

Organometallic complexes for nonlinear optics. 41: Syntheses and quadratic NLO properties of 4-{4-(4-nitrophenyl)diazophenyl}ethynylphenylethynyl complexes

Timothy N. Fondum^a, Katy A. Green^a, Michael D. Randles^a, Marie P. Cifuentes^a, Anthony C. Willis^b, Ayele Teshome^c, Inge Asselberghs^c, Koen Clays^c, Mark G. Humphrey^{a,*}

^a Department of Chemistry, Australian National University, Canberra, ACT 0200, Australia

^b Research School of Chemistry, Australian National University, Canberra, ACT 0200, Australia

^c Department of Chemistry, University of Leuven, Celestijnenlaan 200D, B-3001 Leuven, Belgium

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Vale Professor F. Albert Cotton, who bestrode the inorganic chemistry world like a colossus.

Abstract

The syntheses of $[\text{Au}(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{N}=\text{N}-4-\text{C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)]$ (**3**), *trans*- $[\text{Ru}(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{N}=\text{N}-4-\text{C}_6\text{H}_4\text{NO}_2)\text{Cl}(\text{dppm})_2]$ (**4**), $[\text{Ru}(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{N}=\text{N}-4-\text{C}_6\text{H}_4\text{NO}_2)(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ (**5**), and $[\text{Ni}(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{N}=\text{N}-4-\text{C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ (**6**) are reported, together with a single-crystal X-ray diffraction study of **4**. Quadratic nonlinearities for **3–6** and $[\text{Ru}(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{NO}_2)(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ (**7**) have been determined at 1.064 μm and 1.300 μm by the hyper-Rayleigh scattering (HRS) technique, comparison to related complexes revealing that β values increase on introduction of azo group and π -system lengthening.

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1. Introduction

The nonlinear optical (NLO) properties of organometallic complexes have been studied intensively over the past years [1–6], with the majority of studies focusing on quadratic nonlinearities of complexes with a donor-bridge-acceptor composition. After metallocenyl complexes, alkynyl complexes have probably attracted most attention [7,8]. One area of interest is the effect of π -bridge lengthening on molecular nonlinearities. We have previously reported the series of complexes *trans*- $[\text{Ru}\{\text{C}\equiv\text{C}(-4-\text{C}_6\text{H}_4\text{C}\equiv\text{C})_n-4-$

$\text{C}_6\text{H}_4\text{NO}_2\}\text{Cl}(\text{dppm})_2]$ ($n = 0-2$) [9], for which quadratic nonlinearity increased slightly on proceeding from $n = 0$ to $n = 1$, but significantly on further progression to $n = 2$. We have also described bridge modifications in the series $[\text{M}(\text{C}\equiv\text{C}-4-\text{C}_6\text{H}_4\text{XY}-4-\text{C}_6\text{H}_4\text{NO}_2)\text{L}_n]$ [$\text{ML}_n = \text{trans-RuCl}(\text{dppm})_2, \text{Ru}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5), \text{Au}(\text{PPh}_3)$; XY = Z and *E* CH=CH, N=N, N=CH, C≡C, nothing (i.e. biphenylene)] [10–14], for which quadratic nonlinearity peaked at the azo-linked examples. These observations prompted us to examine longer π -bridge alkynyl ligands incorporating an azo linkage. We report herein the synthesis of 4-O₂NC₆H₄N=N-4-C₆H₄C≡C-4-C₆H₄C≡CH and gold and ruthenium alkynyl complex derivatives, together with a nickel alkynyl complex derived from 4-O₂NC₆H₄N=N-4-C₆H₄C≡CH, and their quadratic non-

* Corresponding author. Tel.: +61 2 6125 2927; fax: +61 2 6125 0760.
E-mail address: Mark.Humphrey@anu.edu.au (M.G. Humphrey).

linearities β_{zzz} from hyper-Rayleigh scattering studies at 1.064 and 1.300 μm .

2. Experimental

2.1. General experimental conditions and starting materials

All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. Dichloromethane was dried by distilling over CaH_2 , and methanol was dried by distilling over Mg/I_2 ; other solvents were used as received. The term “petrol” refers to a fraction of petroleum ether with a boiling range of 60–80 °C. Column chromatography was performed using either Merck silica gel 60 (0.063–0.200 mm) or Sigma–Aldrich aluminium oxide, activated, basic, Brockmann 1, standard grade ~150 mesh, 58 Å. Thin layer preparative chromatography was performed using Fluka silica gel GF₂₅₄. NaOMe was prepared as needed from metallic sodium and dry methanol. The following were prepared by the literature procedures: $[\text{AuCl}(\text{PPh}_3)]$ [15], $[\text{NiCl}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]$ [16], $[\text{RuCl}(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ [17], *cis*- $[\text{RuCl}_2(\text{dppm})_2]$ [18], $[\text{Ru}(\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{NO}_2)(\text{dppe})(\eta\text{-C}_5\text{Me}_5)]$ [19] 1-ethynyl-4-(triisopropylsilylethynyl)benzene [20], 4-iodo-4'-nitroazobenzene [14], 4-ethynyl-4'-nitroazobenzene [14], 1-ethynyl-4-nitrobenzene [21]. Tetra-*n*-butylammonium fluoride (1 M solution in tetrahydrofuran) (Aldrich), sodium hexafluorophosphate (Aldrich), and tetrakis(triphenylphosphine)palladium(0) (Aldrich) were used as received.

2.2. Instrumentation

Electrospray ionization (ESI) mass spectra were recorded using a Micromass/Waters LC-ZMD single quadrupole liquid chromatograph–MS, high resolution ESI mass spectra were carried out utilizing a Bruker Apex 4.7T FTICR-MS instrument and EI mass spectra were recorded using a VG Quattro II triple quadrupole MS; all mass spectrometry peaks are reported as *m/z* (assignment, relative intensity). Microanalyses were carried out at the Research School of Chemistry, Australian National University. Infrared spectra were recorded using a Perkin–Elmer System 2000 FT-IR spectrometer as CH_2Cl_2 solutions using CaF_2 cells. UV–Vis spectra were recorded on a Cary 5 spectrometer as THF solutions in 1 cm cells. ^1H , ^{13}C and ^{31}P NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer (300, 75 and 121 MHz, respectively) and referenced to residual CHCl_3 (7.24 ppm), solvent CDCl_3 (77.0 ppm) and external H_3PO_4 (0.0 ppm), respectively.

2.3. Synthesis of 4- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{N-4-C}_6\text{H}_4\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{C}\equiv\text{CSiPr}_3^i$ (1)

4-Iodo-4'-nitroazobenzene (502 mg, 1.42 mmol), copper(I) iodide (17 mg, 0.089 mmol) and tetrakis(triphenylphosphine)palladium(0) (32 mg, 0.028 mmol) were

dissolved in triethylamine (30 mL) and dichloromethane (20 mL). 1-Ethynyl-4-(triisopropylsilylethynyl)benzene (648 mg, 2.29 mmol) was added and the mixture refluxed under N_2 for 15 h. The solvent was removed on a rotary evaporator and the residue was passed through a 7 cm pad of silica with CH_2Cl_2 (200 mL). The solvent was removed and the residue was washed well with petrol (4 × 10 mL). The product was obtained as an orange powder (456 mg, 63%). Anal. Calc. for $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_2\text{Si}$: C, 73.34; H, 6.55; N, 8.28. Found: C, 73.38; H, 6.72; N, 8.17%. UV–Vis (λ_{max} , nm [ϵ , $\text{M}^{-1}\text{cm}^{-1}$]): 382 [18100]. IR (cm^{-1}): $\nu(\text{NO}_2)$, 1347 (s), 1527 (s); $\nu(\text{C}\equiv\text{C})$ 2154 (m). ^1H NMR: δ 8.38, 8.03 (AB system, 4H, $\text{C}_6\text{H}_4\text{NO}_2$), 7.96 and 7.68 (AB system, 4H, C_6H_4), 7.47 (s, 4H, $\text{C}_2\text{C}_6\text{H}_4\text{C}_2$), 1.15–1.11 (m, 21H, SiPr_3^i). ^{13}C NMR: δ 11.3 (SiC), 18.7 (Me), 90.7, 92.7 (C_9 , C_{10}), 93.4 (C_1), 106.5 (C_2), 122.5, 124.0, 127.3 (C_3 , C_6 , C_{11}), 123.6 (C_4 , C_5), 124.8 (C_{12}), 131.5, 132.1, 132.6 (C_{13} , C_{18} , C_{19}), 148.8, 151.7, 155.7 (C_{14} , C_{17} , C_{20}). EI MS: 507 ($[\text{M}]^+$, 35), 464 ($[\text{M-Pr}^i]^+$, 100). HR EI MS: Calculated $\text{C}_{31}\text{H}_{33}\text{N}_3\text{O}_2\text{Si}$: 507.2342, Found: 507.2353.

2.4. Synthesis of 4- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{N-4-C}_6\text{H}_4\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{C}\equiv\text{CH}$ (2)

4- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{N-4-C}_6\text{H}_4\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{C}\equiv\text{CSiPr}_3^i$ (399 mg, 0.79 mmol) was dissolved in CH_2Cl_2 (50 mL). Tetra-*n*-butylammonium fluoride in tetrahydrofuran (1 M, 1 mL, 1 mmol) was added to the orange solution to afford an immediate colour change to black. The reaction mixture was stirred for a further 1 h. The solvent was removed on a rotary evaporator and the residue was passed through a 7 cm pad of silica with CH_2Cl_2 (200 mL). The solvent was removed and the residue was washed with petrol (2 × 10 mL). The product was obtained as an orange powder (202 mg, 73%). Anal. Calc. for $\text{C}_{22}\text{H}_{13}\text{N}_3\text{O}_2$: C, 75.20; H, 3.73; N, 11.96. Found: C, 75.89; H, 4.17; N, 11.29%. UV–Vis (λ_{max} , nm [ϵ , $\text{M}^{-1}\text{cm}^{-1}$]): 379 [17100]. IR (cm^{-1}): $\nu(\text{NO}_2)$ 1346 (s); $\nu(\text{C}\equiv\text{C})$ 2203 (w). ^1H NMR: δ 8.40, 8.05 (AB system, 4H, $\text{C}_6\text{H}_4\text{NO}_2$), 7.98, 7.70 (AB system, 4H, C_6H_4), 7.50 (s, 4H, $\text{C}_2\text{C}_6\text{H}_4\text{C}_2$), 3.19 (s, 1H, $\text{HC}\equiv\text{C}$). ^{13}C NMR: δ 79.3 (C_1), 83.1 (C_2), 92.3 (C), 103.6 (C), 123.5, 124.8, 131.6, 132.2, 132.6 ($\text{CH} \times 5$), 92.3, 103.6, 122.4, 123.1, 127.1, 155.6. ESI MS: 352 ($[\text{M+H}]^+$, 20).

2.5. Synthesis of $[\text{Au}(\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{N}=\text{N-4-C}_6\text{H}_4\text{NO}_2)(\text{PPh}_3)]$ (3)

$[\text{AuCl}(\text{PPh}_3)]$ (55 mg, 0.11 mmol) and 4- $\text{O}_2\text{NC}_6\text{H}_4\text{N}=\text{N-4-C}_6\text{H}_4\text{C}\equiv\text{C-4-C}_6\text{H}_4\text{C}\equiv\text{CH}$ (40 mg, 0.11 mmol) were dissolved in CH_2Cl_2 (15 mL) to form an orange solution. Addition of 1 mL of sodium methoxide in methanol solution (ca. 0.5 M) caused the solution to rapidly change colour to brown. The mixture was stirred for 15 h. The volume was reduced to ca. 10 mL under reduced pressure and 20 mL of methanol added. A precipitate

formed and was collected by filtration and washed with iced MeOH (3×5 mL) to yield a red-brown powder (40 mg, 45%). Anal. Calc. for $C_{40}H_{27}N_3O_2PAu$: C, 59.34; H, 3.36; N, 5.19. Found: C, 59.36; H, 3.51; N, 5.12%. UV–Vis (λ_{max} , nm [ϵ , $M^{-1}cm^{-1}$]): 392 [40000], 378 [41000], 313 [48000], 278 [178000], 234 [257000]. IR (cm^{-1}) $\nu(NO_2)$ 1346 (s); $\nu(C\equiv C)$ 2211 (m), 2112 (w). 1H NMR: δ 8.40, 8.04 (AB system, 4H, $C_6H_4NO_2$), 7.96, 7.68 (AB system, 4H, $C_6H_4N_2$), 7.51–7.42 (m, 19H, $PPh_3 + C_2C_6H_4C_2$). ^{31}P NMR: δ 42.8 (PPh_3). ^{13}C NMR: δ 90.1, 93.3, 104.0, 120.8, 127.7, 130.0 ($C_2, C_3, C_6, C_7, C_8, C_9$), 123.5, 124.8, (C_{16}, C_{17}), 129.2 (d, C_m , $J_{CP} = 12$ Hz), 131.4 (C_p), 131.59, 131.62 (C_4, C_5), 132.4, 132.5 (C_{10}, C_{11}), 134.4 (d, C_o , $J_{CP} = 14$ Hz), 148.7 (C_{18}), 151.4 (C_{12}), 155.7 (C_{15}). ESI MS: 832 ($[M + Na]^+$, 10), 810 ($[M + H]^+$, 8), 721 ($[Au(PPh_3)_2]^+$, 100), 459 ($[Au(PPh_3)]^+$, 80).

2.6. Synthesis of *trans*-[Ru($C\equiv C$ -4- C_6H_4 - $C\equiv C$ -4- $C_6H_4N=N$ -4- $C_6H_4NO_2$)Cl(dppm) $_2$] (**4**)

cis-[RuCl $_2$ (dppm) $_2$] (108 mg, 0.111 mmol) and NaPF $_6$ (158 mg, 0.940 mmol) were dissolved in CH $_2$ Cl $_2$ (15 mL) and 4-O $_2$ NC $_6$ H $_4$ N=N-4- C_6 H $_4$ C \equiv C-4- C_6 H $_4$ C \equiv CH (40 mg, 0.11 mmol) was added. The orange/red mixture was stirred at reflux for 4 h. The addition of sodium methoxide in methanol solution (0.5 M, 0.3 mL, 0.015 mmol) caused an instant colour change to purple-black. The reaction mixture was passed through a short pad of alumina eluting with CH $_2$ Cl $_2$. The solvent was removed from the eluate on a rotary evaporator to yield the dark purple product (81 mg, 59%). Anal. Calc. for $C_{72}H_{56}N_3O_2P_4ClRu$: C, 68.87; H, 4.49; N, 3.35. Found: C, 68.52; H, 4.50; N, 3.77%. UV–Vis (λ_{max} , nm [ϵ , $M^{-1}cm^{-1}$]): 510 [5000], 380 [19000]. IR (cm^{-1}) $\nu(NO_2)$ 1346 (s); $\nu(C\equiv C)$ 2072 (m); $\nu(C\equiv C)$ 2199 (w). 1H NMR: δ 8.38, 8.03 (AB system, 4H, $C_6H_4NO_2$), 7.94, 7.62 (AB system, 4H, C_6H_4), 7.41–7.03 (m, 42 H, PPh_2, H_5), 5.98 (d, 2H, $H_4, J_{HH} = 9$ Hz), 4.90 (m, 4H, PCH_2). ^{31}P NMR: δ -6.0 (dppm). ^{13}C NMR: δ 50.3 (CH_2), 89.2, 95.1, 113.6, 115.2 (C_2, C_3, C_7, C_8), 123.4, 123.5, 124.8 (C_5, C_{10}, C_{11}), 127.6 (C_p), 128.4 (C), 129.1, 129.3 (C_m), 130.1, 130.5, 132.1 (C_4, C_{16}, C_{17}), 131.8 (C), 133.3, 133.7 (C_o), 134.0 (C_i), 134.9 (t, $C_1, J_{CP} = 12$ Hz), 147.7, 148.8 (C_{12}, C_{15}), 155.7 (C_{18}). ESI MS: 1256 ($[M + H]^+$, 50), 1220 ($[M - Cl]^+$, 83), 905 ($[RuCl(dppm)_2]^+$, 20), 869 ($[Ru(dppm)_2 - H]^+$, 25). HR ESI MS: Calculated $C_{74}H_{59}N_4O_2P_4Ru$ $[M - Cl + MeCN]^+$: 1261.2632, Found: 1261.2530.

2.7. Synthesis of [Ru($C\equiv C$ -4- C_6H_4 - $C\equiv C$ -4- $C_6H_4N=N$ -4- $C_6H_4NO_2$)(dppe)(η - C_5Me_5)] (**5**)

[RuCl(dppe)(η - C_5Me_5)] (81 mg, 0.12 mmol), NaPF $_6$ (195 mg, 1.2 mmol) and 4-O $_2$ NC $_6$ H $_4$ N=N-4- C_6 H $_4$ C \equiv C-4- C_6 H $_4$ C \equiv CH (43 mg, 0.12 mmol) were dissolved in CH $_2$ Cl $_2$ (20 mL) and the reaction was stirred for 48 h. Triethylamine (5 mL) was added, resulting in a rapid colour

change to black and the mixture stirred for 10 min. The reaction mixture was passed through a short pad of alumina eluting with CH $_2$ Cl $_2$. The solvent was removed from the eluant to yield a black powder that was further purified by passing through an alumina column with CH $_2$ Cl $_2$. The solvent was removed from the eluent to yield a fine dark purple powder, which was recrystallised by slow diffusion of methanol into a dichloromethane solution (41 mg, 34%). Anal. Calc. for $C_{58}H_{51}N_3O_2P_2Ru \cdot CH_3OH$: C, 69.67; H, 5.45; N, 4.13. Found: C, 68.85; H, 5.78; N, 4.22%. UV–Vis (λ_{max} , nm [ϵ , $M^{-1}cm^{-1}$]): 522 [8600], 387 [31000], 237 [27000]. IR (cm^{-1}) $\nu(NO_2)$ 1346 (s), 1589 (s); $\nu(C\equiv C)$ 2056 (s); $\nu(C\equiv C)$ 2203 (w). 1H NMR: δ 8.39, 8.03 (AB system, 4H, $C_6H_4NO_2$), 7.94, 7.63 (AB system, 4H, $C_6H_4N_2$), 7.74, 7.35–7.21, 6.97 (m, 22H, PPh_2, H_5), 6.72 (d, 2H, $H_4, J_{HH} = 8$ Hz), 3.49 (s, 3H, CH_3OH), 2.67 (m, 2H, $CH_2/dppe$), 2.06 (m, 2H, $CH_2/dppe$), 1.57 (s, 15H, $C_5(CH_3)_5$). ^{31}P NMR: δ 81.3 (dppe). ^{13}C NMR: δ 10.0 (C_5Me_5), 30.0 (m, PCH_2), 89.1 (C), 92.7 (C_5Me_5), 95.2, 111.4, 115.5 (C), 123.5 (d, $PPh_2, J_{CP} = 7$ Hz), 124.7, 130.1, 131.1, 132.1 (4 of $C_4, C_5, C_{10}, C_{11}, C_{16}, C_{17}$), 125.5 (PPh_2), 127.3 (d of t, $PPh_2, J_{CP} = 4$ Hz, $J_{CP} = 17$ Hz), 128.2, 128.5 (C), 128.9 (d, $PPh_2, J_{CP} = 6$ Hz), 131.7 (C), 133.3 (d of t, $PPh_2, J_{CP} = 5$ Hz, $J_{CP} = 33$ Hz), 135.7, 136.3, 137.0, 138.6 (C), 148.6 (CN), 151.0 (CN), 155.7 (CN). HR ESI MS: Calculated $C_{58}H_{52}N_3O_2P_2Ru$ $[M + H]^+$: 986.2573, Found: 986.2502.

2.8. Synthesis of [Ni($C\equiv C$ -4- $C_6H_4N=N$ -4- $C_6H_4NO_2$)(PPh_3)(η - C_5H_5)] (**6**)

[NiCl(PPh_3)(η - C_5H_5)] (58 mg, 0.15 mmol), 4-HC \equiv CC $_6$ H $_4$ N=N-4- C_6 H $_4$ NO $_2$ (41 mg, 0.16 mmol) and CuI (6 mg, 0.03 mmol) were stirred in triethylamine (20 mL) for 18 h. The solvent was removed under reduced pressure, and the residue extracted with CH $_2$ Cl $_2$ (50 mL) and filtered through a short pad of silica. Removal of the solvent afforded a black residue, which was washed with methanol (2×5 mL) to isolate the product, a fine black powder (40 mg, 42%). Anal. Calc. for $C_{37}H_{28}N_3O_2PNi$: C, 69.84; H, 4.44; N, 6.60. Found: C, 68.87; H, 4.71; N, 6.56%. UV–Vis (λ_{max} , nm [ϵ , $M^{-1}cm^{-1}$]): 519 [9000], 396 [17000], 309 [19000], 259 [25000]. IR (cm^{-1}) $\nu(NO_2)$ 1345 (s); $\nu(C\equiv C)$ 2088 (m). 1H NMR: δ 8.32, 7.91 (AB system, 4H, $C_6H_4NO_2$), 7.72 (m, 6H, H_o), 7.59, 6.73 (AB system, 4H, C_6H_4), 7.41 (m, 9H, H_m, H_p), 5.28 (s, 5H, C_5H_5). ^{31}P NMR: δ 42.0 (PPh_3). ^{13}C NMR: δ 92.9 (C_5H_5), 94.4 (C_1), 123.0, 124.7, 129.7 (C_5, C_{10}, C_{11}), 128.4 (d, $C_m, J_{CP} = 10$ Hz), 130.4 (C_p), 131.6 (C_4), 133.9 (d, $C_o, J_{CP} = 11$ Hz), 134.1 (d, $C_i, J_{CP} = 4$ Hz), 134.4 (C_3), 156.0 (C_9). ESI MS: 647 ($[Ni(PPh_3)_2(C_5H_5)]^+$, 15), 385 ($[Ni(PPh_3)(C_5H_5)]^+$, 65).

2.9. Structure determination

A suitable crystal of **4** was obtained by slow diffusion of petrol into a dichloromethane solution. A single crystal

was mounted on a fine glass capillary, and data were collected at 200 K on a Nonius KappaCCD diffractometer using graphite-monochromated Mo K α radiation ($\lambda = 0.71073$ Å). The unit cell parameters were obtained by least-squares refinement [22] of 163 428 reflections with $2.6 \leq \theta \leq 25.0^\circ$. The reduced data [22] were corrected for absorption using numerical methods [23] implemented from within MAXUS [24]; equivalent reflections were merged. The structure was solved by direct methods and expanded using Fourier techniques [25], and refined using the software package CRYSTALS [26].

Crystal refinement data: C_{73.5}H₅₉Cl₄N₃O₂P₄Ru, $M = 1383.07$. Monoclinic, $C2/c$, $a = 44.5509(8)$, $b = 11.3619(2)$, $c = 28.0643(5)$ Å, $\beta = 92.2274(6)^\circ$, $V = 14194.9(4)$ Å³. D_c ($Z = 8$) = 1.294 g cm⁻³. $\mu_{\text{Mo}} = 0.51$ mm⁻¹; specimen: 0.45 × 0.28 × 0.11 mm; $T_{\text{min/max}} = 0.891/0.986$. $2\theta_{\text{max}} = 50.0^\circ$; $N_{\text{total}} = 98760$ (CCD diffractometer, monochromatic Mo K α radiation, $\lambda = 0.71073$ Å; T 200 K) merging to $N = 12520$ unique ($R_{\text{int}} = 0.08$), $N_o = 12499$ ($I > 3\sigma(I)$) refining to $R = 0.0470$, $R_w = 0.0509$.

The crystallographic asymmetric unit consists of one molecule of **4** and one and a half molecules of dichloromethane. The second dichloromethane site lies close to an inversion centre and, as a result, close intermolecular contacts arise with itself. It was thus set to have half occupancy. Due to the length of the alkynyl ligand, the atoms at the end of the alkynyl ligand remote from the metal atom were too disordered to be solved anisotropically, and so were made isotropic. Restraints on the bond lengths and angles of the end of the chain were thus also made so as to help resolve this disorder. All other non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in the refinement at idealized positions, riding on the atoms to which they were bonded and frequently recalculated.

2.10. Hyper-Rayleigh scattering measurements

For studies at 1.064 μm , an injection-seeded Nd:YAG laser (Q-switched Nd:YAG Quanta Ray GCR5, 1.064 μm , 8 ns pulses, 10 Hz) was focused into a cylindrical cell (7 mL) containing the sample. The intensity of the incident beam was varied by rotation of a half-wave plate placed between crossed polarizers. Part of the laser pulse was sampled by a photodiode to measure the vertically polarized incident light intensity. The frequency doubled light was collected by an efficient condenser system and detected by a photomultiplier. The harmonic scattering and linear scattering were distinguished by appropriate filters; gated integrators were used to obtain intensities of the incident and harmonic scattered light. The absence of a luminescence contribution to the harmonic signal was confirmed by using interference filters at different wavelengths near 532 nm. All measurements were performed in tetrahydrofuran using 4-nitroaniline ($\beta = 21.4 \times 10^{-30}$ esu) as a reference. Solutions were sufficiently dilute that absorption of scattered light was negligible.

For studies at 1.300 μm , a Tsunami-pumped OPAL (model Spectra-Physics) was used. With a high repetition rate of the laser, high frequency demodulation of fluorescence contributions can be effected, a full description being given in ref. [27]. All measurements were performed in tetrahydrofuran using disperse red 1 (DR1, $\beta = 54 \times 10^{-30}$ esu in chloroform) as a reference. Experiments utilized low chromophore concentrations, the linearity of the HRS signal as a function of the chromophore concentration confirming that no significant self-absorption of the SHG signal occurred.

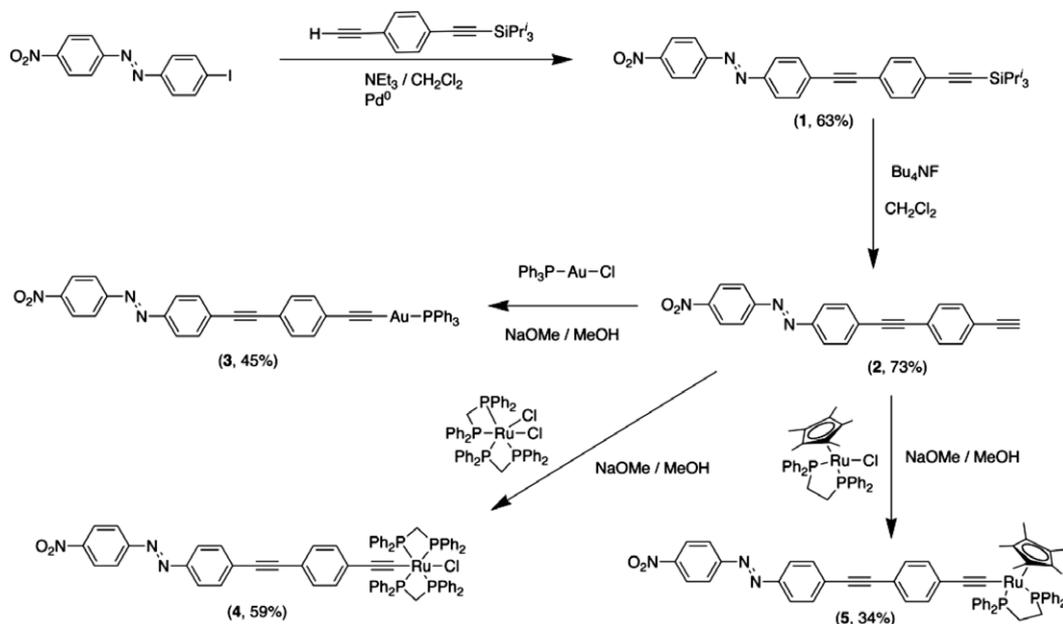
3. Results and discussion

3.1. Synthesis and characterization

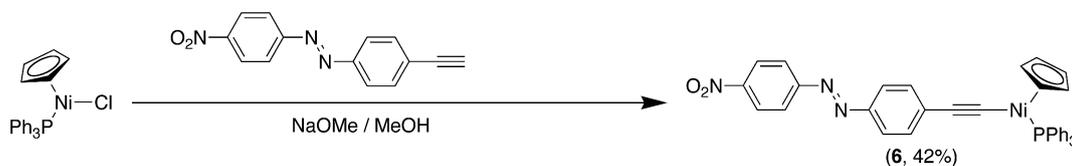
The new acetylenes that were required for alkynyl complex synthesis were prepared by standard organic synthetic procedures: a Sonogashira coupling of 4-iodo-4'-nitroazobenzene with 1-ethynyl-4-(triisopropylsilylethynyl)benzene afforded 4-O₂NC₆H₄N=N-4-C₆H₄C \equiv C-4-C₆H₄C \equiv CSi-Pr₃ (**1**), subsequent desilylation with tetra-*n*-butylammonium fluoride giving 4-O₂NC₆H₄N=N-4-C₆H₄C \equiv C-4-C₆H₄C \equiv CH (**2**) (Scheme 1). Compounds **1** and **2** were characterized by a combination of ¹H and ¹³C NMR, IR, and UV-Vis spectroscopy.

The preparation of the new alkynyl complexes **3** and **4** (Scheme 1) proceeded by adaptation of the published procedures for the preparation of the 4-nitrophenylethynyl complex analogues [11,13]. The synthesis of the gold complex **3** was achieved by coupling [AuCl(PPh₃)] to **2** in methanol in the presence of sodium methoxide, its identity being confirmed by ¹H, ¹³C and ³¹P NMR spectroscopy and ESI mass spectrometry. The ESI spectrum displays a signal at 810 mass units assigned to [M+H]⁺ and a fragment at 721 mass units assigned to [Au(PPh₃)₂]⁺, the latter typical for (triphenylphosphine)gold alkynyl complexes [11]. The synthesis of **4** proceeded by way of a vinylidene intermediate that was not isolated, deprotonation in situ affording the alkynyl complex **4** which was characterized by ¹H, ¹³C and ³¹P NMR spectroscopy and ESI mass spectrometry. The ESI spectrum shows a protonated molecular ion at 1256 mass units, as well as fragments corresponding to the loss of chlorine and alkynyl ligands at 1220 ([M-Cl]⁺) and 905 mass units ([RuCl(dppm)₂]⁺), respectively. A high resolution ESI mass spectrum obtained using acetonitrile as a solvent revealed a peak corresponding to the replacement of chloride by acetonitrile, mirroring solution chemistry of RuClX(L₂)₂ (X = Cl, C₂R) complexes [28,29]. Complex **5**, which incorporates a very electron-rich metal centre, was similarly prepared by adaptation of the published procedure for the 4-nitrophenylethynyl analogue **7** [19] and characterized by the usual spectroscopic techniques complemented by a high-resolution ESI mass spectrum of the protonated molecular ion.

The preparation of **6** (Scheme 2) proceeded by adaptation of the published procedure for the 4-nitrophenylethynyl complex analogue [30]. Its identity was confirmed by



Scheme 1. Preparation of 1–5.



Scheme 2. Synthesis of 6.

^1H , ^{13}C and ^{31}P NMR spectroscopy, with the ESI mass spectrum showing peaks corresponding to the fragment ion $[\text{Ni}(\text{PPh}_3)(\eta\text{-C}_5\text{H}_5)]^+$ and the ion–molecule product $[\text{Ni}(\text{PPh}_3)_2(\eta\text{-C}_5\text{H}_5)]^+$.

3.2. X-ray structural study of 4

A single-crystal X-ray diffraction study of **4** was undertaken. A comparison of selected interatomic bond distances and angles of **4** with those from the previously-determined structural study of the related complex *trans*- $[\text{Ru}(\text{C}\equiv\text{C}-4\text{-C}_6\text{H}_4\text{N}=\text{N}-4\text{-C}_6\text{H}_4\text{NO}_2)\text{Cl}(\text{dppm})_2]$ (**8**) [14] is given in Table 1. Fig. 1 contains ORTEP depictions of the molecular geometries of **4** and **8**.

The bond lengths and angles around the Cl–Ru–C(1)–C(2)–C(3) chain in **4** are comparable to those in **8**, with Cl–Ru–C(1) and Ru–C(1)–C(2) angles close to the idealized 180° and a short Ru–C distance, the latter having been shown semi-empirically to lead to large quadratic nonlinearities [31]. The bond distances and angles involving the diphosphine ligands are unexceptional. Phenyl rings C(3)–C(8) and C(11)–C(16) are not co-planar, the angle between them being 21.9° . Phenyl ring C(1701)–C(2201) lies in a plane between those of the other two rings, with

an angle of 4.3° and 17.8° separating it from the C(11)–C(16) and C(3)–C(8) rings, respectively. The reduction in coplanar character of adjacent phenyl rings has been previously demonstrated to reduce computationally-derived quadratic NLO merit [32].

Fig. 2 shows cell-packing diagrams for **4** and **8**. Both complexes pack pair-wise in the lattice with dipoles aligned antiparallel, arrangements that would result in zero NLO bulk susceptibility.

3.3. HRS studies

Quadratic optical nonlinearities of compounds **3–7** were determined by the hyper-Rayleigh scattering (HRS) technique at $1.064\ \mu\text{m}$ employing ns pulses and at $1.300\ \mu\text{m}$ employing fs pulses. Table 2 includes these results together with important linear optical absorption data, and relevant data from related compounds. For complexes of this type, the NLO properties are dominated by the energy of the lowest-lying charge-transfer state, and frequency-independent nonlinearities calculated using the two-level model would be expected to have some applicability. The data obtained at two wavelengths provides a test of the applicability – if the two-level model is appropriate, $\beta_{0(1.064)}$ and

Table 1
Important bond lengths and angles for **4** and *trans*-[Ru(C≡C-4-C₆H₄N=N-4-C₆H₄NO₂)Cl(dppm)₂] (**8**)

	4 ^a	8 ^b		4 ^a	8 ^b
Ru–Cl	2.507(14)	2.508(2)	C(1)–C(2)	1.187(8)	1.224(9)
Ru–P(1)	2.354(16)	2.322(2)	C(2)–C(3)	1.435(8)	1.406(9)
Ru–P(2)	2.360(16)	2.352(2)	N(1)–N(2)	1.227(12)	1.263(9)
Ru–P(3)	2.329(15)	2.349(2)	C(20/12)–N(3)	1.509(14)	1.47(1)
Ru–P(4)	2.364(16)	2.355(2)	N(3)–O(1)	1.263(16)	1.22(1)
Ru–C(1)	2.001(7)	1.974(7)	N(3)–O(2)	1.176(13)	1.18(1)
P(1)–Ru–P(2)	71.78(5)	72.20(7)	C(1)–C(2)–C(3)	178.1(7)	179.8(9)
P(3)–Ru–P(4)	72.04(5)	71.47(7)	C(14/6)–N(1)–N(2)	118.5(10)	112.9(8)
Cl–Ru–C(1)	175.1(17)	173.1(2)	N(1)–N(2)–C(17/9)	111.4(9)	111.5(8)
Ru–C(1)–C(2)	177.7(5)	175.2(6)	O(1)–N(3)–O(2)	127.9(13)	124(1)

^a This work.

^b Ref. [14].

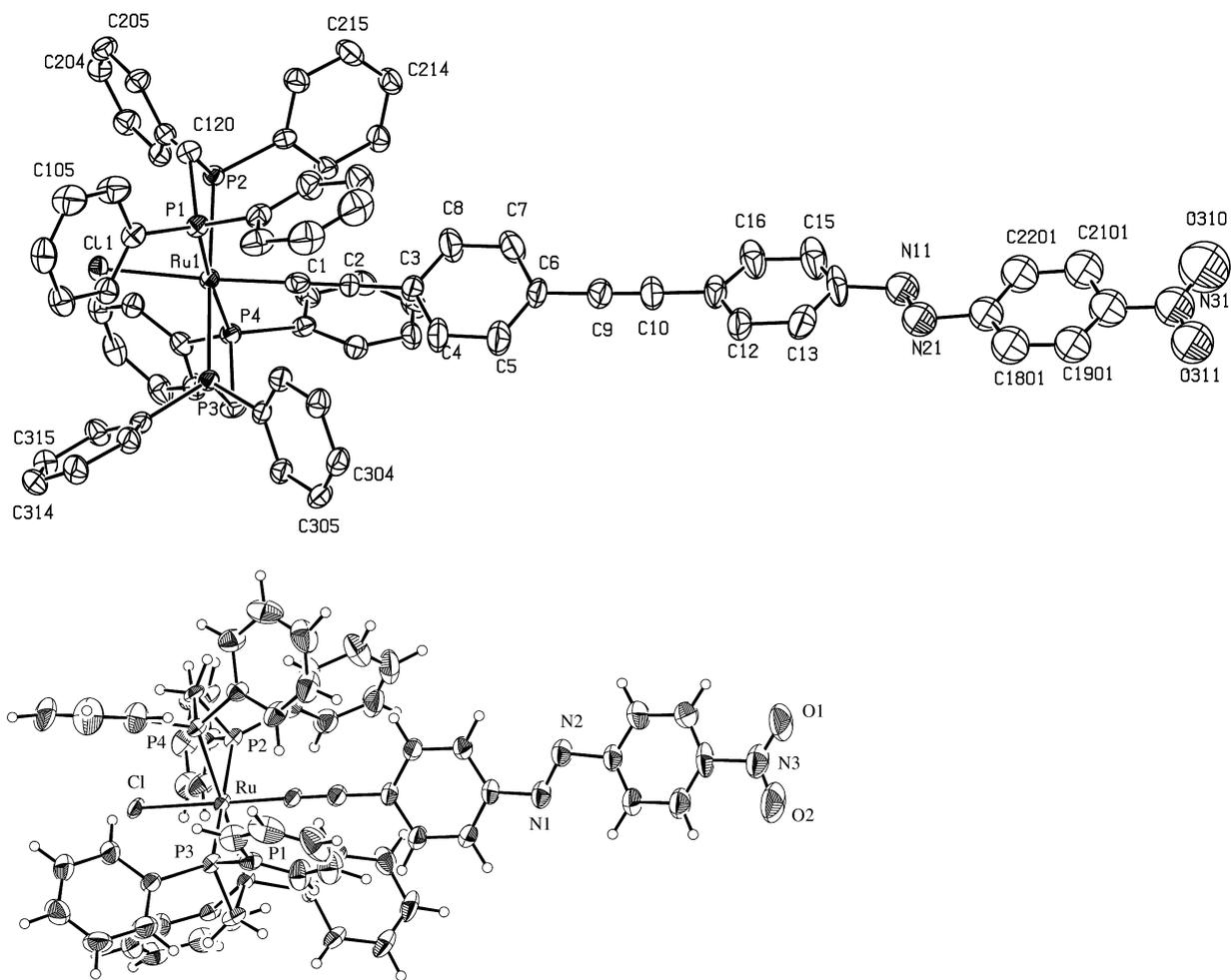


Fig. 1. Molecular geometry and labelling schemes for **4** and *trans*-[Ru(C≡C-4-C₆H₄N=N-4-C₆H₄NO₂)Cl(dppm)₂] (**8**) [14]. Non-hydrogen atoms have been depicted with 30% thermal ellipsoids; for **8**, hydrogen atoms have been placed in calculated positions with arbitrary bond lengths of 0.95 Å.

$\beta_{0(1.300)}$ should be identical, but this is not the case, so the β_0 data should be treated with caution.

The complexes in Table 2 have been grouped by metal and by co-ligand set (for ruthenium). Compounds **3** and **6** have the largest quadratic nonlinearities reported for gold and nickel alkynyl complexes thus far, a result that can be attributed to the longer π -system in **3** than previously reported gold complexes (see below), and to the introduc-

tion of an azo-linkage in **6** compared to earlier nickel alkynyl complexes for which π -bridge lengthening was achieved by ene or yne linkages. Compounds **5** and **7** both have an [Ru(alkynyl)(dppe)(η -C₅Me₅)] centre and display large β , though values are marginally lower than those of their analogues with a [Ru(alkynyl)Cl(dppm)₂] composition.

We have previously noted the difficulty in developing structure–NLO activity relationships for nickel and ruthenium

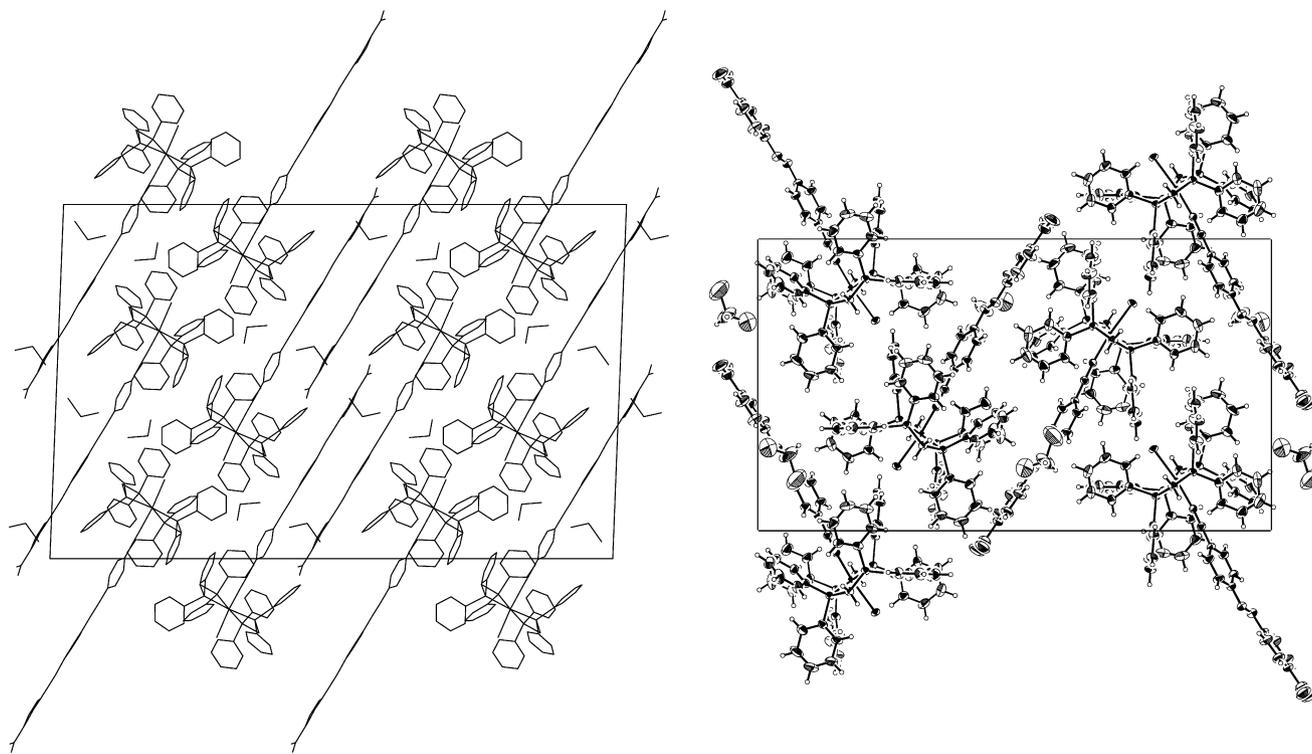


Fig. 2. Molecular packing of **4** and *trans*-[Ru(C≡C-4-C₆H₄N=N-4-C₆H₄NO₂)Cl(dppm)₂] **8**.

nium complexes with these ligand sets, due to the proximity of optical absorptions to the second-harmonic wavelength corresponding to the fundamental frequency of the laser. In contrast, (triphenylphosphine)gold complexes with alkynyl ligands of this type are transparent at 532 nm, permitting assessment of the effect of structural change on NLO merit. [Our earlier studies contrasted these specific ligated metal units, permitting us to derive “figures of merit” for the efficiency of the various metal–ligand combinations [30]; the (phosphine)gold unit was shown to be a weaker donor, but the lack of resonance enhancement in data from its alkynyl complexes is very useful in developing structure–property relationships for alkynyl ligand modification.] Inspection of the data in Table 2 reveals progressively increasing $\beta_{1,064}$ and $\beta_{0(1,064)}$ values on π -bridge lengthening (proceeding from [Au(C≡C-4-C₆H₄NO₂)(PPh₃)] to [Au(C≡C-4-C₆H₄-*E*-CH=CH-4-C₆H₄NO₂)(PPh₃)] and from [Au(C≡C-4-C₆H₄N=N-4-C₆H₄NO₂)(PPh₃)] to **3**) and replacement of ene-linkage by azo linkage (proceeding from [Au(C≡C-4-C₆H₄-*E*-CH=CH-4-C₆H₄NO₂)(PPh₃)] to [Au(C≡C-4-C₆H₄N=N-4-C₆H₄NO₂)(PPh₃)]). Proceeding from gold to nickel, and then to ruthenium centres for the present series of complexes results in red-shifted optical absorption maxima, and larger $\beta_{1,064}$ values, but with progressively increasing resonance enhancement for which the two-level model is increasingly inappropriate at accommodating. The $\beta_{1,300}$ values similarly increase in proceeding from gold, to nickel, and then ruthenium complex.

4. Conclusion

The present studies have afforded several examples of complexes incorporating the new alkynyl 4-O₂NC₆H₄N=N-4-C₆H₄C≡C-4-C₆H₄C≡CH as an alkynyl ligand. The new complexes have significant quadratic nonlinearities, and the enhanced magnitude of these data compared to those of previously reported related complexes can be ascribed to a combination of π -system lengthening and incorporation of the azo group. We have previously reported molecular NLO switching by protic and electrochemical means [9]. The azo group itself is a photoisomerizable unit whose incorporation potentially affords the possibility of switching nonlinearity – this will be the subject of a future report.

Acknowledgements

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Table 2
Quadratic nonlinearities for compounds 3–7 and related compounds

	$\lambda_{\max}(\text{nm})$ [$\epsilon(10^4 \text{ M}^{-1} \text{ cm}^{-1})$]	HRS, 1.064 μm		HRS, 1.300 μm		Reference
		β_{zzz} (10^{-30} esu)	β_0^a (10^{-30} esu)	β_{zzz} (10^{-30} esu)	β_0^b (10^{-30} esu)	
<i>Au complexes</i>						
[Au(C \equiv C-4-C ₆ H ₄ NO ₂)(PPh ₃)]	338 (2.5)	22	12			[11]
[Au(C \equiv C-4-C ₆ H ₄ -E-CH=CH-4-C ₆ H ₄ NO ₂)(PPh ₃)]	368 (3.8)	120	49			[11]
[Au(C \equiv C-4-C ₆ H ₄ N=N-4-C ₆ H ₄ NO ₂)(PPh ₃)]	398 (3.3)	180	68			[14]
[Au(C \equiv C-4-C ₆ H ₄ C \equiv C-4-C ₆ H ₄ N=N-4-C ₆ H ₄ NO ₂)(PPh ₃)] (3)	392 (4.0)	213 \pm 20	91 \pm 9	83	51	This work
<i>Ni complexes</i>						
[Ni(C \equiv C-4-C ₆ H ₄ NO ₂)(PPh ₃)(η -C ₅ H ₅)]	439 (0.9)	221	59			[33]
[Ni(C \equiv C-4-C ₆ H ₄ -E-CH=CH-4-C ₆ H ₄ NO ₂)(PPh ₃)(η -C ₅ H ₅)]	437 (2.8)	445	120			[30]
[Ni(C \equiv C-4-C ₆ H ₄ N=N-4-C ₆ H ₄ NO ₂)(PPh ₃)(η -C ₅ H ₅)] (6)	519 (0.9)	605 \pm 72	46 \pm 6	98	34	This work
<i>trans-[Ru(alkynyl)Cl(dppm)₂] complexes</i>						
<i>trans</i> -[Ru(C \equiv C-4-C ₆ H ₄ NO ₂)Cl(dppm ₂)]	473 (1.8)	767	129			[13]
<i>trans</i> -[Ru(C \equiv C-4-C ₆ H ₄ -E-CH=CH-4-C ₆ H ₄ NO ₂)Cl(dppm ₂)]	490 (2.6)	1964	235			[13]
<i>trans</i> -[Ru(C \equiv C-4-C ₆ H ₄ N=N-4-C ₆ H ₄ NO ₂)Cl(dppm ₂)]	583 (2.7)	1649	232			[14]
<i>trans</i> -[Ru(C \equiv C-4-C ₆ H ₄ C \equiv C-4-C ₆ H ₄ C \equiv C-4-C ₆ H ₄ NO ₂)Cl(dppm ₂)]	439 (2.0)	1379	365			[9]
<i>trans</i> -[Ru(C \equiv C-4-C ₆ H ₄ C \equiv C-4-C ₆ H ₄ N=N-4-C ₆ H ₄ NO ₂)Cl(dppm ₂)] (4)	510 (0.5)	1215 \pm 146	51 \pm 6	225	70	This work
<i>[Ru(alkynyl)(L)₂(η-C₅R₅)] complexes</i>						
[Ru(C \equiv C-4-C ₆ H ₄ NO ₂)(PPh ₃) ₂ (η -C ₅ H ₅)]	460 (8.5)	468	96			[10]
[Ru(C \equiv C-4-C ₆ H ₄ N=N-4-C ₆ H ₄ NO ₂)(PPh ₃) ₂ (η -C ₅ H ₅)]	565 (2.9)	1627	149			[14]
[Ru(C \equiv C-4-C ₆ H ₄ NO ₂)(dppe)(η -C ₅ Me ₅)] (7)	479 (1.7)	544 \pm 133	82 \pm 20	50	19	This work
[Ru(C \equiv C-4-C ₆ H ₄ C \equiv C-4-C ₆ H ₄ N=N-4-C ₆ H ₄ NO ₂)(dppe)(η -C ₅ Me ₅)] (5)	522 (0.9)	1136 \pm 150	^c	220	60	This work

Errors \pm 15% unless otherwise indicated.

$$^a \beta_0 = \beta[1 - (2\lambda_{\max}/1064)^2][1 - (\lambda_{\max}/1064)^2].$$

$$^b \beta_0 = \beta[1 - (2\lambda_{\max}/1300)^2][1 - (\lambda_{\max}/1300)^2].$$

^c Not applicable: the two-level model diverges when the SHG wavelength becomes identical to λ_{\max} .

Appendix A. Supplementary material

CCDC 662443 contains the supplementary crystallographic data for compound **4**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2007.11.004](https://doi.org/10.1016/j.jorganchem.2007.11.004).

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