Organometallic complexes for nonlinear optics. 52. Syntheses, structural, spectroscopic, quadratic nonlinear optical, and theoretical studies of Ru(C2C6H4R-4)(κ²-dppf)(η⁵-C5H5) (R = H, NO2)

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ARTICLE INFO

ABSTRACT

The synthesis of Ru(C≡CC6H4-4-NO2)(κ²-dppf)(η⁵-C5H5) (**1**) is reported, together with spectroscopic, X-ray structural, linear optical and quadratic nonlinear optical (NLO) studies of **1** and Ru(C≡CPh) (κ²-dppf)(η⁵-C5H5) (**2**), the last-mentioned using the hyper-Rayleigh scattering technique at 1064 nm. Quadratic nonlinearities for these dppf-containing complexes are comparable to those of their dppe-containing analogues and significantly greater than carbonyl-containing analogues. The linear optical and quadratic NLO properties of **1**, **2** and their dppe-containing analogues have been rationalized by time-dependent density functional theory calculations.

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1. Introduction

The nonlinear optical (NLO) properties of organometallic complexes have come under considerable scrutiny during the past twenty years [1–4], the majority of studies being focused on quadratic nonlinearities and on complexes with a donor-bridge-acceptor composition. The field of organometallics in nonlinear optics was given initial impetus from the promising outcomes of studies with metallocenyl complexes [5], but more recently alkynyl complexes have also attracted significant attention [6–8]. Amongst metal alkynyl complexes, those of ruthenium are some of the most important due to their facile high-yielding syntheses [9,10], enhanced NLO coefficients [11,12], ease of use in construction of multimetallic complexes such as dendrimers [13], and reversible redox properties which afford the possibility of NLO switching [14].

We have previously probed the effect of acceptor group incorporation and π-bridge modification at metal alkynyl complexes, reporting the syntheses and NLO properties (by both electric field-induced second-harmonic generation, EFISH, and the hyper-Rayleigh scattering technique, HRS) of complexes of general formula Ru(4-C≡CC6H4X)(PPh3)2(η⁵-C5H5). Nonlinearities of these complexes increase on proceeding to a strongly dipolar system (replacing X = H by X = NO2) and π-system lengthening (proceeding from X = NO2 to X = C6H4-4-NO2, C≡CC6H4-4-NO2, N=CHC6H4-4-NO2, and Z- and E-CH=CHC6H4-4-NO2, with the last-mentioned being the most efficient in terms of its quadratic NLO performance) [15–18]. We then explored the effect of metal and co-ligand variation in the series of complexes M(4-C≡CC6H4-4-NO2)(L2)(η⁵-C5H5) (M = Fe, Ru, Os, L2 = dppe; M = Ru, Os, L = PPh3; M = Ru, L = CO), for which quadratic nonlinearities increase as M = Fe ≤ Ru ≤ Os and L = CO < phosphines [19]. The more subtle co-ligand modification (replacing 2 × PPh3 with dppe) afforded unclear results, with β_{HRS} data for M(4-C≡CC6H4-4-NO2)(L2)(η⁵-C5H5) suggesting (M = Ru, L2 = 2PPh3) < (M = Ru,

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L_2 = dppe) and (M = Os, L_2 = 2PPh$_3$) $\approx$ (M = Os, L_2 = dppe) (within the error margins of the experiment). We have now returned to this question of the effect of co-ligand variation on quadratic non-linearity in metal alkynyl complexes (and thereby the potential of tuning the response), and report herein the synthesis of the new complex Ru(C≡CC$_6$H$_4$-4-NO$_2$)(κ^2-dppf)(η^5-C$_5$H$_5$) incorporating the electro-active bidentate ligand 1,2-bis(diphenylphosphino)ferrocene, structural studies of both this complex and its non-nitro analogue Ru(C≡CPh)(κ^2-dppf)(η^5-C$_5$H$_5$), spectroscopic and electrochemical characterization of these complexes, quadratic non-linearities from hyper-Rayleigh scattering measurements at 1064 nm, comparison to related extant experimental data, and theoretical studies employing density functional theory (DFT) and time-dependent DFT (TD-DFT) to rationalize the experimental outcomes.

2. Experimental

2.1. General experimental conditions and starting materials

All reactions were performed under a nitrogen atmosphere with the use of Schlenk techniques unless otherwise stated. Dichloromethane was dried by distilling over calcium hydride; all other solvents were used as received. Petrol is a fraction of petroleum spirits of boiling range 60–80 °C. Chromatography was performed on ungraded basic alumina. Phenylacetylene (Aldrich) was used as received. The following were prepared by the literature procedures: RuCl(κ^2-dppf)(η^5-C$_5$H$_5$) [20], HC≡CC$_6$H$_4$-4-NO$_2$ [21].

2.2. Instrumentation

Microanalyses were carried out at the Australian National University. UV–vis spectra of solutions in 1 cm quartz cells were recorded using a Cary 5 spectrophotometer; bands are reported in the form wavelength (nm) [extinction coefficient, 10^4 M^{-1} cm^{-1}]. The infrared spectra were recorded as KBr discs using a Perkin–Elmer System 2000 FT-IR; peaks are reported in cm^{-1}. ^{1}H (300 MHz) and ^{13}C (75 MHz) NMR spectra were recorded using an Inova-300 NMR spectrometer and ^{31}P NMR spectra (121 MHz) were recorded using a Varian Mercury-300 FT NMR spectrometer. The spectra are referenced to residual chloroform (7.26 ppm), CDCl$_3$ (77.0 ppm), or external H$_3$PO$_4$ (0.0 ppm), respectively; atom labelling follows the numbering scheme in Chart 1. The high resolution ESI mass spectrum (HR ESI MS) was obtained utilizing a Bruker Apex 4.7T FTICR-MS instrument. Cyclic voltammetry measurements were recorded using a MacLab 400 interface and MacLab potentiostat from ADInstruments. The supporting electrolyte was 0.1 M (NBu$_4^n$)PF$_6$ in distilled, deoxygenated CH$_2$Cl$_2$.
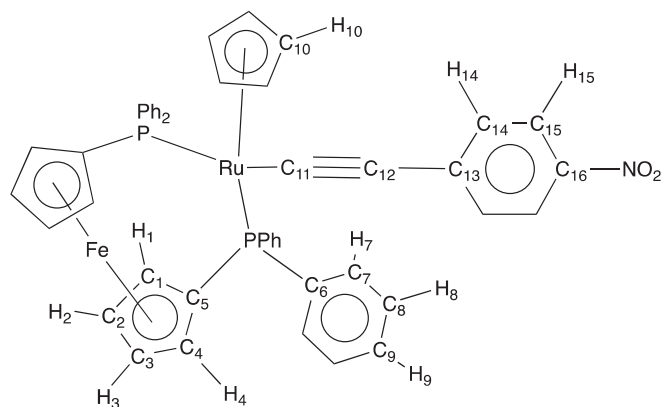

Chart 1. NMR labelling scheme for **1**.

Solutions containing ca 1 × 10^{-3} M complex were maintained under nitrogen. Measurements were carried out at room temperature using Pt disc working-, Pt wire auxiliary- and Ag/AgCl reference electrodes, such that the ferrocene/ferrocenium redox couple was located at 0.56 V (peak separation ca. 0.10 V). Scan rates were typically 100 mV s^{-1}.

2.3. Synthesis of Ru(C≡CC$_6$H$_4$-4-NO$_2$)(κ^2-dppf)(η^5-C$_5$H$_5$) (**1**)

RuCl(κ^2-dppf)(η^5-C$_5$H$_5$) (210.2 mg, 0.278 mmol) and HC≡CC$_6$H$_4$-4-NO$_2$ (41.5 mg, 0.282 mmol) were added to a flask containing MeOH (20 ml). A solution of NaOMe in MeOH (7.00 ml, 0.1 M) was added and the orange mixture was stirred at reflux until the formation of a red solution (ca. 15 min). The red solution was cooled to room temperature, resulting in the precipitation of a red powder that was collected by filtration, affording **1** (184.3 mg, 77%). Crystals of **1** suitable for single-crystal X-ray structural study were grown by slow diffusion of methanol into a dichloromethane solution at room temperature. Elemental analysis (C$_{47}$H$_{37}$FeNO$_2$P$_2$Ru): calcd.: C: 65.14, H: 4.30, N: 1.62%. Found: C: 65.30, H: 4.18, N: 1.35%. HR ESI MS (C$_{47}$H$_{37}$FeNO$_2$P$_2$Ru): calculated: 882.0927, found: 882.0944. UV–vis (CH$_2$Cl$_2$): 469 nm (1.74), 273 nm (1.42). ^{1}H NMR (CDCl$_3$): 3.95, 4.04, 4.11, 5.06 (4 s, 4 × 2H, H$_1$, H$_2$, H$_3$, H$_4$), 4.27 (s, 5H, H$_{10}$), 7.08 (d, J_{HH} = 9 Hz, 2H, H$_{14}$), 7.18–7.73 (m, 20H, H$_7$, H$_8$, H$_9$), 7.99 (d, J_{HH} = 9 Hz, 2H, H$_{15}$). ^{13}C NMR (CDCl$_3$): 68.3, 71.3, 73.2, 76.0 (C$_1$, C$_2$, C$_3$, C$_4$), 80.8 (C$_{12}$), 85.0 (C$_{10}$), 88.3 (t, J_{CP} = 35 Hz, C$_5$), 115.6 (C$_{11}$), 123.9 (C$_{14}$), 127.3 (m), 128.8, 129.3, 134.0 (m) (C$_7$, C$_8$, C$_9$), 130.5 (C$_{15}$), 137.5 (C$_{13}$), 140.4 (m, C$_6$), 142.7 (C$_{16}$). ^{31}P NMR (CDCl$_3$): 55.9.

2.4. Synthesis of Ru(C≡CPh)(κ^2-dppf)(η^5-C$_5$H$_5$) (**2**)

This complex has been prepared previously by an alternative procedure in 98% yield [22]. RuCl(κ^2-dppf)(η^5-C$_5$H$_5$) (113.7 mg, 0.15 mmol) and HC≡CPh (0.05 ml, 0.46 mmol) were added to a flask containing MeOH (15 ml). A solution of NaOMe in MeOH (7.00 ml, 0.1 M) was added and the orange mixture was stirred at reflux until the formation of a red solution (ca. 15 min). The red solution was cooled to room temperature, resulting in the precipitation of a yellow powder that was collected by filtration, affording **2** (103.0 mg, 83%). Crystals of **2** suitable for X-ray diffraction study were grown by slow diffusion of methanol into a dichloromethane solution at room temperature. UV–vis (CH$_2$Cl$_2$): 402 nm (0.14), 311 nm (2.18), 273 nm (1.36). ^{31}P NMR (CDCl$_3$): 56.0.

2.5. Structure determinations

Intensity data were collected using an Enraf-Nonius KAPPA CCD at 200 K with Mo Kα radiation (λ = 0.7170 Å). Suitable crystals were immersed in viscous hydrocarbon oil and mounted on a glass fibre that was mounted on the diffractometer. Using psi and omega scans N_t (total) reflections were measured, which were reduced to N_o unique reflections, with $F_o > 2\sigma(F_o)$ being considered "observed". Data were initially processed and corrected for absorption using the programs DENZO [23] and SORTAV [24]. The structures were solved using direct methods, and observed reflections were used in least squares refinement on F^2, with anisotropic thermal parameters refined for non-hydrogen atoms. Hydrogen atoms were constrained in calculated positions and refined with a riding model. Structure solutions and refinements were performed using the programs SHELXS-97 and SHELXL-97 [25] through the graphical interface Olex2 [26], which was also used to generate the figures. Crystal data for **1**: C$_{47}$H$_{37}$FeNO$_2$P$_2$Ru, M = 866.64, red block, 0.10 × 0.10 × 0.09 mm^3, triclinic, space group P-1 (no. 2), a = 9.926(2), b = 12.406(3), c = 15.571(3) Å, α = 97.23(3),