecules but organometallic complexes have been much less studied. Most published SHG research on organometallic systems has focused on ferrocene and its derivatives [6–14]. However, the charge transfer (metal-cyclopentadienyl) axis in ferrocene derivatives is at right angles to a cyclopentadienyl-coordinated chromophore, which may not be ideal for maximum response. Recent studies have suggested that for optimal organometallic NLO response some metal–carbon multiple bonding should be introduced, and the metal should lie in the same plane as the π-system of the chromophore [9]. We have therefore initiated an investigation into the NLO properties of metal-vinylidene, -carbene and -carbyne complexes, which might be expected to satisfy these criteria.

We recently reported the syntheses and structural authentication of some (vinylidene)ruthenium complexes [15–18]. Structural studies have indicated that a formal M=C double bond is present in such compounds, the X-ray study of $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**1**) showing planarity of the Ru=C=C–N=N–Ar chromophore [15]. Thus, the (aryldiazovinylidene)ruthenium complexes satisfy both

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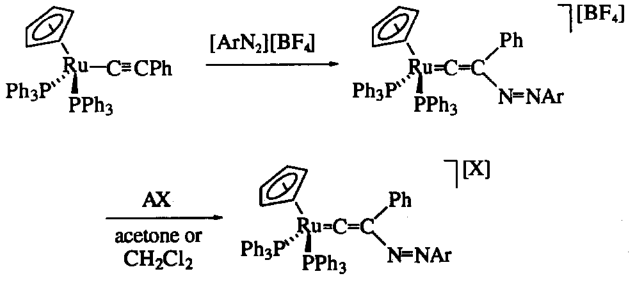

Fig. 1. Synthetic scheme for the preparation of (aryldiazovinylidene)ruthenium complexes. Ar=Ph, $C_6H_3(NO_2)_2$-3,5, $C_6H_4NO_2$-4, C_6H_4OMe-2, C_6H_4OMe-4. AX = $[NEt_4]Br$, $[N^nPr_4]I$, $[NMe_4]Cl$, $Na[CH_3C_6H_4SO_3$-4], $NaNO_3$.

selection criteria, and we present below our initial NLO results for representative samples from this system.

2. Results and discussion

2.1. Syntheses and spectroscopic characterization

The synthetic method employed was analogous to that previously used and is summarized in Fig. 1.

The new complexes have similar spectral properties to other (aryldiazovinylidene)ruthenium compounds. Thus, the IR spectra contain medium intensity C=C and N=N bands between 1530 and 1600 cm^{-1}. The ^1H and ^{13}C NMR spectra have characteristic singlets for the cyclopentadienyl rings between 5.3 and 5.4 ppm, and 96–98 ppm, respectively, and a low-field signal due to the metal-bound carbon of the vinylidene ligand occurs between 350 and 360 ppm in the ^{13}C NMR spectra.

2.2. Solvatochromic behaviour

The solvatochromic responses of the complexes as tetrafluoroborate salts were determined and the results are shown in Table 1. The salts are of limited solubility in less polar solvents, thus restricting the solvent polarity range for the solvatochromic studies. The shifts observed are quite small; however, a solvatochromic shift is not an indicator of the magnitude of an NLO response [19]. As the aryldiazovinylidene complexes showed modest solvatochromic behaviour, their powder SHG efficiencies were measured.

TABLE 1. Solvatochromic behaviour of (aryldiazovinylidene)ruthenium complexes

Complex	λ_{max} (nm)		
	CH_2Cl_2	CH_3CN	DMF
$[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**2a**)	363	368	374
$[Ru\{C{=}CPhN{=}NC_6H_3(NO_2)_2\text{-}3,5\}(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**3a**)	400	402	407
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**4a**)	374	378	382
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}2)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**5a**)	371	373	376
$[Ru(C{=}CPhN{=}NC_6H_4NO_2\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)]$[BF4] (**6a**)	413	417	425

TABLE 2. Powder SHG measurements (at 1.064 μm) on (aryldiazovinylidene)ruthenium complexes

Complex	SHG response (urea = 1)
$[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**2a**)	0.48
$[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][CH_3C_6H_4SO_3\text{-}4]$ (**2b**)	0.50
$[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][NO_3]$ (**2c**)	0.57
$[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][Cl]$ (**2d**)	0.50
$[Ru(C{=}CPhN{=}NPh)(PPh_3)_2(\eta\text{-}C_5H_5)][I]$ (**2e**)	0.53
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**4a**)	1.05
$[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}2)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**5a**)	0.63

2.3. Powder SHG measurements

The powder SHG responses of the aryldiazovinylidene complexes were measured by the Kurtz method [20]; significant responses (> 0.05 × urea) are shown in Table 2. The samples were ground, unsized microcrystalline powders; as was pointed out by Marder *et al.* [10], this can give rise to some uncertainties in the measured efficiencies, perhaps involving a factor of 2 or more.

Significant responses are restricted to the three (aryldiazovinylidene)ruthenium complex cations with electron-donating chromophores (Ar = Ph, C_6H_4OMe-2, C_6H_4OMe-4). This suggests that the electron deficient metal-stabilized vinylidene group is functioning as an acceptor, in line with the ^{13}C NMR shift of the metal-bound carbon (*vide supra*), and propensity of this carbon to undergo nucleophilic attack [21]. The powder SHG responses are a combination of molecular responses and crystal alignment. Thus, the moderate results obtained could be due to low molecular β values or large β values with unfavourable (centrosymmetric) crystal packing. In order to distinguish between these possibilities an X-ray structural study of the

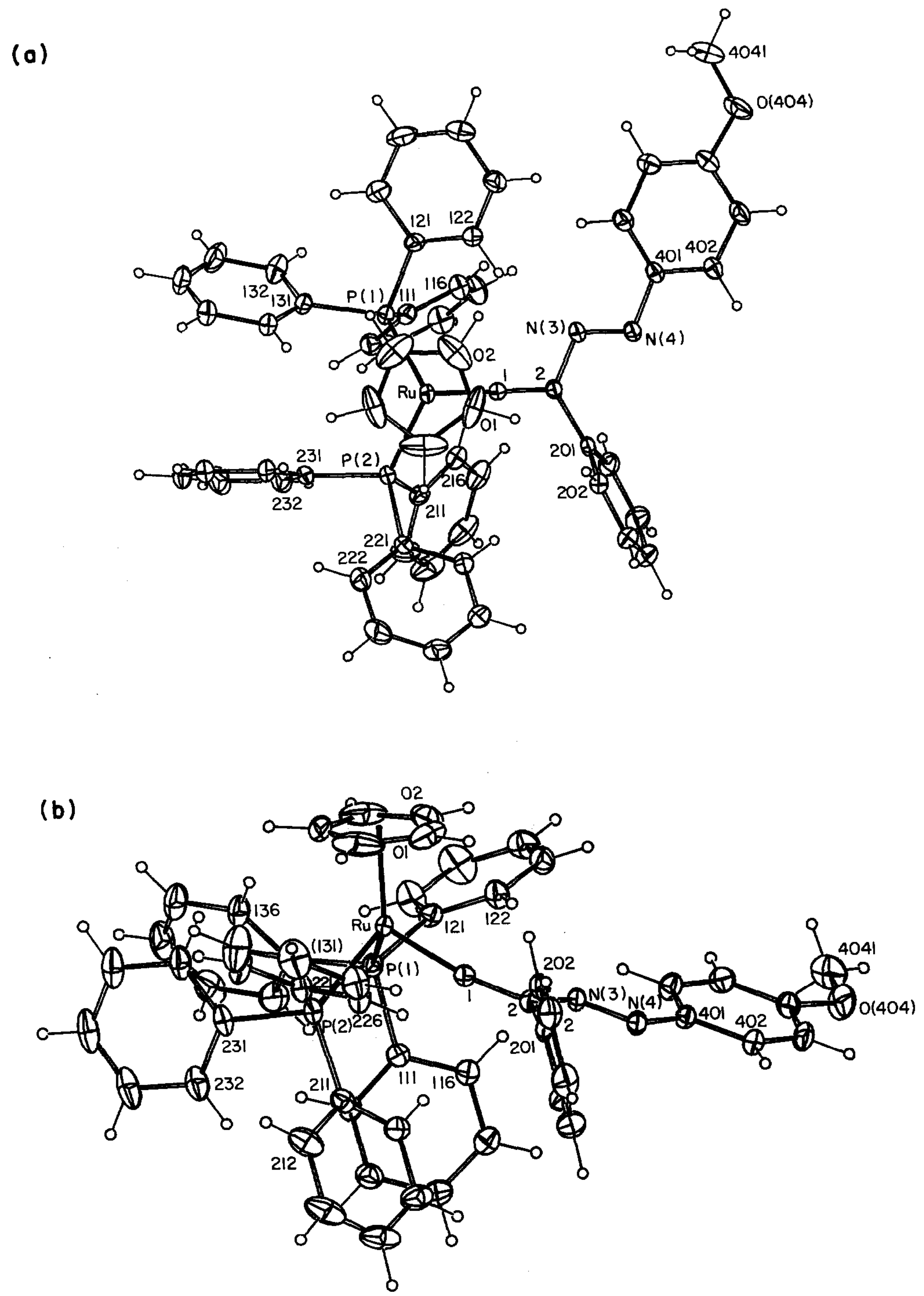

Fig. 2. The cation of $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4].CH_2Cl_2$ (**4a**) viewed (a) onto the plane of the cyclopentadienyl ligand and (b) oblique to the cyclopentadienyl ligand plane. 20% thermal ellipsoids and atom numbering are shown for the non-hydrogen atoms. Hydrogen atoms have arbitrary radii of 0.1 Å.

complex with the largest response, $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**4a**) was carried out.

TABLE 3. Atomic coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms in $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**4a**)

Atom	x	y	z	U_{eq} (Å^2)
Ru	0.16413(2)	0.30743(3)	0.22749(3)	0.0368(1)
C(01)	0.1284(5)	0.4879(4)	0.2047(5)	0.109(4)
C(02)	0.0896(4)	0.4729(4)	0.2954(6)	0.112(3)
C(03)	0.1443(5)	0.4255(5)	0.3616(4)	0.122(4)
C(04)	0.2214(4)	0.4109(4)	0.3129(6)	0.107(3)
C(05)	0.2155(4)	0.4472(5)	0.2102(5)	0.123(4)
P(1)	0.12300(7)	0.18028(9)	0.34246(8)	0.0425(4)
C(111)	0.1079(3)	0.0657(3)	0.2791(3)	0.047(2)
C(112)	0.1756(3)	−0.0311(3)	0.2564(3)	0.054(2)
C(113)	0.1664(3)	−0.1155(4)	0.2037(4)	0.067(2)
C(114)	0.0898(3)	−0.1059(4)	0.1711(4)	0.076(2)
C(115)	0.0221(3)	−0.0109(4)	0.1934(4)	0.079(2)
C(116)	0.0312(3)	0.0744(4)	0.2466(4)	0.060(2)
C(121)	0.0182(2)	0.2476(3)	0.4192(3)	0.047(2)
C(122)	−0.0442(3)	0.3277(4)	0.3741(3)	0.061(2)
C(123)	−0.1243(3)	0.3740(4)	0.4289(4)	0.067(2)
C(124)	−0.1440(3)	0.3450(4)	0.5308(4)	0.076(2)
C(125)	−0.0822(4)	0.2668(5)	0.5771(4)	0.102(3)
C(126)	−0.0013(3)	0.2197(5)	0.5231(4)	0.082(2)
C(131)	0.1882(3)	0.1134(3)	0.4447(3)	0.053(2)
C(132)	0.1800(4)	0.0194(4)	0.4940(4)	0.077(2)
C(133)	0.2262(4)	−0.0260(4)	0.5775(4)	0.094(3)
C(134)	0.2785(3)	0.0229(5)	0.6101(4)	0.095(3)
C(135)	0.2863(3)	0.1164(5)	0.5642(4)	0.084(3)
C(136)	0.2409(3)	0.1618(4)	0.4808(3)	0.063(2)
P(2)	0.28952(6)	0.18257(9)	0.13546(8)	0.0435(4)
C(211)	0.2851(3)	0.0859(3)	0.0370(3)	0.051(2)
C(212)	0.3593(3)	0.0365(4)	−0.0329(4)	0.081(2)
C(213)	0.3603(4)	−0.0378(4)	−0.1077(4)	0.099(3)
C(214)	0.2890(4)	−0.0628(4)	−0.1150(4)	0.094(3)
C(215)	0.2148(4)	−0.0134(4)	−0.0480(4)	0.077(3)
C(216)	0.2140(3)	0.0607(3)	0.0277(3)	0.055(2)
C(221)	0.3459(2)	0.2600(3)	0.0492(3)	0.050(2)
C(222)	0.4206(3)	0.2736(5)	0.0649(4)	0.082(3)
C(223)	0.4580(3)	0.3334(6)	−0.0063(5)	0.112(3)
C(224)	0.4224(3)	0.3770(5)	−0.0941(4)	0.090(3)
C(225)	0.3485(3)	0.3653(4)	−0.1112(4)	0.075(2)
C(226)	0.3097(3)	0.3071(4)	−0.0400(4)	0.063(2)
C(231)	0.3671(2)	0.0976(4)	0.2174(3)	0.054(2)
C(232)	0.3985(3)	−0.0154(4)	0.2072(4)	0.075(2)
C(233)	0.4586(3)	−0.0771(5)	0.2708(5)	0.100(3)
C(234)	0.4858(3)	−0.0264(5)	0.3426(4)	0.097(3)
C(235)	0.4559(3)	0.0841(5)	0.3534(4)	0.088(3)
C(236)	0.3959(3)	0.1465(4)	0.2911(3)	0.069(2)
C(1)	0.0973(2)	0.2958(3)	0.1319(3)	0.038(1)
C(2)	0.0428(2)	0.3070(3)	0.0616(3)	0.039(1)
C(201)	0.0713(2)	0.3197(3)	−0.0527(3)	0.043(1)
C(202)	0.0973(3)	0.4083(3)	−0.0865(3)	0.050(2)
C(203)	0.1284(3)	0.4175(4)	−0.1916(3)	0.063(2)
C(204)	0.1327(3)	0.3414(5)	−0.2636(4)	0.080(2)
C(205)	0.1054(3)	0.2527(4)	−0.2325(4)	0.074(2)
C(206)	0.0743(3)	0.2433(4)	−0.1274(3)	0.059(2)
N(3)	−0.0387(2)	0.3059(2)	0.1038(2)	0.042(1)
N(4)	−0.0897(2)	0.3191(3)	0.0357(2)	0.045(1)
C(401)	−0.1724(2)	0.3221(3)	0.0824(3)	0.045(2)
C(402)	−0.2313(3)	0.3357(3)	0.0120(3)	0.053(2)
C(403)	−0.3136(3)	0.3436(4)	0.0504(4)	0.065(2)
C(404)	−0.3386(3)	0.3396(4)	0.1584(4)	0.059(2)
O(404)	−0.4221(2)	0.3483(3)	0.1885(3)	0.088(2)
C(4041)	−0.4512(3)	0.3422(5)	0.2979(5)	0.100(3)
C(405)	−0.2814(3)	0.3258(4)	0.2299(4)	0.059(2)
C(406)	−0.1981(3)	0.3172(4)	0.1901(3)	0.058(2)
F(1)	0.2905(3)	0.3955(5)	0.5906(5)	0.233(4)
F(2)	0.4174(4)	0.2971(4)	0.5964(5)	0.237(4)
F(3)	0.3902(5)	0.4600(5)	0.5720(6)	0.269(5)
F(4)	0.3723(4)	0.3673(6)	0.4549(3)	0.232(5)
B	0.3689(4)	0.3802(5)	0.5541(5)	0.075(3)
Cl(1)	0.3658(1)	0.6098(2)	0.2463(2)	0.141(1)
Cl(2)	0.3370(1)	0.7542(2)	0.4250(2)	0.146(1)
C(0)	0.4007(4)	0.6318(5)	0.3628(6)	0.112(3)

*2.4. X-Ray structural study of $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**4a**)*

The solid-state structure of the cation in **4a** is shown in Fig. 2; atomic coordinates are listed in Table 3 and selected bond lengths and angles in Table 4. The structural study also confirmed the presence of the BF_4^- anion and revealed the presence of a solvent molecule of crystallization; further discussion is restricted to details of the cation geometry and its implications for materials design.

The cation geometry is pseudooctahedral about ruthenium on the assumption that the cyclopentadienyl group takes up three coordination sites. The Ru–C(Cp) and Ru–P distances are normal. Our interest in this structure is with the metal-vinylidene interaction. The Ru–C(1) distance [1.813(4) Å] is very short, and similar to that reported previously for the analogue $[Ru(C{=}CPhN{=}NC_6H_3Me_2\text{-}3,4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$

TABLE 4. Selected bond lengths (Å) and angles (°) for $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}4)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**4a**)

Ru–C(01)	2.227(5)	Ru–C(02)	2.227(5)
Ru–C(03)	2.252(6)	Ru–C(04)	2.277(7)
Ru–C(05)	2.240(7)	Ru–P(1)	2.363(1)
Ru–P(2)	2.370(1)	P(1)–C(111)	1.821(5)
P(1)–C(121)	1.838(4)	P(1)–C(131)	1.825(4)
P(2)–C(211)	1.832(5)	P(2)–C(221)	1.830(5)
P(2)–C(231)	1.827(4)	Ru(1)–C(1)	1.813(4)
C(1)–C(2)	1.341(6)	C(2)–C(201)	1.485(5)
C(2)–N(3)	1.403(5)	N(3)–N(4)	1.272(5)
N(4)–C(401)	1.423(5)	C(404)–O(404)	1.371(5)
O(404)–C(4041)	1.415(7)		
P(1)–Ru–P(2)	97.76(4)	P(1)–Ru–C(1)	91.9(1)
P(2)–Ru–C(1)	94.0(1)	Ru–C(1)–C(2)	169.7(3)
C(1)–C(2)–N(3)	116.0(3)	C(2)–N(3)–N(4)	114.7(3)
N(3)–N(4)–C(401)	112.8(3)	C(1)–C(2)–C(201)	119.2(3)
N(3)–C(2)–C(201)	124.8(3)		

(**1**) [15,16] [1.823(9) Å]. (For purposes of comparison, distances in the latter complex are given in parentheses following those for **4a**.) Similarly, the angle Ru–C(1)–C(2) is almost linear 169.7(3)° (169.9(7)°). The distance C(1)–C(2) [1.341(6) Å, (1.34(1) Å)] and the angles about C(2) [C(1)–C(2)–N(3) 116.0(3)° (114.4(8)°), C(1)–C(2)–C(201) 119.2(3)° (121.4(8)°), C(201)–C(2)–N(3) 124.8(3)° (124.2(7)°) are consistent with an sp^2-hybridized C(2) and a "normal" C=C double bond. The values of C(2)–C(Ph) 1.485(5) Å (1.48(1) Å), C(2)–N(3) 1.403(5) Å (1.42(1) Å), N(3)–N(4) 1.272(5) Å (1.27(1) Å), and N(4)–C(401) 1.423(5) Å (1.42(1) Å) are all comparable with those in **1**, and consistent with a C=C(Ph)–N=N–Ph chromophore. Figure 2 shows that the phenyl group attached to C(2) is twisted out of the plane of the chromophore, with an interplanar dihedral angle of 62.2(1)°; thus, substantial metal π-overlap is restricted to the diazo chromophore.

The crystal structure was solved in a centrosymmetric space group, suggesting that the molecular β value is substantial. Possible reasons for observed SHG in centrosymmetric space groups include effects originating in the non-centrosymmetric crystal surface, small contributions from a non-centrosymmetric phase, or minor deviations from centrosymmetry [22]. A result of this type is not unprecedented; indeed, in the diiron-stabilized carbene complex $[(\eta\text{-}C_5H_5)_2Fe_2(CO)_2(\mu\text{-}CO)(\mu\text{-}(E)\text{-}CCH{=}CHC_6H_4N(CH_3)_2\text{-}4)][BF_4]$, a powder SHG response of 0.77 times that of urea was observed, despite the fact that the crystal structure was solved in the centrosymmetric space group $P2_1/n$ [22]. The results for the (aryldiazovinylidene)ruthenium and (alkenylidyne)diiron systems certainly suggest that metal-stabilized acceptors merit investigation as potential NLO materials; our current studies in the ruthenium system are directed towards improvement of the chromophore alignment in the crystal lattice and the preparation of neutral analogues, for which molecular hyperpolarizabilities can be determined by the EFISH technique [23].

3. Experimental details

3.1. General conditions

All preparations were carried out under dinitrogen but no special precautions were taken to exclude air during work-up of products. Solvents used were dried by standard methods; diethyl ether was distilled from Na/benzophenone, CH_2Cl_2 from CaH_2, methanol from Mg/I_2 and acetone from $CaSO_4$.

3.2. Instruments

The IR spectra were recorded on a Perkin-Elmer model 1725 Fourier transform spectrophotometer with CaF_2 or NaCl optics. The NMR spectra were recorded on a Bruker AM300 spectrometer, the ^1H spectra at 300.13 MHz and the ^{13}C at 75.47 MHz with a recycle delay of 10 s. Elemental analyses were by Dr. N. Jacobsen of the Microanalytical Service, Department of Chemistry, University of Queensland. Melting points were determined in a Reichert melting point apparatus.

3.3. Starting materials

The salts used in metatheses were obtained from commercial sources and used as received. The aryldiazonium salts were prepared by standard methods [24], involving diazotization of the appropriately substituted aniline, as the tetrafluoroborate salt. $Ru(C\equiv CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ was synthesized by the method used by Bruce *et al.* [25], and the known (aryldiazovinylidene)ruthenium complexes were prepared by the method we reported previously [16].

3.4. Preparation of aryldiazovinylidene complexes

3.4.1. $[Ru(C{=}CPhN{=}NC_6H_3(NO_2)_2\text{-}3,5)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$

$[N\equiv NC_6H_3(NO_2)_2\text{-}3,5][BF_4]$ (200 mg, excess) was added to a suspension of $Ru(C\equiv CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) in tetrahydrofuran (10 ml), the yellow suspension immediately becoming a red solution. After stirring for 10 min, the solvent was removed *in vacuo* and the residue extracted with dichloromethane. The extract was filtered and methanol was added, and the solution allowed to evaporate slowly to give red crystals of $[Ru(C{=}CPhN{=}NC_6H_3(NO_2)_2\text{-}3,5)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**3a**), (147 mg, 54%) m.p. 147–150°C (dec). Anal. Found: C, 61.26; H, 4.15; N, 4.78. $RuC_{55}H_{43}N_4O_4P_2BF_4$ calc: C, 61.52; H, 4.04; N 5.22%. Infrared (Nujol): ν(C=C) 1539m, ν(N=N) 1581w, ν(BF) 1052s cm^{-1}; other bands at 1974w 1569w, 1356s, 1317m, 1254m, 1207m, 1162w, 1090m, 1070m, 998m, 980m, 920w, 857w, 747w, 729m, 697m cm^{-1}. ^1H NMR($CDCl_3$): δ 5.42 (s, 5H, C_5H_5); 7.02–7.45 (35H, Ph); 8.26 (2H, d, $J(HH) = 2$ Hz, C_6H_2H); 8.82 (1H, t, $J(HH) = 2$ Hz, C_6H_2H). ^{13}C NMR ($CDCl_3$): δ 97.16 (C_5H_5); 117.27, 121.53, 125.20, 128.60–133.74, 148.68, 154.56 (RuC=C + Ph + N=NC$_6$); 354.05 (t, $J(CP) = 15$Hz, RuC).

3.4.2. $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}2)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$

By use of the same procedure, $Ru(C\equiv CPh)(PPh_3)_2(\eta\text{-}C_5H_5)$ (200 mg, 0.253 mmol) and $[N\equiv NC_6H_4OMe\text{-}2][BF_4]$ (200 mg, excess) afforded $[Ru(C{=}CPhN{=}NC_6H_4OMe\text{-}2)(PPh_3)_2(\eta\text{-}C_5H_5)][BF_4]$ (**5a**) (159 mg, 62%) m.p. 134–137°C (dec). Anal. Found:

C, 65.62; H, 4.79; N, 2.58. $C_{56}H_{47}BF_4N_2OP_2Ru$ calc: C, 66.34; H, 4.67; N 2.76%. Infrared (Nujol): ν(C=C) 1585m, ν(N=N) 1600m, ν(BF) 1057s cm^{-1}; other bands at 1777w, 1279w, 1244w, 1230w, 1175w, 1160w, 1091m, 1024m, 1000w, 973w, 929w, 897w, 762m, 750m, 709m, 695m cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 3.79 (s, 3H, OMe); 5.36 (s, 5H, C_5H_5); 6.76–7.42 (m, 39H, Ph + C_6H_4). ^{13}C NMR ($CDCl_3$): δ 56.64 (OMe); 96.89 (C_5H_5); 113.13 (RuC=*C*); 117.30, 120.75, 128.78–132.72, 155.50, 159.82 (Ph + N=NC_6); 354.08 (t, *J*(CP) = 15Hz, RuC).

3.4.3. *[Ru(C=CPhN=NC$_6$H$_4$NO$_2$-4)(PPh$_3$)$_2$(η-C$_5$H$_5$)][BF$_4$]* (**6a**) [16]

^{13}C NMR ($CDCl_3$): δ 96.81 (C_5H_5), 122.39, 124.25, 124.98, 128.67–133.60, 147.08, 156.69, 161.18 (Ph + N = NC_6 + RuC = *C*), 356.74 (t, *J*(CP) = 16 Hz, RuC).

3.5. *Anion metatheses*

Anion metatheses were accomplished by adding solid $[NEt_4]Br$, $[N^nPr_4]I$, $[NMe_4]Cl$, Na$[CH_3C_6H_4SO_3$-4] or $NaNO_3$ to a solution of the BF_4^- salt in acetone or CH_2Cl_2 and stirring for 15 min; the resulting solutions or suspensions were filtered into an excess of diethyl ether, and the precipitated solid collected. Successful metathesis was confirmed by the absence of the 1050 cm^{-1} ν(BF) of the BF_4^- anion.

3.6. *Solvatochromic behaviour*

The solvatochromic behaviour of the BF_4^- salts were measured in CH_2Cl_2, CH_3CN and dimethylformamide (DMF) solutions of approximately 50 μM concentration in a quartz cell with a 1 cm path length using a Hitachi U-3200 Spectrophotometer with a 2.00 nm band pass, medium response, and a scan speed of 120 nm/min over the range 250–600 nm.

3.7. *Powder SHG measurements*

Powder SHG efficiencies were determined by use of the 1064 nm output of a Q-switched Nd:YAG laser. The powder SHG measurements were made by the Kurtz powder method on ground, unsized microcrystalline powders. Pulse lengths were 24 ns with pulse energies of the order of 100 mJ/pulse and a 0.8 mm beam diameter. The diffusely back-scattered SH signals were sampled by using a silica fibre bundle at an angle of 45° to the laser beam, filtered to remove the 1064 nm fundamental radiation, detected (Silicon Model 815 photosensor), amplified using a homemade preamplifier, and averaged and displayed (Tektronix TDS 520 digital sampling oscilloscope).

3.8. *X-ray structure determination*

A unique room temperature diffractometer data set ($T \approx 295$K; monochromatic Mo Kα radiation ($\lambda = 0.7107_3$ Å); 2θ–θ scan mode, $2\theta_{max}$ 55°) was obtained, yielding 11831 independent reflections, 8045 of these with $I > 3\sigma(I)$) being considered "observed" and used in the full matrix least squares refinement after Gaussian absorption correction. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x,y,z,U_{iso})_H$ were included constrained at estimated values. Difference map artefacts were modelled acceptably as a molecule of dichloromethane of solvation, the population being constrained at unity despite high thermal motion after testing its refinement behaviour. High thermal motion on the Cp ring is probably reflecting some disorder, an attempt was made to deconvolute a pair of seemingly half-weighted components without total success, and the "ordered" model retained. Conventional residuals R, R_w or $|F|$ at convergence were 0.049, 0.050, statistical reflection weights derivative of $\sigma^2(I) = \sigma^2(I_{diff}) + 0.0004\sigma^4(I_{diff})$ being used. Computation used the XTAL 3.2 program system implemented by Hall [26]. Pertinent results are given in Fig. 2 and Tables 3 and 4. Tables of hydrogen atom coordinates and thermal parameters and a complete list of bond lengths and angles for non-hydrogen atoms have been deposited at the Cambridge Crystallographic Data Centre.

3.9. *Crystal data*

$[C_{56}H_{47}N_2OP_2Ru]BF_4 \cdot CH_2Cl_2$, $M = 1098.8$. Triclinic, space group $P\bar{1}$ (C_i^1, No. 2), $a = 16.836(3)$, $b = 12.936(4)$, $c = 12.716(5)$ Å, $\alpha = 87.58(3)$, $\beta = 81.73(3)$, $\gamma = 70.59(2)°$, $V = 2585(1)$ Å^3. D_c ($Z = 2$) = 1.41 g cm^{-3}; $F(000) = 1124$. $\mu_{Mo} = 5.3$ cm^{-1}; specimen: 0.15 × 0.17 × 0.50 mm^3; $A^*_{min,max} = 1.09, 1.13$.

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