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Highly polarized ruthenium alkynyls with nitrothienyl substituents

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This paper is dedicated with deep respect and appreciation to Professor Andrew Wojcicki on the occasion of his retirement from Ohio State University

Abstract

Me₃SiC=CC₄H₂S-5-NO₂ was synthesized in good yield by palladium-catalyzed cross-coupling of ethynyltrimethylsilane and 2bromo-5-nitrothiophene or 2-iodo-5-nitrothiophene. Reactions of Me₃SiC=C(C₄H₂S)NO₂ with a series of ruthenium chloride complexes [RuClLL'(Cp')] gave the alkynyls [Ru(2-C=CC₄H₂S-5-NO₂)LL'(Cp')] (L, L' = CO, PMe₂Ph or PPh₃; Cp' = C₅H₅ or C₅Me₅). These metal complexes, each with a strongly electron-donating metal center at one end and an electron-accepting organic substituent at the other end of a π -conjugated chain, are strongly polarized and are expected to demonstrate non-linear optical activity. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Alkynyl; Heterocycle; Ruthenium; Solvatochromism; Non-linear optical activity

1. Introduction

Non-linear optical materials have attracted interest among physicists, chemists, and materials scientists [1,2]. In particular, materials that double [3-6] or triple [7-10]the frequency of an incident beam of light are under intense study. Current NLO devices generally rely on inorganic crystals such as lithium niobate, titanyl phosphate, quartz, and gallium arsenide, but such materials can be expensive, fragile, and difficult to integrate into devices. [11,12,2]. Organic materials offer several advantages, such as large non-linear coefficients, high optical damage thresholds, ease of processing, and the possibility of tailoring compounds to the precise requirements of the device [13,14,9,6,10]. Organometallic compounds, distinguished by unique metal-ligand interactions, have received increasing attention [15-17,8,5,18]. Metal-to-ligand or ligand-to-metal charge transfer gives intense optical absorption bands in the

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UV and visible regions, which are often associated with large second-order optical non-linearities. Organometallic compounds with non-linear second-order [5], third-order and optical-limiting [8] properties have been recently reviewed. Some organometallic compounds display second harmonic generation (SHG) efficiencies as good as or better than organic reference compounds. Ferrocene derivatives have been particularly well investigated, but they have the disadvantage that the donor-acceptor interaction is perpendicular to the metal-ligand axis, leading to an unfavorable alignment [16]. On the other hand, metal alkynyls with conjugated aryl substituents have the metal in the same plane as the arylalkynyl and display large second-order non-linear optical susceptibilities [19-53]. Humphrey and others have particularly investigated the synthesis and NLO properties of ruthenium alkynyl complexes [19-25,27-31,33,35,36,39-44,46-48].

We report here a series of ruthenium σ -thienylalkynyl complexes, [Ru(2-C=CC₄H₂S-5-NO₂)LL'(Cp')] (L = CO, PMe₂Ph, or PPh₃; Cp' = C₅H₅ or C₅Me₅). Each complex features a π -conjugated chain with an electron-donating metal center at one end and electron-accepting nitro group at the other [40].

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2. Experimental

Unless otherwise noted, all preparations and manipulations were carried out under a dry, nitrogen atmosphere using standard Schlenk techniques or a Vacuum Atmospheres HE-493 dry box. Methanol was distilled from magnesium turnings. Pyridine, triethylamine and diisopropylamine were distilled from calcium hydride. Ethynyltrimethylsilane (Farchan Laboratories) was passed through a short bed of Grade 1 neutral alumina. Triphenylphosphine (Aldrich Chemical) was recrystallized from ethanol. Palladium acetate (Pressure Chemical), 2-bromothiophene, 2-iodothiophene and copper (I) iodide (Aldrich Chemical) were used without further purification. 2-Bromo-5-nitrothiophene was made according to Babasinian [54].

2.1. Preparation of 2-trimethylsilylethynyl-5nitrothiophene (1)

2-Bromo-5-nitrothiophene (2.080 g, 10.00 mmol) was dissolved in THF (20 ml). Pd(OAc)₂ (0.050 g, 0.20 mmol), PPh₃ (0.100 g, 0.400 mmol), and CuI (0.038 g, 0.20 mmol) were added. Ethynyltrimethylsilane (1.100 g, 11.00 mmol) was added dropwise from a syringe. The mixture was refluxed for an hour and cooled to ambient temperature. After filtration, the solvent was removed in vacuo to give a brown solid residue. It was sublimed to give a light yellow, crystalline solid (1.500 g, 70%). Melting point (m.p.): 60 °C. ¹H NMR (200 MHz, CDCl₃, $\delta_{\rm H}$): 0.25 (s, 9H), 7.07 (d, 1H, J = 4.2 Hz), 7.75 (d, 1H, J = 4.2 Hz).

2.2. Preparation of 2-ethynyl-5-nitrothiophene (2)

2-Trimethylsilylethynyl-5-nitrothiophene (0.225 g, 1.00 mmol) (1) was dissolved in methanol (20 ml). Potassium carbonate (0.028 g, 0.20 mmol) was added. After stirring at ambient temperature for 2 h, the solvent was removed in vacuo to give a brown residue, which was sublimed to give light yellow crystals (0.100 g, 70%). M.p.: 65 °C. ¹H NMR (200 MHz, CDCl₃, $\delta_{\rm H}$): 3.55 (s, 1H), 7.15 (d, 1H, J = 4.0 Hz), 7.77 (d, 1H, J = 4.0 Hz).

2.3. Preparation of $[Ru(2-C \equiv CC_4H_2S-5-NO_2)(CO)_2(Cp)]$ (3)

2-Trimethylsilylethynyl-5-nitrothiophene (0.045 g, 0.20 mmol) and [RuCl(CO)₂(Cp)] (0.052 g, 0.20 mmol) were dissolved in methanol (20 m;). KF (0.018 g, 0.30 mmol) was added. The mixture was refluxed for 20 h and cooled to room temperature (r.t.). The solvent was removed in vacuo. The brown residue was purified on a neutral Grade 1 alumina column with hexane to give a yellow solid (0.038 g, 50%). M.p.: 130 °C. ¹H NMR (200 MHz, CDCl₃,

 $δ_{\rm H}$: 5.49 (s, 5H), 6.76 (d, J = 4.4 Hz, 1H), 7.74 (d, J = 4.4 Hz, 1H). ¹³C{¹H} NMR (100 MHz, CDCl₃, $δ_{\rm C}$): 88.0 (d, J = 182 Hz, Cp), 102.9, 105.8 (s, C=C), 127.9 (d, J = 116 Hz), 129.1 (d, J = 116 Hz) (thienyl), 136.4 (s), 146.5 (s), (thienyl), 195.6 (s, CO). IR (KBr, cm⁻¹): 1995.8 (s, CO), 2046.1 (s, CO), 2102.0 (s, C= C). UV–Vis (CH₂Cl₂, $λ_{max}$, nm): 420 ($\varepsilon = 2.13 \times$ 10⁴). MS (EI): 375 (M^+), 347 (M^+ –CO), 319 (M^+ –2CO). Calc. for ¹²C₁₃⁻¹H₇⁻¹⁴N¹⁶O₄⁻¹⁰²Ru³²S: 375 amu. Analysis of C₁₃H₇NO₄RuS: Calc.: C, 41.6; H, 1.87; N, 3.73. Found: C, 41.7; H, 2.00; N, 3.33%.

2) 2-Ethynyl-5-nitrothiophene (2) (0.076 g, 0.50 mmol) and [RuCl(CO)₂(Cp)] (0.130 g, 0.500 mmol) were dissolved in CH₂Cl₂ (10 ml). TlBF₄ (0.175 g, 0.600 mmol) was added. The mixture was stirred at ambient temperature for 10 h and filtered. The solvent was removed in vacuo and the residue was dissolved in MeOH (20 ml). K₂CO₃ (0.020 g, 0.14 mmol) was added. After stirring the mixture at ambient temperature for 1 h, the solvent was removed in vacuo. The ¹H NMR spectrum indicated only 20% yield of **3**, with remaining [RuCl(CO)₂(Cp)] (80%).

2.4. Preparation of $[Ru(2-C \equiv CC_4H_2S-5-NO_2)(CO)(PPh_3)(Cp)]$ (4)

2-Trimethylsilylethynyl-5-nitrothiophene (1, 0.045 g, 0.20 mmol) and [RuCl(CO)(PPh₃)(Cp)] (0.052 g, 0.20 mmol) were dissolved in MeOH (20 ml). KF (0.018 g, 0.30 mmol) was added. The mixture was refluxed for 4 h, then cooled to ambient temperature. The solvent was removed in vacuo. The solid residue was purified on a neutral Grade 1 alumina column with hexane to give orange crystals of **4** (0.073 g, 60%). M.p.: 160 $^{\circ}$ C. ¹H NMR (200 MHz, CDCl₃, $\delta_{\rm H}$): 5.01 (s, 5H), 6.28 (d, J =4.4 Hz, 1H), 7.62 (d, J = 4.4 Hz, 1H), 7.42 (m, 15H). ¹³C NMR (50 MHz, CDCl₃, $\delta_{\rm C}$): 84.4, 104.7 (C=C), 85.9 (d, $J_{\rm CP} = 1.5$ Hz, Cp), 125.2, 128.3 (s, thienyl), 126.9, (d, ${}^{3}J_{\rm CP} = 10$ Hz), 131.9 (d, ${}^{4}J_{\rm CP} = 10$ Hz) (C_m, C_o of Ph), 128.9 (d, ${}^{5}J_{\rm CP} = 2.3$ Hz), 133.7 (d, ${}^{2}J_{\rm CP} = 50$ Hz, C_{ipso} of Ph), 137.1, 143.3 (s, thienyl), 201.0 (d, $J_{CP} = 28$ Hz, CO). IR (KBr, cm⁻¹): 1961.3 (s, CO), 2071.2 (s, C=C). UV-Vis (CH₂Cl₂, λ_{max} , nm): 462 ($\varepsilon = 2.20 \times 10^4$). MS (EI): 609 (M^+). Calc. for ${}^{12}\text{C}_{30}{}^{1}\text{H}_{22}{}^{14}\text{N}{}^{16}\text{O}_{3}{}^{31}\text{P}{}^{102}\text{Ru}{}^{32}\text{S}$: 609 amu. Analysis for C₃₀H₂₂NO₃PRuS: Calc.: C, 59.1; H, 3.19; N, 2.03. Found: C, 58.8; H, 3.59; N, 2.25%.

2.5. Preparation of $[Ru(2-C \equiv CC_4H_2S-5-NO_2)(PPh_3)_2(Cp)]$ (5) [48]

2-Trimethylsilylethynyl-5-nitrothiophene (0.045 g, 0.20 mmol) and $[\text{RuCl}(\text{PPh}_3)_2(\text{Cp})] (0.145 \text{ g}, 0.200 \text{ mmol})$ were dissolved in methanol (20 ml). KF (0.018 g, 0.30 mmol) was added. The mixture was stirred at ambient temperature for 4 h. The solvent was removed

in vacuo. The solid residue was purified on a Grade 1 neutral alumina column with 1:1 hexane-Et₂O to give purple crystals of 5 (0.100 g, 60%) m.p.: 202 °C. ¹H NMR (200 MHz, CDCl₃, $\delta_{\rm H}$): 4.39 (s, 5H, Cp), 6.39 (d, J = 4.4 Hz, 1H), 7.78 (d, J = 4.4 Hz, 1H), 7.20 (m, 30H). ¹³C{¹H} NMR (100 MHz, CDCl₃, $\delta_{\rm C}$, gated decoupled): 86.1 (d, J = 163 Hz, Cp), 90.5, 111.6 (s, C= C), 125.2 (d, J = 169 Hz, thienyl), 130.8 (d, J = 167 Hz, thienyl), 127.5 (d, J = 160 Hz), 133.6 (d, J = 167 Hz) $(J_{CP} = 4.8 \text{ Hz}, C_m, C_o \text{ of Ph}), 128.9 \text{ (d, } J = 161 \text{ Hz},$ $J_{\rm CP} = 7.4$ Hz, C_p of Ph), 131.1, 133.1 (s, thienyl), 138.1 (d, ${}^{2}J_{CP} = 20$ Hz, C_{ipso} of Ph). IR (KBr, cm⁻¹): 2020.9 (s, C=C). UV–Vis (CH₂Cl₂, λ_{max} , nm): 533.5 (δ = 3.07×10^4). MS (EI, amu): 843 (M⁺). Calc. for ¹²C₄₇¹H₃₇¹⁴N¹⁶O₂³¹P₂¹⁰²Ru³²S: 843 amu. Analysis for $C_{47}H_{37}NO_2P_2RuS:\ Calc.:\ C,\ 66.9;\ H,\ 4.40;\ N,\ 1.66.$ Found: C, 67.1; H, 4.60; N, 1.72%.

2.6. Preparation of $Ru(2-C \equiv CC_4H_2S-5-NO_2)(PMe_2Ph)_2(Cp^*)$] (6)

2-Trimethylsilylethynyl-5-nitrothiophene (0.045 g, 0.20 mmol) and [RuCl(PMe₂Ph)₂(Cp*)] (0.110 g, 0.200 mmol) were dissolved in methanol (20 ml). KF (0.018 g, 0.30 mmol) was added. The resulting blue mixture was stirred at ambient temperature for 4 h. The solvent was removed in vacuo to give a blue, solid residue, which was purified on a neutral alumina column with 1:1 hexane- Et_2O to give a brown solid of 6 (0.113 g, 85%). M.p.: 160 °C (dec). ¹H NMR (200 MHz, CDCl₃, $\delta_{\rm H}$): 1.48 (bs, 15H, Cp*), 1.54 (m, 12H, PMe₂Ph), 6.49 (d, J = 4.4 Hz), 7.85 (d, J = 4.4 Hz) (thienyl), 7.34–7.63 (m, 10H, phenyl). ¹³C{¹H} NMR (100 MHz, CDCl₃, δ_{C} , gated decoupled): 10.2 (q, J = 127 Hz, Me of Cp*), 19.3, 20.6 (d, J = 136 Hz, Me of PMe₂Ph), 93.7 (s, C of Cp*), 107.6 (s, C=C), 124.2 (d, J = 172 Hz), 131.6 (d, J = 175Hz) (thienyl), 127.8 (d, J = 160 Hz), 130.6 (d, J = 160Hz) (C_m, C_o, of Ph), 128.8 (d, J = 158 Hz, C_p of Ph), 141.5 (m, C_{ipso} of Ph). IR (KBr, cm⁻¹): 2008 (s, C=C). UV–Vis (CH₂Cl₂, λ_{max} , nm): 582.5 ($\varepsilon = 2.42 \times 10^4$). MS (EI, amu): 665 (M^+). Calc. for C₃₂H₃₉NO₂P₂RuS: 665. Analysis for C₃₂H₃₉NO₂P₂RuS: Calc.: C, 57.7; H, 5.86; N, 2.10. Found: C, 57.6; H, 6.13; N, 2.00%.

2.7. Thermogravimetric analysis of $[Ru(2-C=CC_4H_2S-5-NO_2)(PPh_3)_2(Cp)]$ (5)

Compound 5 (0.017 g, 0.020 mmol) was analyzed on a platinum pan by using a TA Instruments 2950 Thermogravimetric Analyzer. The furnace was heated from 30 to 600 °C at 20 °C min⁻¹ under an air atmosphere.

3. Results

3.1. Synthesis

 $Me_3SiC \equiv CC_4H_2SNO_2$ (1) [55] was synthesized in good yield by palladium-catalyzed cross-coupling of ethynyltrimethylsilane and 2-bromo-5-nitrothiophene (or 2-iodo-5-nitrothiophene). The reaction of 1 with a series of ruthenium chloride complexes [RuClLL'(Cp')] gave corresponding [RuLL'(C=CC_4H_2S)NO_2(Cp')] products (Scheme 1). [Ru(2-C=CC_4H_2S-5-NO_2)(PPh_3)_2(Cp)] has been previously prepared by Wu and coworkers [48].

The reaction was slow for the ruthenium complexes with CO ligands. Whereas the reaction of **1** and $[RuCl(CO)_2(Cp)]$ required refluxing methanol, more electron-rich $[RuCl(PMe_2Ph)_2(Cp^*)]$ reacted almost instantly with **1** at ambient temperature. The relative reaction rates and yields decrease with decreasing electron density on the metal center in the order $[RuCl(PMe_2Ph)_2(Cp^*)] > [RuCl(PPh_3)_2(Cp)] >$ $[RuCl(CO)(PPh_3)(Cp)] > [RuCl(CO)_2(Cp)].$

Compounds 3-5 are air-stable and their solutions in CDCl₃ are stable for several days. Compound **6** is moderately air-sensitive in solution, oxidizing slowly in CDCl₃, but air-stable as a solid.

3.2. Characterization

The ruthenium σ -thienylalkynyl complexes were characterized by ¹H and ¹³C NMR, IR, UV–Vis, MS, and microanalysis. Selected spectroscopic data are listed in Table 1 and discussed below. Thermogravimetric analysis of **5** showed that it is stable up to 200 °C in the air, then gradually decomposes by losing its ligands.

4. Discussion

4.1. Synthesis

Me₃SiC=CC₄H₂S-5-NO₂ (1) was prepared by the cross-coupling reaction of ethynyltrimethylsilane and 2-bromo-5-nitrothiophene in triethylamine. The protecting trimethylsilyl group of 1 was removed by reaction with K₂CO₃ to give HC=CC₄H₂S-5-NO₂ (2). Overall,



Scheme 1. Preparation of [Ru(2-C=CC₄H₂S-5-NO₂)LL'(Cp')].

Table 1	
Selected spectroscopic data for	$[Ru(2-C=CC_4H_2S-5-NO_2)LL'(Cp')]$ (3–6)

	L, L′	Cp′	$\delta_{\rm H} \ {\rm Cp'}$	$\delta_{\rm H} {\rm C_4H_2S}$	$\delta_{\rm C}{\rm Cp'}$	v(C=C) (cm ⁻¹)	$\lambda_{\rm max}$ (ϵ , M ⁻¹ cm ⁻¹ × 10 ⁻⁴ , CH ₂ Cl ₂)
3	(CO) ₂	C_5H_5	5.49	6.76, 7.77	88.0	2102	420.0 (2.13)
4	(CO)(PPh ₃)	C_5H_5	5.01	6.28, 7.62	85.9	2071	462.5 (2.20)
5	$(PPh_3)_2$	C_5H_5	4.39	6.39, 7.78	86.1	2021	533.5 (3.07)
6	$(PMe_2Ph)_2$	C_5Me_5	1.48	6.49, 7.85	93.7	2008	582.5 (2.42)

the method is more convenient than the dehydrobromination of Z-2-(2-bromovinyl)-5-nitrothiophene [55]. Sonogashira conditions have been similarly used to prepare substituted 2-ethynyl-5-nitrothiophenes [47,46] and related alkynes [48].

A general synthetic methodology for ruthenium σ alkynyls is to react a 1-alkyne, RC=CH, with a ruthenium chloride, [RuClL₂(Cp')], in a polar solvent, followed by deprotonation of the vinylidene products, [RuL₂(C=CHR)(Cp')]⁺. The reaction has been used extensively in the preparation of ruthenium alkynyls with NLO properties [19–25,27–31,33,35,36,39–44,46– 48]. We find it convenient to carry out the deprotection of the trimethylsilyl alkyne **2** with KF in methanol in the presence of an organoruthenium chloride, giving the ruthenium alkynyl in a single step.

4.2. Spectroscopy

The spectroscopic features of complexes 3-6 depend in the usual way on electron density at the metal center, induced by the electron-donor abilities of the ancillary ligands. The ¹H chemical shifts of the Cp ligands of complexes 3-5 shift upfield by about a half ppm as each weakly electron-donating CO ligand is replaced by a more basic PPh₃ ligand. The ¹³C NMR Cp shifts of 3-5show a slight upfield shift as CO is replaced by PPh₃.

Decreasing infrared v(C=C) with increasing electron density on the metal center of alkynyl complexes is a well-known phenomenon that has been attributed to several causes: increasing metal- $d\pi$ to alkynyl- π backbonding, decreasing metal- $d\pi$ to alkynyl- π filled-filled interaction, and increasing $M\delta^+ - C\delta^-$ bond polarity [56]. Calculations [57] and photoelectron spectroscopy [58–60] indicate that metal- $d\pi$ to alkynyl- π backbonding actually plays a minor role in the properties of $[M(C=CR)L_2(Cp)]$. Regardless of the origin, we observe an approximately 100 cm⁻¹ decrease in v(C=C) with increasing electron-donor ability of the ancillary ligand in the series 3-6. Humphrey and coworkers stress the importance of the extent of π -conjugation along the chain of ruthenium alkynyls in determining NLO properties [43,44,61,8,5]. They and Lewis et al. [62] found that π -conjugation along the chain is favored by strongly electron-donating phosphine ancillary ligands.

Ruthenium alkynyls 3–6 showed strong ($\varepsilon \sim 10^4$) UV-Vis absorptions. The λ_{max} value is dependent on the ancillary ligands, moving to longer wavelength with increasing electron-richness from 420.0 nm ($\varepsilon = 2.13 \times$ 10⁴) for **3** to 582.5 nm ($\varepsilon = 2.42 \times 10^4$) for **6** (both in CH₂Cl₂). The absorption is apparently a metal-ligand charge-transfer band. Stronger electron-donating ligands in 5 and 6 lower the HOMO-LUMO gap. Solvatochromic behavior of an absorbance maximum is a general indication of appreciable quadratic molecular hyperpolarizability (β), i.e. a large dipole moment difference between the ground and first excited states [29,63,64]. We observe substantial positive solvatochromism for compounds 3-6. Absorption maxima in the moderately polar solvent dichloromethane (dielectric constant = 8.93) are listed in Table 1. In the nonpolar solvent cyclohexane (dielectric constant = 2.02), the UV-Vis absorptions shift to shorter wavelength (400.5 nm for 3, 435.5 nm for 4, 485.0 nm for 5 and 503.0 nm for 6). The effect is particularly striking for 6, with a shift of nearly 80 nm. Positive solvatochromism indicates charge transfer from the electron-rich metal to the acceptor upon excitation, [29,63,64] i.e. a more polar excited state according to Scheme 2.

The non-linear optical properties of these complexes remain to be investigated; unfortunately, we lack the equipment to make the measurements. We expect 3-6 to display significant second-order or third-order nonlinear optical activity, based on comparison to similar ruthenium alkynyls with nitrophenyl and nitropyridyl substituents. Extending the length of the conjugated chain by adding alkynyl, alkenyl, aromatic or heteroaromatic spacers would likely increase their activity [5,8].

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Scheme 2. Increased polarity of an excited-state ruthenium alkynyl.

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