Journal of Organometallic Chemistry, 403 (1991) 365–372
Elsevier Sequoia S.A., Lausanne
JOM 21426

Synthesis and nonlinear optical properties of some substituted ruthenium(II) η^5-cyclopentadienyl η^5- or η^6-arene salts

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(Received July 16th, 1990)

Abstract

Treatment of a suspension of $AgBF_4$ in absolute methanol with a solution of η^5-$C_5H_5Ru(PPh_3)_3Cl$ (**1**) and an arene gives [(η^5- or η^6-arene)Ru(η^5-C_5H_5)]BF_4; where the η^5 or η^6-arenes are thiophene (**2**), nitrobenzene (3), *N*,*N*-dimethyl-4-nitroaniline (**4**), 2-methyl-4-nitroaniline (**5**) and *N*-(4-nitrophenyl)-(L)-prolinol (**6**). The relative efficiency of second-harmonic generation (1064 nm → 532 nm) for compounds (**1–6**) is 0.7 to 1.0 × urea.

Introduction

Theoretical and experimental investigations concerning nonlinear optics have grown exponentially in recent years [1]. Some of the applications that depend upon the nonlinear response of materials include: frequency doubling (second-harmonic generation) or tripling (third-harmonic generation); frequency modulation of a laser carrier beam; optical parametric oscillation and amplification; optical bistability or switching and degenerate four wave mixing including phase conjugate reflection. These techniques may play important roles in optical signal processing, telecommunications, electrophotography and in the construction of optical computers if improvements in the nonlinear optical properties of materials can be made. While compounds presently available are adequate for use with higher power lasers, new compounds are needed for use with the relatively lower power semiconductor lasers (200–500 mW, cw operation) with fundamental wavelengths in the range of 800 to 1500 nm. The semiquantitative testing procedure introduced by Kurtz and Perry [2] for the second-harmonic efficiency of powder samples provides a starting point for the study of the nonlinear optical properties of solids. The usual method is to monitor either the reflected or the transmitted second harmonic intensity when a powder sample held between quartz plates is irradiated with a high power laser pulse (for example, 532 nm, harmonic from a Nd : YAG fundamental of 1064 nm). Often the beam is split and the ratio of $I^{2\omega}$(sample)/$I^{2\omega}$(reference) is measured.

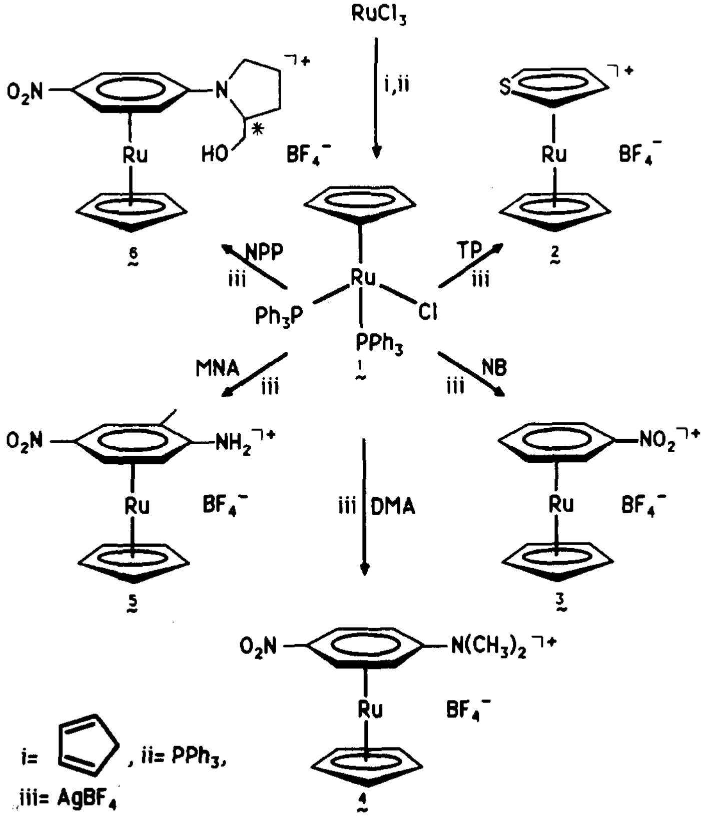
0022-328X/91/$03.50

The reference is commonly KDP, quartz, or urea. An interference filter that allows only the second harmonic frequency to pass helps eliminate the fundamental and spurious signals resulting perhaps from multiphoton fluorescence. Although a large number of inorganic and organic compounds have been tested for their efficiency as frequency doubling media, organometallic compounds are a class of materials that only recently have been intensively examined [3]. A cursory survey of these compounds would initially suggest that this should not be a good group of materials to study because of the low energy *d–d* transitions that give rise to the so-called "transparency-efficiency trade-off". For a substance to be used in a frequency doubling capacity, it must not absorb the harmonic light that is produced. Certainly absorption of visible light would limit the useful frequency doubling capability of these materials. However, the attractive feature of this group is the rather polarizable extended π-electron network of ligands, which in conjugation with the *d*-electrons of a transition metal, could give rise to useful nonlinear optical response. Previous research on the nonlinear optical properties of organic compounds has shown that an intramolecular donor–acceptor combination which allows for a large charge-transfer transition, such as occurs in *p*-nitroaniline, is a primary factor in producing materials with desirable nonlinear optical properties [1].

Reported herein is the synthesis and preliminary nonlinear optical study of several new arene–Cp–ruthenium complexes ($Cp = \eta^5\text{-}C_5H_5$). In three of these organometallic ruthenium compounds, *p*-nitroaniline derivatives were used as ligands in an effort to increase the molecular hyperpolarizability of the compounds.

Results and discussion

There are three general procedures for preparing arene–Cp–ruthenium complexes. Nesmeyanov and co-workers [4] have synthesized ruthenium complexes by exchanging one Cp ligand of ruthenocene for various arenes. Zelonica and Baird [5] have shown that the chlorines in the dimeric complex, $[(\eta^6\text{-}C_6H_6)RuCl_2]_2$, are readily substituted via thallium cyclopentadienide in acetonitrile thus producing $[(\eta^6\text{-}C_6H_6)Ru(\eta^5\text{-}C_5H_5)]Cl$ in good yield. Recently, Spies and Angelici [6] have developed a new and very convenient route leading to $[\eta^5\text{-}C_4H_4S)Ru(\eta^5\text{-}C_5H_5)]BF_4$ **2**. This method involves refluxing, under N_2, $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ **1**, thiophene and $AgBF_4$ in absolute methanol for 72 h. We chose this last procedure since it could provide arene–Cp–ruthenium complexes with nitro-(electron acceptor) and amino- or *N,N*-disubstituted amino-(electron donor) substituents in the arene ligand. However, we have found that stirring the reaction mixture for 24 h at 25 °C under Ar gave better yields than refluxing the solution 3 d under N_2. The sample procedure was as follows: $(\eta^5\text{-}C_5H_5)Ru(PPh_3)_2Cl$ **1**, $AgBF_4$, and nitrobenzene, in absolute methanol, were stirred for 24 h at 25 °C, the solvent was removed *in vacuo* and the residue was extracted with methylene chloride. The product, $[(\eta^6\text{-}NO_2C_6H_5)Ru(\eta^5\text{-}C_5H_5)]BF_4$ **3**, was recrystallized from acetone/diethyl ether (60% yield). The IR spectrum exhibits absorption bands at 1350 and 1560 cm^{-1} ($-NO_2$), and 1000–1150 cm^{-1} (BF_4^-). The ^1H NMR spectrum shows a singlet at δ 5.50 (Cp) and multiplets centered at δ 6.45 (3H, aromatic protons) and 7.15 (2H, aromatic protons adjacent to NO_2). Compounds **4**, **5**, and **6** were also obtained in a similar fashion, except the *p*-nitroaniline derivatives (*N,N*-dimethyl-4-nitroaniline = DMNA, 2-methyl-4-nitroaniline = MNA, or (*S*)(−)-2-hydroxymethyl-1-(4-



Scheme 1

nitrophenyl)-pyrrolidine(NPP)) were used in the place of nitrobenzene. These reactions are depicted in Scheme 1. The crystalline ruthenium complexes (**2**, **3**, **4**, **5**, and **6**) are stable in air and are soluble in methylene chloride and acetonitrile. Solutions of these complexes, however, are somewhat air sensitive and show gradual decomposition after several days.

A comparison of the ^{1}H NMR spectra of compounds **3**, **4**, **5**, and **6** shows that the influence of the amino-donor group on the chemical shift of the Cp-ligand protons is between 0.1 and 0.2 ppm. See the experimental section. The IR spectra of these complexes are consistent with the presence of the $-NO_2$ group, with the bands at 1350 and 1550 cm^{-1}, and BF_4^- between 1000–1300 cm^{-1}. The UV-Vis spectra of **4**, **5**, and **6** basically show two large absorptions in the UV region. The UV absorptions, at longer wavelengths, are 291 ($\log \epsilon = 3.91$), 276 (3.80), and 300 nm (3.93), for **4**, **5**, and **6**, respectively. The pattern of the UV spectrum of **3**, however, is quite different from the others exhibiting only weak *d–d* absorptions between 300 and 500 nm. That is, there is no band due to a charge-transfer transition. As all of the *p*-nitroaniline ligands used here display an intense charge-transfer absorption band in the near ultraviolet region, it is noteworthy that the UV absorptions of the corresponding ruthenium complexed ligands show charge-transfer absorptions which are blue-shifted. This trend is illustrated in Figs. 1 and 2 where the electronic

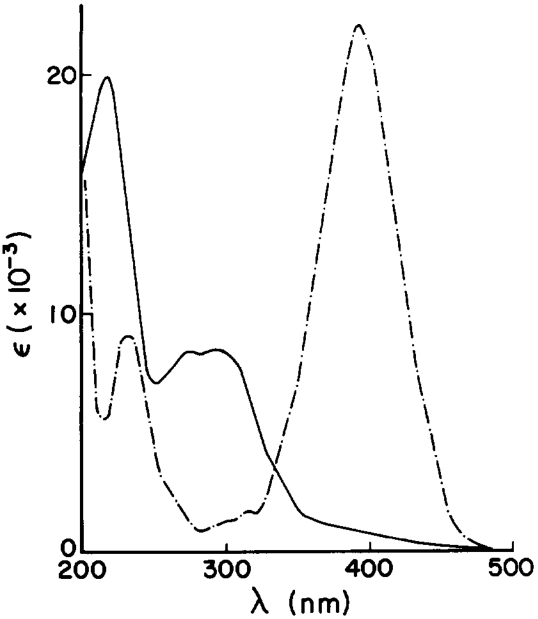


Fig. 1. Electronic absorption spectra of NPP (·—·—·) and **6** (———) in absolute methanol at 25°C.

spectrum of the free ligand NPP is compared with that of the corresponding ruthenium complex. In terms of practical laser frequency doubling, the absorption edge should be near, but not include, the wavelength of the second harmonic as was noted for these compounds when 1064 nm radiation is used.

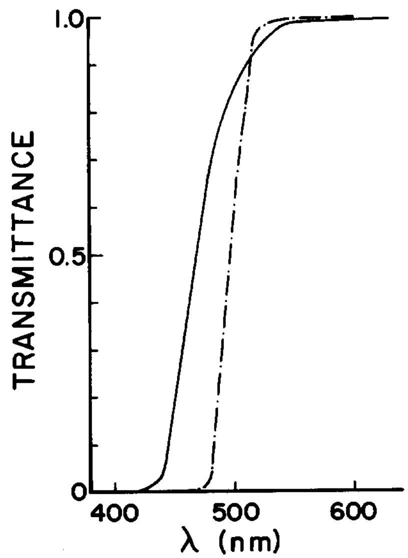


Fig. 2. Absorption cutoffs of 10^{-2} *M* solutions in absolute methanol of NPP (·—·—·) and **6** (———).

Table 1

Second harmonic intensity for a series of powders [a]

Compound	Relative second-harmonic intensity [b]	Compound	Relative second-harmonic intensity [b]
Urea	1.0	**4**	0.9
1	0.7	**5**	1.0
2	0.7	**6**	0.7
3	0.7		

[a] The fundamental radiation is supplied by a Quantel International Q-switched Nd:YAG laser, with about 0.9 J/pulse at 1064 nm and with a repetition rate of 10 Hz, and a pulse width of 15 ns. [b] Relative to SHG intensity of urea.

The relative efficiency of second-harmonic generation [7] (SHG) for these compounds is summarized in Table 1. The SHG efficiency of each ruthenium complex is on the order of that for urea, although it is substantially lower than the best organic compounds. We also measured the SHG efficiency of $[(\eta^5\text{-dienyl})\text{Ru}(\eta^6\text{-arene})]\text{X}$ listed in ref. 8, and again observed similar efficiencies (0.7–1.0 relative to that of urea). All of the ruthenium complexes studied decomposed to some extent in the radiation field (1064 nm) generated by Nd : Yag laser source (0.9 J/pulse).

Even though two of the organometallic compounds, **5**, **6**, incorporate ligands which in themselves are among the most efficient SHG materials (NPP, 50 × urea; MNA, 22 × urea) the resulting organometallic salts have only modest SHG efficiencies.

The low SHG efficiency could be the result of either a molecular or crystal structure problem. On the molecular level, the electric dipole moment (μ) induced in a molecule by the presence of a local field (E) can be expressed in a power series. It is the first hyperpolarizability tensor (β) that directly influences the SHG efficiency.

$$\mu = \alpha E + \beta EE + \gamma EEE$$

Two factors at the molecular level could contribute to this rather dramatic effect. First, the d_π–p_π interaction of the metal with the ligand may interrupt the donor-acceptor interaction which is predominantly responsible for the nonlinearity in the ligand. This would be consistent with the large changes noted in the electronic absorption spectra. Second, if the two factors which give rise to the hyperpolarizability tensor β (the change in dipole moment between the ground and excited state and the electronic transition moment) are not aligned, individual components of the tensor will not reach their maximum values. While this may account for part of the reduction in SHG efficiency it seems unlikely to account for it entirely.

Even when β is large if these molecules are not incorporated in the solid so that they contribute in an additive fashion to the second-order electric susceptibility (χ^2), then the SHG efficiency can still be low. The susceptibility (χ^2) is defined by the following equation

$$p = \chi^1 E + \chi^2 EE + \chi^3 EEE$$

Where p is the induced polarization of the solid, χ^n is the n^{th} order electric susceptibility and E is the optical field. It is possible that the reduction in SHG efficiency (NPP → **6** of almost 80 ×) is due to both crystal packing and molecular structure, but this will remain uncertain until β is measured via electric-field-induced second-harmonic (EFISH) studies.

Experimental

Melting points were determined in sealed capillaries on a Thomas–Hoover Unimelt melting point apparatus and are uncorrected. IR spectra were obtained with a Perkin–Elmer 347 IR spectrophotometer. UV-Visible spectra were taken in CH_3OH on a Varian–Cary 219 spectrometer. ^1H NMR spectra were recorded at 80 MHz, in CD_3CN or acetone-d_6 on a Varian CFT-20 spectrometer. Chemical shifts are reported in ppm downfield from an internal standard, tetramethylsilane. Elemental analysis was performed by Galbraith Laboratories, Inc., Knoxville, TN. (*S*)(–)-2-Hydroxymethyl-1-(4-nitrophenyl)pyrrolidine or *N*-(4-nitrophenyl)-(L)-prolinol (NPP) was prepared according to a published procedure [9]. For the SHG studies, the instrumentation and procedure was the same as that described in a previous publication [7].

[(η^5-Thiophene)Ru(η^5-C_5H_5)]BF_4 (2) [6]

A solution of (η^5-C_5H_5)Ru(PPh_3)$_2$Cl (**1**) [10] (1.00 g, 1.38 mmol) in thiophene (12 mL) was added to a suspension of $AgBF_4$ (0.35 g, 1.80 mmol) in absolute methanol (10 mL) and thiophene (7 mL), and the mixture was stirred under Ar at 25 °C for 24 h. The solvents were evaporated *in vacuo*, the residue was taken up in methylene chloride (20 mL) and filtered to remove AgCl. Addition of diethyl ether (20 mL) to the filtrate gave **2** (242 mg, 73%) as a white solid: m.p. 295 °C (dec); ^1H NMR (acetone-d_6) δ 5.49 (s, 5H, C_5H_5), 6.50 (m, 2H, thiophene H (2, 5)), and 6.57 (m, 2H, thiophene H (3, 4)).

[(η^6-Nitrobenzene)Ru(η^5-C_5H_5)]BF_4 (3)

A solution of **1** (1.00 g, 1.38 mmol) in nitrobenzene (20 mL) was added to a suspension of $AgBF_4$ (0.30 g, 1.54 mmol) in absolute methanol (10 mL) and the mixture was stirred under argon at 25 °C for 24 h. After filtration of AgCl addition of diethyl ether (150 mL) to the filtrate gave a pale brownish-yellow solid. The solid was then dissolved in acetone (5 mL) and slow addition of diethyl ether (50 mL) gave **3** as pale yellow crystals in 47% yield: m.p. 308–312 °C (dec); UV (methanol) 312 nm (log $\epsilon = 3.04$), 368 (2.81), 410 (2.59), 470 (2.24), and 500 (2.12); IR (KBr) 3045, 3030, 3000, 2950, 2900, 2820, 1560, 1350, 1150–1000 (BF_4^-), 855, 845, 682 cm^{-1}; ^1H NMR (CD_3CN) δ 5.50 (s, 5H, C_5H_5), 6.45 (m, 3H, nitrobenzene (3, 4, 5)) and 7.15 ppm (m, 2H, nitrobenzene (2, 6)); Anal. Found: C, 35.17; H, 2.69; N, 3.73. $C_{11}H_{10}BF_4NO_2Ru$ calcd.: C, 35.13; H, 2.68; N, 3.72%.

[(η^6-N,N-Dimethyl-4-nitroaniline)Ru(η^5-C_5H_5)BF_4 (4)

A solution of **1** (1.00 g, 1.38 mmol) and *N,N*-dimethyl-4-nitroaniline (3 g, 18 mmol) in methylene chloride (140 mL) was added to a suspension of $AgBF_4$ (0.3 g, 1.54 mmol) in absolute methanol (10 mL) and the mixture was stirred under argon at 25 °C for 24 h. After the filtration of AgCl, addition of diethyl ether (150 mL) to the filtrate gave a brownish-yellow solid. The solid was then dissolved in acetonitrile (10 mL) and slow addition of diethyl ether (50 mL) gave **4** (310 mg, 62%) as a yellow solid: m.p. 282–285 °C; UV (methanol) 216 nm (log $\epsilon = 4.35$), 270 (3.94), and 294

(3.91); IR (KBr) 3105, 2900, 2820, 1560, 1350, 1080–1040 (BF_4^-), 750, 650, 610 cm^{-1}; ^1H NMR (CD_3CN) δ 2.85 (s, 6H, methyl), 5.30 (s, 5H, C_5H_5), 5.65 (d, 2H, $J = 9$ Hz), and 6.90 (d, 2H, $J = 9$ Hz); Anal. Found: C, 37.16; H, 3.63; N, 6.62. $C_{13}H_{15}BF_4N_2O_2Ru$ calcd.: C, 37.25; H, 3.61; N, 6.68%.

[(η^6-2-Methyl-4-nitroaniline)Ru(η^5-C_5H_5)]BF_4 (5)

Compound **5** was prepared in an analogous manner using 2-methyl-4-nitroaniline (MNA) (2.25 g, 14.8 mmol). Yield 310 mg, 55.5%: m.p. 185–187 ° C; UV (methanol) 206 nm (log $\epsilon = 4.29$), 244 (3.82), 276 (3.80); IR (KBr) 3450, 3360, 3250, 3090, 2900, 1640, 1560, and 1350 (NO_2), 1100 ~ 1000 (BF_4^-), 850, 820, 760, and 670 cm^{-1}; ^1H NMR (acetone-d_6) δ 2.50 (s, 3H, methyl), 2.81 (s, 2H, NH_2), 5.40 (s, 5H, C_5H_5), 6.35 (d, 1H, $J = 8$ Hz), 7.05 (d, 1H, $J = 8$ Hz), and 7.20 (1H, s). Anal. Found: C, 35.85; H, 3.49; N, 6.73. $C_{12}H_{13}BF_4N_2O_2Ru$ calcd.: C, 35.58; H, 3.23; N, 6.91%.

[(η^6-N-(4-Nitrophenyl)-(L)-prolinol)Ru(η^5-C_5H_5)BF_4 (6)

Complex **6** was prepared in an analogous manner using *N*-(4-nitrophenyl)-(L)-prolinol (2.7 g, 12.2 mmol). Yield 330 mg, 50.3%: m.p. 192–195 ° C; UV (methanol) 217 nm (log $\epsilon = 4.30$), 276 (3.93), and 300 (3.93); IR (KBr) 3560, 3300, 2920, 2870, 1550, and 1340 (-NO_2), 1010–1100 (BF_4^-), and 650 cm^{-1}; ^1H NMR δ (CD_3CN) 2.70–4.00 (m, 10H), 5.30 (s, 5H, C_5H_5), 5.93 (d, 1H, $J = 7.2$ Hz), 5.95 (d, 1H, $J = 7.2$ Hz), and 6.9 (d, 2H, $J = 7.2$ Hz); Anal. Found: C, 40.37; H, 4.18; N, 5.76. $C_{16}H_{18}BF_4N_2O_3Ru$ calcd.: C, 40.53; H, 3.83; N, 5.91%.

Acknowledgment

Support of the Air Force Office of Scientific Research under Grant AFOSR-84-0363 and the National Science Foundation under Grants DMR-8615305 and DMR-8921071 is gratefully acknowledged. One of us (DWR) was supported by a grant from the Research Corporation. We wish to thank Richard D. McCullough and Allan B. Bailey for their helpful discussions and Professor Andreas Ludi (Universität Bern) for samples of the ruthenium compounds listed in Table 1 of ref. 8.

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