Organometallic Complexes for Nonlinear Optics. 11.[1] Molecular Quadratic and Cubic Hyperpolarizabilities of Systematically Varied (Cyclopentadienyl)(triphenylphosphine)nickel σ-Arylacetylides

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The complexes $Ni(C\equiv CR)(PPh_3)(\eta-C_5H_5)$ (R = $4-C_6H_4NO_2$ (**3**), $4,4'-C_6H_4C_6H_4NO_2$ (**4**), (*E*)-$4,4'-C_6H_4CH=CHC_6H_4NO_2$ (**5**), (*Z*)-$4,4'-C_6H_4CH=CHC_6H_4NO_2$ (**6**), $4,4'-C_6H_4C\equiv CC_6H_4NO_2$ (**7**), $4,4'-C_6H_4N=CHC_6H_4NO_2$ (**8**)) have been prepared. Electrochemical data for the series of complexes $NiCl(PPh_3)(\eta-C_5H_5)$ (**1**), $Ni(C\equiv CPh)(PPh_3)(\eta-C_5H_5)$ (**2**), and **3**−**8** have been determined. Introduction of nitro substituent (in progressing from **2** to **3**) results in a substantial increase in the $Ni^{II/III}$ oxidation potential, all of which is lost on progressing from a one-ring (**3**) to two-ring (**4**−**8**) chromophore. The molecular quadratic and cubic optical nonlinearities of the series of complexes have been determined by hyper-Rayleigh scattering (HRS) and Z-scan techniques, respectively. HRS measurements at 1064 nm are consistent with an increase in β upon chromophore chain-lengthening (in progressing from **3** to **7** to **5**), replacing *Z* by *E* stereochemistry (in progressing from **6** to **5**), and in replacing N by CH (in progressing from **8** to **5**), general trends that are maintained with the two-level-corrected data. Nonlinearities for the 18-electron nickel complexes are larger than those for related 14-electron (triphenylphosphine)gold acetylides, but smaller than those for the more easily oxidizable 18-electron (cyclopentadienyl)bis(phosphine)ruthenium acetylide analogues. Z-scan data at 800 nm reveal a negative γ for the nitro-containing complexes, consistent with the dispersion effect of two-photon states contributing to the nonlinearities. An increase in γ upon chromophore chain-lengthening (in progressing from **3** to **5**, **4** and **7**) and replacing *Z* by *E* stereochemistry (in progressing from **6** to **5**) is observed. Nonlinearities for the extended-chromophore acetylide complexes **5** and **7** are significantly less than those for the (triphenylphosphine)gold acetylide analogues.

Introduction

The optical nonlinearities of organometallic complexes have been the subject of intense investigation recently.[2] Many organic molecules with enhanced nonlinear optical (NLO) responses have a donor−bridge−acceptor composition. Organometallic complexes can be constructed similarly, but with additional flexibility due to the potential of a variable d electron count, oxidation state, and ligand environment, all of which may impact significantly on the NLO performance. However, few investigations correlating systematic changes in these parameters against NLO merit have been reported. Our studies have focussed on metal σ-acetylide complexes,[1,3] which are frequently accessible by modification or extension of established synthetic methodologies and are in general thermally and oxidatively stable. They also satisfy a suggested organometallic NLO chromophore design criterion (incorporation of the metal into the

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⊗ Abstract published in *Advance ACS Abstracts,* May 1, 1997.
(1) Part 10: Whittall, I. R.; Cifuentes, M. P.; Humphrey, M. G.; Luther-Davies, B.; Samoc, M.; Houbrechts, S.; Persoons, A.; Heath, G. A.; Hockless, D. C. R. *J. Organomet. Chem.*, submitted for publication.
(2) (a) Nalwa, H. S. *Appl. Organomet. Chem.* **1991,** *5,* 349. (b) Marder, S. R. In *Inorganic Materials;* Bruce, D. W., O'Hare, D., Eds.; Wiley: Chichester, England, 1992; p 115. (c) Long, N. J. *Angew. Chem., Int. Ed. Engl.* **1995,** *34,* 21.

plane of the π-system) not fulfilled by, for example, the extensively investigated ferrocenyl system.[4] We have recently reported optical nonlinearities for 18-electron (cyclopentadienyl)bis(phosphine)ruthenium acetylides,[1,3a–c,3i] for which electrochemical studies confirmed facile oxidizability of the metal, and 14-electron (triphenylphosphine)gold acetylides,[3g–i] for which difficulty in metal oxidation was found. The 18-electron, more easily oxidizable, ruthenium complexes exhibit uniformly larger quadratic nonlinearities β than the 14-electron, less readily oxidizable, gold compounds. In contrast, cubic nonlinearities γ for metal acetylides bearing "extended chromophore" ligands (4,4'-$C\equiv CC_6H_4C\equiv CC_6H_4NO_2$ and (E)-4,4'-$C\equiv CC_6H_4$-$CH=CHC_6H_4NO_2$) are larger for the gold complexes than their ruthenium analogues. Clearly, further studies examining the impact on optical nonlinearities of modifying the valence electron count and the ease of oxidation are required. We have now extended our investigations to embrace 18-electron (cyclopentadienyl)(triphenylphosphine)nickel acetylide complexes, which are expected to be less oxidizable than their ruthenium analogues. This paper reports the synthesis and spectroscopic and electrochemical characterization of these complexes, their molecular quadratic optical nonlinearities at 1064 nm and two-level-corrected values, as determined by hyper-Rayleigh scattering (HRS), and their cubic NLO data at 800 nm, as measured by Z-scan, together with comparisons to the relevant data for the analogous ruthenium and gold complexes.

Experimental Section

All organometallic reactions were carried out under an atmosphere of nitrogen with the use of standard Schlenk techniques; no attempt was made to exclude air during work-up of the products. Petroleum ether refers to a fraction of boiling range 60–80 °C. Copper(I) iodide (Aldrich) and triethylamine (BDH) were used as received. NiCl(PPh$_3$)(η-C$_5$H$_5$),[5] Ni(C$\equiv$CPh)(PPh$_3$)(η-C$_5$H$_5$),[6] 4-HC$\equiv$CC$_6$H$_4$NO$_2$,[7] 4-HC$\equiv$CC$_6$H$_4$C$_6$H$_4$NO$_2$,[1] (E)-4,4'-HC$\equiv$CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$,[3b] 4,4'-HC$\equiv$CC$_6$H$_4$C$\equiv$CC$_6$H$_4$NO$_2$,[1] and 4,4'-HC$\equiv$CC$_6$H$_4$N=CH-C$_6$H$_4$NO$_2$[3b] were prepared following the literature methods. Column chromatography was carried out using 7734 Kieselgel 60 silica (Merck). Microanalyses were performed at the Research School of Chemistry, Australian National University. Infrared spectra were recorded using a Perkin-Elmer System 2000 FT-IR spectrometer. UV–vis spectra were recorded

(3) (a) Whittall, I. R.; Humphrey, M. G.; Hockless, D. C. R.; Skelton, B. W.; White, A. H. *Organometallics* **1995**, *14*, 3970. (b) Whittall, I. R.; Humphrey, M. G.; Persoons, A.; Houbrechts, S. *Organometallics* **1996**, *15*, 1935. (c) Whittall, I. R.; Humphrey, M. G.; Samoc, M.; Swiatkiewicz, J.; Luther-Davies, B. *Organometallics* **1995**, *14*, 5493. (d) McDonagh, A. M.; Whittall, I. R.; Humphrey, M. G.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *519*, 229. (e) McDonagh, A. M.; Whittall, I. R.; Humphrey, M. G.; Hockless, D. C. R.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1996**, *523*, 33. (f) McDonagh, A. M.; Cifuentes, M. P.; Whittall, I. R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B.; Hockless, D. C. R. *J. Organomet. Chem.* **1996**, *526*, 99. (g) Whittall, I. R.; Humphrey, M. G.; Houbrechts, S.; Persoons, A.; Hockless, D. C. R. *Organometallics* **1996**, *15*, 5738. (h) Whittall, I. R.; Humphrey, M. G.; Samoc, M.; Luther-Davies, B. *Angew. Chem.* **1997**, *109*, 386; *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 370. (i) Houbrechts, S.; Clays, K.; Persoons, A.; Cadierno, V.; Gamasa, M. P.; Gimeno, J.; Whittall, I. R.; Humphrey, M. G. *Proc. SPIE-Int. Soc. Opt. Eng.* **1996**, *2852*, 98. (j) Humphrey, M. G. *Chem. Aust.* **1996**, *63*, 442.
(4) Calabrese, J. C.; Cheng, L.; Green, J. C.; Marder, S. R.; Tam, W. *J. Am. Chem. Soc.* **1991**, *113*, 7227.
(5) Barnett, K. W. *J. Chem. Educ.* **1974**, *51*, 422.
(6) Bruce, M. I.; Humphrey, M. G.; Matisons, J. G.; Roy, S. K.; Swincer, A. G. *Aust. J. Chem.* **1984**, *37*, 1955.
(7) Takahashi, S.; Kuroyama, Y.; Sonogashira, K.; Hagihara, N. *Synthesis* **1980**, 627.
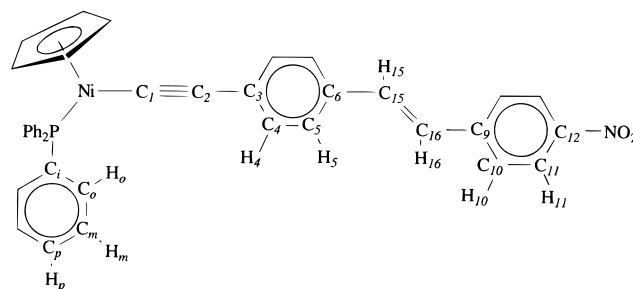

Figure 1. Numbering scheme for NMR spectral assignment of **5**. Analogous scheme for **2**–**4** and **6**–**8**.

using a Cary 5 spectrophotometer. Electrochemical measurements were carried out using a Princeton Applied Research Model 170 Potentiostat. The supporting electrolyte was [NBu$^n_4$][PF$_6$] in distilled deoxygenated CH$_2$Cl$_2$. Solutions (1 × 10^{-3} M) were made under a purge of nitrogen and measured versus a Ag/AgCl reference electrode at −50 °C, such that the ferrocene/ferrocenium redox couple was located at 0.55 V.

^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded using a Varian Gemini-300 FT NMR spectrometer and are referenced to residual CHCl$_3$, 7.24 ppm and CDCl$_3$, 77.0 ppm, and external 85% H$_3$PO$_4$, 0.0 ppm, respectively. NMR spectral assignments for **5** follow the numbering scheme shown in Figure 1. Compounds **2**–**4** and **6**–**8** are numbered analogously.

Characterization of Ni(C≡CPh)(PPh$_3$)(η-C$_5$H$_5$) (2). Complex **2** was prepared following the literature method.[6] IR: (cyclohexane) ν(C≡C) 2107 cm^{-1}; (CH$_2$Cl$_2$) ν(C≡C) 2098 cm^{-1}. ^{1}H NMR (δ, 300 MHz, CDCl$_3$): 5.24 (s, 5H, C$_5$H$_5$), 6.64 (d, J_{HH} = 8 Hz, 2H, H$_4$), 6.90 (m, 3H, H$_5$, H$_6$), 7.38 (m, 9H, H$_m$, H$_p$), 7.73 (dd, J_{HH} = 8 Hz, J_{HP} = 12 Hz, 6H, H$_o$). ^{13}C NMR (δ, 75 MHz, CDCl$_3$): 86.1 (d, J_{CP} = 48 Hz, C$_1$), 92.6 (C$_5$H$_5$), 119.7 (C$_2$), 124.6 (C$_6$), 127.2 (C$_5$), 128.1 (d, J_{CP} = 10 Hz, C$_m$), 129.6 (C$_3$), 130.2 (C$_p$), 130.8 (C$_4$), 133.7 (d, J_{CP} = 11 Hz, C$_o$), 133.9 (d, J_{CP} = 48 Hz, C$_i$). ^{31}P NMR (δ, 121 MHz, CDCl$_3$): 41.6. FAB MS m/z (fragment, relative intensity): 486 ([M]$^+$, 100), 385 ([M − C≡CPh]$^+$, 41), 320 ([M − C≡CPh − C$_5$H$_5$]$^+$, 31).

Synthesis of Ni(4-C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (3). NiCl(PPh$_3$)(η-C$_5$H$_5$) (200 mg, 0.47 mmol) and 4-HC≡CC$_6$H$_4$NO$_2$ (77 mg, 0.52 mmol) were stirred in NEt$_3$ (20 mL) with CuI (5 mg, 0.03 mmol) for 16 h. The solvent was removed under reduced pressure, and the residue was extracted with dichloromethane (50 mL) and then filtered through a plug of silica. Petroleum ether (10 mL) and ethanol (2 mL) were added to the eluate, and then the dichloromethane was removed under reduced pressure, precipitating the microcrystalline product which was collected by filtration (152 mg, 60%). Anal. Calcd for C$_{31}$H$_{24}$NNiO$_2$P: C, 69.95; H, 4.55; N, 2.63. Found: C, 69.54; H, 4.58; N, 2.60. IR: (cyclohexane) ν(C≡C) 2101 cm^{-1}; (CH$_2$Cl$_2$) ν(C≡C) 2091 cm^{-1}. ^{1}H NMR (δ, 300 MHz, CDCl$_3$): 5.25 (s, 5H, C$_5$H$_5$), 6.60 (d, J_{HH} = 9 Hz, 2H, H$_4$), 7.40 (m, 9H, H$_m$, H$_p$), 7.69 (dd, J_{HH} = 9 Hz, J_{HP} = 13 Hz, 6H, H$_o$), 7.79 (d, J_{HH} = 9 Hz, 2H, H$_5$). ^{13}C NMR (δ, 75 MHz, CDCl$_3$): 92.8 (C$_5$H$_5$), 103.6 (d, J_{CP} = 47 Hz, C$_1$), 119.3 (C$_2$), 123.0 (C$_5$), 128.3 (d, J_{CP} = 10 Hz, C$_m$), 130.4 (C$_p$), 131.0 (C$_4$), 133.5 (d, J_{CP} = 48 Hz, C$_i$), 133.7 (d, J_{CP} = 11 Hz, C$_o$), 134.8 (C$_3$), 144.1 (C$_6$). ^{31}P NMR (δ, 121 MHz, CDCl$_3$): 42.5. FAB MS m/z (fragment, relative intensity): 531 ([M]$^+$, 100), 385 ([M − C≡CC$_6$H$_4$NO$_2$]$^+$, 55), 320 ([M − C≡CC$_6$H$_4$NO$_2$ − C$_5$H$_5$]$^+$, 56).

Synthesis of Ni(4,4'-C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (4). Following the method for **3**, NiCl(PPh$_3$)(η-C$_5$H$_5$) (300 mg, 0.71 mmol), 4,4'-HC≡CC$_6$H$_4$C$_6$H$_4$NO$_2$ (170 mg, 0.76 mmol), and CuI (5 mg, 0.03 mmol) afforded **4** as a brown microcrystalline solid (300 mg, 69%). Anal. Calcd for C$_{37}$H$_{28}$NNiO$_2$P: C, 73.06; H, 4.65; N, 2.30. Found: C, 72.75; H, 4.51; N, 2.19. IR: (cyclohexane) ν(C≡C) 2103 cm^{-1}; (CH$_2$Cl$_2$) ν(C≡C) 2094 cm^{-1}. ^{1}H NMR (δ, 300 MHz, CDCl$_3$): 5.25 (s, 5H, C$_5$H$_5$), 6.70 (d, J_{HH} = 8 Hz, 2H, H$_4$), 7.22 (d, J_{HH} = 8 Hz, 2H, H$_5$), 7.40 (m, 9H, H$_m$, H$_p$), 7.58 (d, J_{HH} = 9 Hz, 2H, H$_{10}$), 7.69 (dd, J_{HH} = 8 Hz, J_{HP} = 12 Hz, 6H, H$_o$), 8.18 (d, J_{HH} = 9 Hz, 2H, H$_{11}$). ^{13}C NMR

(δ, 75 MHz, CDCl$_3$): 92.0 (d, J_{CP} = 48 Hz, C$_1$), 92.7 (C$_5$H$_5$), 119.3 (C$_2$), 123.9 (C$_{11}$), 126.3, 127.0 (C$_5$, C$_{10}$), 128.2 (d, J_{CP} = 10 Hz, C$_m$), 129.0 (C$_3$), 129.7 (C$_6$), 130.2 (C$_p$), 130.2 (C$_4$), 133.8 (d, J_{CP} = 11 Hz, C$_o$), 133.8 (d, J_{CP} = 48 Hz, C$_i$), 146.4 (C$_9$), 147.3 (C$_{12}$). ^{31}P NMR (δ, 121 MHz, CDCl$_3$): 42.0. FAB MS m/z (fragment, relative intensity): 607 ([M]$^+$, 100), 385 ([M − C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$]$^+$, 82), 320 ([M − C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$ − C$_5$H$_5$]$^+$, 62).

Synthesis of Ni((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)-(PPh$_3$)(η-C$_5$H$_5$) (5). Following the method for **3**, NiCl(PPh$_3$)(η-C$_5$H$_5$) (130 mg, 0.31 mmol), (E)-4,4′-HC≡CC$_6$H$_4$CH=CHC$_6$-H$_4$NO$_2$ (80 mg, 0.32 mmol), and CuI (5 mg, 0.03 mmol) afforded **5** as a brown microcrystalline solid (110 mg, 56%). Anal. Calcd for C$_{39}$H$_{30}$NNiO$_2$P: C, 73.84; H, 4.77; N, 2.21. Found: C, 73.47; H, 4.47; N, 2.22. IR: (cyclohexane) ν(C≡C) 2100 cm^{-1}; (CH$_2$Cl$_2$) ν(C≡C) 2093 cm^{-1}. ^{1}H NMR (δ, 300 MHz, CDCl$_3$): 5.24 (s, 5H, C$_5$H$_5$), 6.61 (d, J_{HH} = 8 Hz, 2H, H$_4$), 6.92 (d, J_{HH} = 16 Hz, 1H, H$_{15}$), 7.07 (d, J_{HH} = 16 Hz, 1H, H$_{16}$), 7.12 (d, J_{HH} = 8 Hz, 2H, H$_5$), 7.38 (m, 9H, H$_m$, H$_p$), 7.51 (d, J_{HH} = 9 Hz, 2H, H$_{10}$), 7.73 (dd, J_{HH} = 8 Hz, J_{HP} = 13 Hz, 6H, H$_o$), 8.15 (d, J_{HH} = 9 Hz, 2H, H$_{11}$). ^{13}C NMR (δ, 75 MHz, CDCl$_3$): 91.7 (d, J_{CP} = 48 Hz, C$_1$), 92.7 (C$_5$H$_5$), 120.0 (C$_2$), 124.1 (C$_{11}$), 124.6 (C$_{15}$), 126.2, 126.5 (C$_5$, C$_{10}$), 128.2 (d, J_{CP} = 10 Hz, C$_m$), 128.8 (C$_3$), 130.2 (C$_p$), 131.3 (C$_4$), 132.2 (C$_6$), 133.3 (C$_{16}$), 133.8 (d, J_{CP} = 11 Hz, C$_o$), 133.9 (d, J_{CP} = 48 Hz, C$_i$), 144.2 (C$_9$), 146.3 (C$_{12}$). ^{31}P NMR (δ, 121 MHz, CDCl$_3$): 41.8. FAB MS m/z (fragment, relative intensity): 633 ([M]$^+$, 100), 385 ([M − C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$]$^+$, 84), 320 ([M − C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$ − C$_5$H$_5$]$^+$, 52).

Synthesis of Ni((Z)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)-(PPh$_3$)(η-C$_5$H$_5$) (6). Following the method for **3**, NiCl(PPh$_3$)(η-C$_5$H$_5$) (200 mg, 0.47 mmol), (Z)-4,4′-HC≡CC$_6$H$_4$-CH=CHC$_6$H$_4$NO$_2$ (120 mg, 0.48 mmol), and CuI (5 mg, 0.03 mmol) afforded **6** as a light brown powder (180 mg, 60%). Anal. Calcd for C$_{39}$H$_{30}$NNiO$_2$P: C, 73.84; H, 4.77; N, 2.21. Found: C, 72.94; H, 4.37; N, 2.35. IR: (cyclohexane) ν(C≡C) 2103 cm^{-1}; (CH$_2$Cl$_2$) ν(C≡C) 2094 cm^{-1}. ^{1}H NMR (δ, 300 MHz, CDCl$_3$): 5.23 (s, 5H, C$_5$H$_5$), 6.41 (d, J_{HH} = 12 Hz, 1H, H$_{15}$), 6.51 (d, J_{HH} = 8 Hz, 2H, H$_4$), 6.60 (d, J_{HH} = 12 Hz, 1H, H$_{16}$), 6.78 (d, J_{HH} = 8 Hz, 2H, H$_5$), 7.27 (d, J_{HH} = 9 Hz, 2H, H$_{10}$), 7.37 (m, 9H, H$_m$, H$_p$), 7.70 (dd, J_{HH} = 8 Hz, J_{HP} = 13 Hz, 6H, H$_o$), 7.99 (d, J_{HH} = 9 Hz, 2H, H$_{11}$). ^{13}C NMR (δ, 75 MHz, CDCl$_3$): 90.3 (d, J_{CP} = 47 Hz, C$_1$), 92.8 (C$_5$H$_5$), 119.8 (C$_2$), 123.4 (C$_{11}$), 126.8 (C$_{15}$), 127.6 (C$_3$), 127.9, 129.5 (C$_5$, C$_{10}$), 128.2 (d, J_{CP} = 10 Hz, C$_m$), 130.2 (C$_p$), 130.9 (C$_4$), 132.3 (C$_6$), 133.8 (d, J_{CP} = 11 Hz, C$_o$), 133.8 (d, J_{CP} = 48 Hz, C$_i$), 134.0 (C$_{16}$), 144.3 (C$_9$), 146.2 (C$_{12}$). ^{31}P NMR (δ, 121 MHz, CDCl$_3$): 41.8. FAB MS m/z (fragment, relative intensity): 633 ([M]$^+$, 100), 385 ([M − C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$]$^+$, 83), 320 ([M − C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$ − C$_5$H$_5$]$^+$, 47).

Synthesis of Ni(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (7). Following the method for **3**, NiCl(PPh$_3$)(η-C$_5$H$_5$) (100 mg, 0.24 mmol), 4,4′-HC≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$ (60 mg, 0.24 mmol), and CuI (5 mg, 0.03 mmol) afforded **7** as a brown powder (100 mg, 66%). Anal. Calcd for C$_{39}$H$_{28}$NNiO$_2$P: C, 74.07; H, 4.47; N, 2.22. Found: C, 73.31; H, 4.47; N, 2.19. IR: (cyclohexane) ν(C≡C) 2101, 2213 cm^{-1}; (CH$_2$Cl$_2$) ν(≡C) 2096, 2212 cm^{-1}. ^{1}H NMR (δ, 300 MHz, CDCl$_3$): 5.26 (s, 5H, C$_5$H$_5$), 6.59 (d, J_{HH} = 8 Hz, 2H, H$_4$), 7.12 (d, J_{HH} = 8 Hz, 2H, H$_5$), 7.40 (m, 9H, H$_m$, H$_p$), 7.55 (d, J_{HH} = 9 Hz, 2H, H$_{10}$), 7.71 (dd, J_{HH} = 8 Hz, J_{HP} = 13 Hz, 6H, H$_o$), 8.16 (d, J_{HH} = 9 Hz, 2H, H$_{11}$). ^{13}C NMR (δ, 75 MHz, CDCl$_3$): 88.1 (C$_{15}$), 92.8 (C$_5$H$_5$), 94.0 (d, J_{CP} = 47 Hz, C$_1$), 95.7 (C$_{16}$), 117.6 (C$_6$), 119.8 (C$_2$), 123.6 (C$_{11}$), 128.3 (d, J_{CP} = 10 Hz, C$_m$), 129.1 (C$_3$), 130.3 (C$_p$), 130.6 (C$_9$), 130.9, 131.0, 131.9 (C$_4$, C$_5$, C$_{10}$), 133.8 (d, J_{CP} = 11 Hz, C$_o$), 133.8 (d, J_{CP} = 48 Hz, C$_i$), 146.6 (C$_{12}$). ^{31}P NMR (δ, 121 MHz, CDCl$_3$): 42.0. FAB MS m/z (fragment, relative intensity): 631 ([M]$^+$, 87), 385 ([M − C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$]$^+$, 100), 320 ([M − C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$ − C$_5$H$_5$]$^+$, 73).

Synthesis of Ni(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (8). Following the method for **3**, NiCl(PPh$_3$)(η-C$_5$H$_5$) (300 mg, 0.71 mmol), 4,4′-HC≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$ (179 mg,

0.72 mmol), and CuI (5 mg, 0.03 mmol) afforded **8** as a brown powder (210 mg, 47%). Anal. Calcd for C$_{38}$H$_{29}$NNiO$_2$P: C, 71.83; H, 4.61; N, 4.41. Found: C, 71.29; H, 4.40; N, 4.31. IR: (cyclohexane) ν(C≡C) (not sufficiently soluble); (CH$_2$Cl$_2$) ν(C≡C) 2094 cm^{-1}. ^{1}H NMR (δ, 300 MHz, CDCl$_3$): 5.24 (s, 5H, C$_5$H$_5$), 6.65 (d, J_{HH} = 8 Hz, 2H, H$_4$), 6.91 (d, J_{HH} = 8 Hz, 2H, H$_5$), 7.38 (m, 9H, H$_m$, H$_p$), 7.73 (dd, J_{HH} = 8 Hz, J_{HP} = 13 Hz, 6H, H$_o$), 7.96 (d, J_{HH} = 9 Hz, 2H, H$_{10}$), 8.26 (d, J_{HH} = 9 Hz, 2H, H$_{11}$), 8.42 (s, 1H, H$_{16}$). ^{13}C NMR (δ, 75 MHz, CDCl$_3$): 90.0 (d, J_{CP} = 47 Hz, C$_1$), 92.6 (C$_5$H$_5$), 119.6 (C$_2$), 120.5 (C$_5$), 123.9 (C$_{11}$), 127.5 (C$_3$), 128.2 (d, J_{CP} = 10 Hz, C$_m$), 129.0 (C$_{10}$), 130.2 (C$_p$), 131.8 (C$_4$), 133.8 (d, J_{CP} = 11 Hz, C$_o$), 133.9 (d, J_{CP} = 48 Hz, C$_i$), 141.8 (C$_9$), 146.8 (C$_6$), 148.9 (C$_{12}$), 155.1 (C$_{16}$). ^{31}P NMR (δ, 121 MHz, CDCl$_3$): 41.8. FAB MS m/z (fragment, relative intensity): 634 ([M]$^+$, 100), 385 ([M − C≡CC$_6$H$_4$-N=CHC$_6$H$_4$NO$_2$]$^+$, 88), 320 ([M − C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$ − C$_5$H$_5$]$^+$, 47).

HRS Measurements. An injection-seeded Nd:YAG laser (Q-switched Nd:YAG Quanta Ray GCR5, 1064 nm, 8 ns pulses, 10 Hz) was focussed 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. Further details of the experimental procedure have been reported elsewhere.[8]

Z-Scan Measurements. Measurements were performed at 800 nm, using a system consisting of a Coherent Mira Ar-pumped Ti−sapphire laser generating a mode-locked train of approximately 100 fs pulses and a home-built Ti−sapphire regenerative amplifier pumped with a frequency-doubled Q-switched pulsed YAG laser (Spectra Physics GCR) at 30 Hz and employing chirped pulse amplification. THF solutions were examined in a glass cell with a 0.1 cm path length. The Z-scans were recorded at two concentrations for each compound, and the real and imaginary part of the nonlinear phase change was determined by numerical fitting.[9] The real and imaginary parts of the hyperpolarizability of the solute were then calculated by assuming linear concentration dependencies of the solution susceptibility. The nonlinearities and light intensities were calibrated using measurements of a 1 mm thick silica plate for which the nonlinear refractive index n_2 = 3 × 10^{-16} cm^2 W^{-1} was assumed.

Results and Discussion

Syntheses and Characterization of σ-Acetylide Complexes. The synthetic methodology employed for the preparation of **2**−**8** (Scheme 1) has been successfully utilized for the preparation of **2** by Bruce and co-workers;[6] applying it to the nitro-containing acetylenes afforded the corresponding acetylides in 46−69% yields. Complexes **3**−**8** were characterized by IR, ^{1}H, ^{13}C, and ^{31}P NMR spectroscopies, FAB mass spectrometry, and satisfactory microanalyses. Characteristic ν(C≡C) in the IR move to lower energy on increasing solvent polarity (a difference of 5−10 cm^{-1} in moving from cyclohexane to dichloromethane), suggestive of in-

(8) (a) Clays, K.; Persoons, A. *Rev. Sci. Instrum.* **1992**, *63*, 3285. (b) Hendrickx, E.; Dehu, C.; Clays, K.; Brédas, J. L.; Persoons, A. In *Polymers for Second-Order Nonlinear Optics*; Lindsay, G. A., Singer, K. D., Eds.; ACS Symposium Series 601; American Chemical Society: Washington, DC, 1995, 82. (c) Houbrechts, S.; Clays, K.; Persoons, A.; Pikramenou, Z.; Lehn, J.-M. *Chem. Phys. Lett.* **1996**, *258*, 485.
(9) Sheikh-bahae, M.; Said, A. A.; Wei, T.; Hagan, D. J.; van Stryland, E. W. *IEEE J. Quantum Electron.* **1990**, *26*, 760.

Scheme 1

Complex	R	% yield
2[a]		
3	—NO$_2$	60
4	—NO$_2$	69
5		56
6		60
7	—C≡C—⟨⟩—NO$_2$	66
8		47
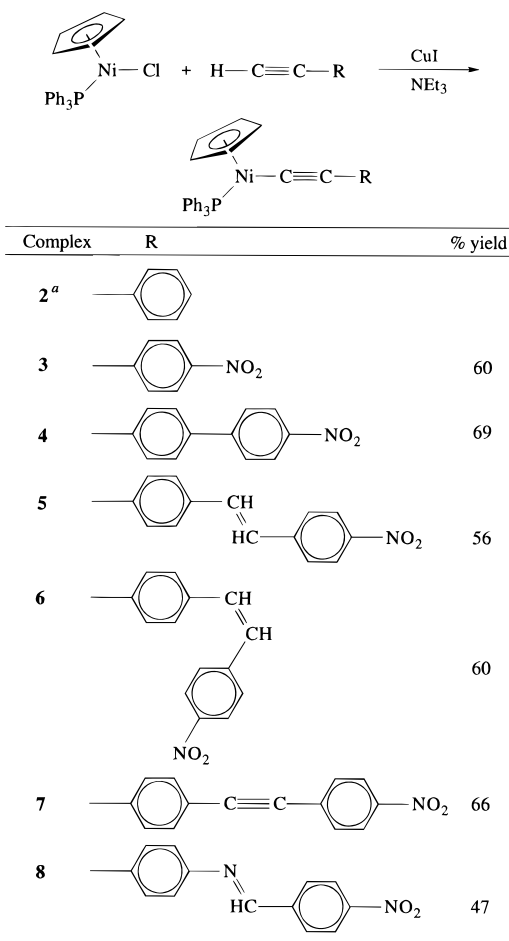
[a] Reference 6.

creased contribution of a vinylidene form (Ni−C≡C ↔ Ni=C=C). Cyclopentadienyl (^{1}H NMR, 5.23−5.26 ppm; ^{13}C NMR, 92.6−92.8 ppm), Ni*C*≡*C* (119.3−120.0 ppm), and ^{31}P NMR phosphine resonances (41.6−42.5 ppm) are insensitive to changes in the acetylide ligand, whereas Ni*C* moves downfield on introduction of a nitro-substituent (**2**, 86.1 ppm; **3**, 103.5 ppm) and then upfield on progressing from a one-ring to two-ring acetylide ligand (**4**−**8**, 90.0−94.0 ppm). We have confirmed the identities of **2**−**5** and **7**−**8** by carrying out single-crystal X-ray diffraction studies, complete details of which will be reported elsewhere.[10] Importantly, no significant increase in the quinoidal vinylidene contribution to the acetylide ground state structure is apparent on introduction of the nitro substituent.

Electrochemical Studies. The results of the cyclic voltammetric investigations of complexes **1**−**8** are summarized in Table 1; to the best of our knowledge, the results for **2**−**8** are the first such data for nickel acetylide complexes. All complexes undergo a one-electron oxidation assigned to the Ni$^{II/III}$ couple. Replacement of the electron withdrawing Cl by C≡CPh in progressing from **1** to **2** leads to a decrease in the oxidation potential, and replacing phenylacetylide by the more electron withdrawing 4-nitrophenylacetylide in progressing from **2** to **3** results in the expected increase in the oxidation potential. Replacing the one-

ring nitrophenylacetylide ligand in **3** by the two-ring nitro-containing ligands in **4**−**8** leads to a decreased $E°_{Ni^{II/III}}$, with the value for the latter similar to that of the phenylacetylide complex **2**. These trends reproduce those observed with (cyclopentadienyl)bis(triphenylphosphine)ruthenium complexes.[1,3a,b] Complexes **3**−**8** undergo a one-electron reduction between −0.80 (**7**) and −1.05 V (**4**), assigned to reduction of the nitro substituent. The oxidation waves are associated with nickel-centered HOMOs and the reduction waves with nitro-centered LUMOs. The ease of electron removal from the donor and addition to the acceptor group may be relevant to the nonlinear optical response. The nitro substituents have similar reduction potentials in analogous ruthenium and nickel complexes, but the nickel complexes are 0.14−0.27 V more difficult to oxidize than the ruthenium analogues, suggesting that polarization of the metal-centered electrons toward the nitro acceptor may be less favorable for nickel than ruthenium.

Quadratic Hyperpolarizabilities. We have previously determined the molecular quadratic optical nonlinearities of (cyclopentadienyl)bis(phosphine)ruthenium and (triphenylphosphine)gold σ-arylacetylide complexes[1,3b,g] and have now extended these studies to the nickel complexes **1**−**8**. Experimentally obtained data at 1064 nm by hyper-Rayleigh scattering and two-level-corrected values are collected in Table 2, together with related data for the ruthenium and gold complexes.

Earlier studies with related ruthenium complexes suggested that replacing L = PMe$_3$ by PPh$_3$ in Ru(4-C≡CC$_6$H$_4$NO$_2$)(L)$_2$(η-C$_5$H$_5$), extending the nitro-containing chromophore in progressing from R = 4-C$_6$H$_4$NO$_2$ to 4,4′-C$_6$H$_4$C$_6$H$_4$NO$_2$, 4,4′-C$_6$H$_4$C≡CC$_6$H$_4$NO$_2$, and then (E)-4,4′-C$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$ in Ru(C≡CR)(PPh$_3$)$_2$(η-C$_5$H$_5$), and replacing bridging N by CH in progressing from Ru(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$) to Ru((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$) all lead to an increase in β_{HRS}.[1,3b] These data were substantially resonance enhanced, although the relative orderings were maintained with two-level-corrected values. Subsequent work with analogous gold complexes which have λ_{max} much further removed from 2ω (ω = irradiating frequency) confirmed these relative trends with both experimentally obtained and two-level-corrected data and also suggested that the E stereochemistry was more efficient than the Z stereochemistry.[3g] The two-level-corrected data for ruthenium and gold complexes suggested that the 18-electron, more easily oxidizable ruthenium is a better donor than the 14-electron, less easily oxidizable gold in these donor−bridge-acceptor complexes. The present studies extend our earlier work by affording data for an 18-electron, but less easily oxidizable metal center. The trends observed in chromophore variation with the ruthenium and gold complexes are maintained with these nickel complexes. Although the absolute value of β_{HRS} for the biphenyl-linked **4** is less than that for the one-ring chromophore **3**, this relative ordering is reversed with two-level-corrected values. All of the nickel data are greater than the β values for the corresponding gold complexes, emphasizing the importance of the valence electron count in determining quadratic optical nonlinearity. Conversely, all of the nickel data are less than the β values for the related ruthenium complexes (with the exception of two-level-corrected values for the imino-

(10) Whittall, I. R.; Humphrey, M. G.; Hockless, D. C. R. Manuscript in preparation.

Table 1. Cyclic Voltammetric Data for Complexes 1–8[a]

	$E°_{Ni}$ (V)	i_{pc}/i_{pa}	$E°_{NO_2}$ (V)	i_{pa}/i_{pc}
NiCl(PPh$_3$)(η-C$_5$H$_5$) (**1**)	0.86	0.5		
Ni(C≡CPh)(PPh$_3$)(η-C$_5$H$_5$) (**2**)	0.81	0.4		
Ni(4-C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**3**)	0.90	0.4	−0.97	0.7
Ni(4,4′-C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**4**)	0.81	0.4	−1.05	0.6
Ni((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**5**)	0.78	0.5	−0.85	0.4
Ni((Z)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**6**)	0.75	0.4	−0.96	0.6
Ni(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**7**)	0.77	0.3	−0.80	0.7
Ni(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**8**)	0.81	0.2	−0.79	1.0

[a] At −50 °C vs Ag/AgCl; 0.5 M [NBu$^n_4$][PF$_6$] in CH$_2$Cl$_2$ with a rate of 100 mV s^{-1} and a switching potential of 1.0 V.

Table 2. Experimental Linear Optical Spectroscopic and Quadratic Nonlinear Optical Response Parameters[a]

compound	λ (nm) (ϵ (10^4 M^{-1} cm^{-1}))	β_{1064}[b]	$\beta_{1064, corr}$[c]	ref
NiCl(PPh$_3$)(η-C$_5$H$_5$) (**1**)	330 (0.6), 263 (1.1)	89	45	this work
Ni(C≡CPh)(PPh$_3$)(η-C$_5$H$_5$) (**2**)	307 → (2.5)	24[d]	15	this work
Ni(4-C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**3**)	439 (0.9), 368 → (1.3)	221	59	this work
Ni(4,4′-C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**4**)	413 (1.6), 310 (2.3), 263 → (2.4)	193	65	this work
Ni((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**5**)	437 (2.8), 313 (2.3)	445	120	this work
Ni((Z)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**6**)	417 (1.0), 307 (2.8)	145	47	this work
Ni(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**7**)	417 (1.5), 313 (2.3)	326	106	this work
Ni(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**8**)	448 (1.4), 282 (2.8)	387	93	this work
RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)	357 (0.3) br, 290 (0.5) sh	<7	<4	1
Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)	310 (2.0)	16	10	3b
Ru(4-C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	460 (1.1), 382 (1.1)	468	96	3b
Ru(4-C≡CC$_6$H$_4$NO$_2$)(PMe$_3$)$_2$(η-C$_5$H$_5$)	477 (1.7), 279 (1.0)	248	38	3b
Ru(4,4′-C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	448 (1.6), 310 (2.3)	560	134	1
Ru((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	476 (2.6), 341 (2.4)	1455	232	3b
Ru(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	446 (1.9), 340 (2.8)	865	212	1
Ru(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	496 (1.3), 298 (2.6)	840	86	3b
Au(C≡CPh)(PPh$_3$)	296 (1.3), 282 (3.0), 268 (2.7)	6	4	3g
Au(4-C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)	338 (2.5)	22	12	3g
Au(4,4′-C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$)(PPh$_3$)	350 (2.9), 287 (1.8), 274 (1.9)	39	20	3g
Au((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)	386 (3.8), 303 (2.0)	120	49	3g
Au((Z)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)	362 (2.0), 298 (2.8)	58	28	3g
Au(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)	362 (3.6), 301 (3.2)	59	28	3g
Au(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)	392 (2.1), 297 (3.2)	85	34	3g

[a] All measurements in THF solvent. All complexes are optically transparent at 1064 nm. [b] HRS at 1064 nm; values ±10%. [c] HRS at 1064 nm corrected for resonance enhancement at 532 nm, using the two-level model with $\beta_o = \beta[1 - (2\lambda_{max}/1064)^2][1 - (\lambda_{max}/1064)^2]$; damping factors not included. [d] Value ±20%.

linked complexes), emphasizing the importance of oxidizability in determining NLO merit. We have previously discussed problems in utilizing the two-level-correction; it is likely that $\beta_{1064,corr}$ for Ru(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$) is an underestimation.[1]

Figure 2 correlates quadratic optical nonlinearities for the nickel complexes with those of the precursor terminal alkynes, with the slopes of the graphs (7.1 (R = 0.93) for uncorrected; 2.8 (R = 0.80) for two-level-corrected) defining a "figure of merit" for the (cyclopentadienyl)-(triphenylphosphine)nickel moiety compared to hydrogen. We had earlier analyzed the related (cyclopentadienyl)bis(triphenylphosphine)ruthenium (24 (R = 0.99) for uncorrected; 6.7 (R = 0.69) for two-level-corrected) and (triphenylphosphine)gold (2.4 (R = 0.99) for uncorrected; 2.0 (R = 0.99) for two-level-corrected) complexes. Although the correlation coefficients for the two-level-corrected values in particular are low (perhaps reflecting the lack of applicability of this model to the ruthenium and nickel complexes), the figures of merit provide a useful comparison of the donor strength of these ligated metal centers, with the Ru(PPh$_3$)$_2$(η-C$_5$H$_5$) unit three times as efficient as the Ni(PPh$_3$)(η-C$_5$H$_5$) moiety.

Cubic Hyperpolarizabilities. Third-order nonlinearities for the nickel complexes were determined by Z-scan at 800 nm. An electronic origin for cubic nonlinearities in these metal acetylide complexes has been demonstrated earlier by degenerate four-wave mixing
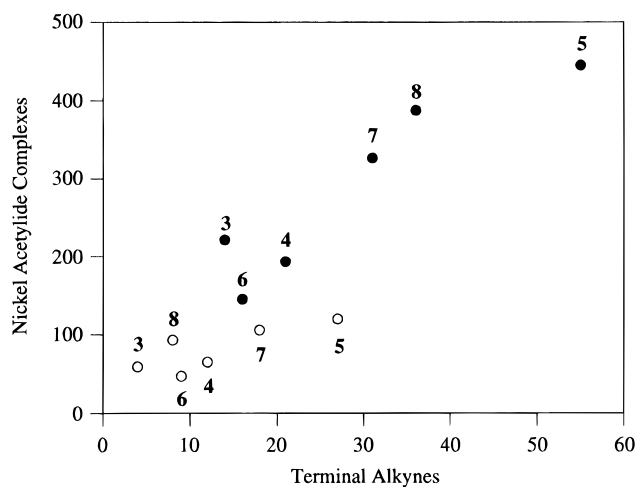

Figure 2. Correlation of molecular quadratic hyperpolarizabilities of complexes **3**–**8** with those of the corresponding terminal alkynes (10^{-30} cm^5 esu^{-1}); ● uncorrected; ○ two-level-corrected. 10% uncertainty.

measurements on the related ruthenium complexes.[3c] Data for the nickel acetylides, together with those from the ruthenium and gold complexes, are collected in Table 3.

The real component of the γ values for the nitro-containing nickel complexes are large, negative, and incorporate substantial error margins; the negative real components and presence of significant imaginary com-

Table 3. Experimental Linear Optical Spectroscopic and Cubic Nonlinear Optical Response Parameters[a]

		γ (10^{-36} esu)[b]		
	λ (nm) (ϵ (10^4 M^{-1} cm^{-1}))	real	imaginary	ref
NiCl(PPh$_3$)(η-C$_5$H$_5$) (**1**)	330 (0.6), 263 (1.1)	c		this work
Ni(C≡CPh)(PPh$_3$)(η-C$_5$H$_5$) (**2**)	307 → (2.5)	15 ± 10	< 10	this work
Ni(4-C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**3**)	439 (0.9), 368 → (1.3)	−270 ± 100	70 ± 50	this work
Ni(4,4′-C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**4**)	413 (1.6), 310 (2.3), 263 → (2.4)	−580 ± 200	300 ± 60	this work
Ni((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**5**)	437 (2.8), 313 (2.3)	−420 ± 100	480 ± 150	this work
Ni((Z)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**6**)	417 (1.0), 307 (2.8)	−230 ± 50	160 ± 80	this work
Ni(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**7**)	417 (1.5), 313 (2.3)	−640 ± 300	720 ± 300	this work
Ni(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)(η-C$_5$H$_5$) (**8**)	448 (1.4), 282 (2.8)	<120	360 ± 100	this work
RuCl(PPh$_3$)$_2$(η-C$_5$H$_5$)	357 (0.3) br, 290 (0.5) sh	150 ± 100		3c
RuCl(PMe$_3$)$_2$(η-C$_5$H$_5$)	347 (0.1)	≤80		3c
Ru(C≡CPh)(PPh$_3$)$_2$(η-C$_5$H$_5$)	310 (2.0)	≤150		3c
Ru(C≡CC$_6$H$_4$Br-4)(PPh$_3$)$_2$(η-C$_5$H$_5$)	325	≤150		3c
Ru(4-C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	460 (1.1), 382 (1.1)	−210 ± 50	≤10	3c
Ru(4-C≡CC$_6$H$_4$NO$_2$)(PMe$_3$)$_2$(η-C$_5$H$_5$)	477 (1.7), 279 (1.0)	−230 ± 70	74 ± 30	3c
Ru(4,4′-C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	448 (1.6), 310 (2.3)	−380 ± 200	320 ± 160	1
Ru((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	476 (2.6), 341 (2.4)	−450 ± 100	210 ± 60	3c
Ru(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	446 (1.9), 340 (2.8)	−450 ± 100	≤20	3c
Ru(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η-C$_5$H$_5$)	496 (1.3), 298 (2.6)	−850 ± 300	360 ± 200	1
AuCl(PPh$_3$)	275 (0.2), 268 (0.3)	180 ± 100		3h
Au(C≡CPh)(PPh$_3$)	296 (1.3), 282 (3.0), 268 (2.7)	39 ± 20		3h
Au(4-C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)	338 (2.5)	120 ± 40	20 ± 15	3h
Au(4,4′-C≡CC$_6$H$_4$C$_6$H$_4$NO$_2$)(PPh$_3$)	350 (2.9), 287 (1.8), 274 (1.9)	540 ± 150	120 ± 50	3h
Au((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)	386 (3.8), 303 (2.0)	1200 ± 200	470 ± 150	3h
Au((Z)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$)	362 (2.0), 298 (2.8)	420 ± 150	92 ± 30	3h
Au(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$)	362 (3.6), 301 (3.2)	1300 ± 400	560 ± 150	3h
Au(4,4′-C≡CC$_6$H$_4$N=CHC$_6$H$_4$NO$_2$)(PPh$_3$)	392 (2.1), 297 (3.2)	130 ± 30	330 ± 60	3h

[a] All measurements as THF solutions (all complexes are optically transparent at 800 nm). [b] All results are referenced to the hyperpolarizability of THF $\gamma = 1.6 \times 10^{-36}$ esu. [c] Insufficiently soluble.

ponents of the nonlinearities indicate two-photon dispersion is contributing to the observed responses. As noted with our previous data from the ruthenium and gold systems, these two-photon states become important for an 800 nm irradiating wavelength when complexes contain $\lambda_{max} > 400$ nm, and real components for the nickel complexes considered here become negative when the optical absorption maximum fulfills this criterion. Despite the large error margins, an increase in the real component of the nonlinearity upon chain-lengthening is evident and an increase in efficiency upon replacing Z by E stereochemistry in progressing from **5** to **6** is suggested. The γ_{real} values for these nickel complexes are the same within the error margins to those of the ruthenium complexes, ease of oxidation making no significant difference to cubic NLO merit. Nonlinearities for Au(4,4′-C≡CC$_6$H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$) and Au((E)-4,4′-C≡CC$_6$H$_4$CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$) are the largest values for any of the complexes in the ruthenium, gold, and nickel systems, despite the gold complexes having the lower valence electron count.

Conclusion

The series of donor−bridge−acceptor (cyclopentadienyl)(triphenylphosphine)nickel σ-acetylide complexes with an 18-electron, less oxidizable metal fill the niche existing between the 18-electron, more oxidizable (cyclopentadienyl)bis(triphenylphosphine)ruthenium acetylides and the 14-electron (triphenylphosphine)gold acetylides and, thus, permit cautious comment on the effect of the ease of oxidation and valence electron count on quadratic and cubic nonlinearities. The ^{13}C NMR chemical shifts of the metal bound α-carbon and Ni$^{II/III}$ redox couple (by cyclic voltammetry) are consistent with the NiC unit becoming less electron rich upon replacement of C≡CPh in **2** by 4-C≡CC$_6$H$_4$NO$_2$ to afford **3**, but

with attenuation of this electron depletion as the nitro group becomes further removed from the metal, on replacement of one-ring acetylide groups by two-ring acetylides to afford **4−8**. These trends in the spectroscopic and electrochemical data mirror those observed for the ruthenium complexes. Experimentally obtained and two-level-corrected quadratic nonlinearities are consistent with an increase in β upon chain-lengthening from a one-ring to two-ring chromophore, replacing Z by E stereochemistry in the 4,4′-C≡CC$_6$H$_4$-CH=CHC$_6$H$_4$NO$_2$ chromophores, replacing N by CH in the 4,4′-C≡CC$_6$H$_4$X=CHC$_6$H$_4$NO$_2$ chromophores, and progressing from a biphenyl to yne-linked and then E-ene-linked chromophore. Where data exist, these trends are also followed by the related ruthenium and gold complexes. Figures of merit for the ligated metal centers defined by comparison to the parent acetylenes as the standard are a necessarily crude approximation. Nevertheless, decreases by factors of three in proceeding from Ru(PPh$_3$)$_2$(η-C$_5$H$_5$) to Ni(PPh$_3$)(η-C$_5$H$_5$) and then to Au(PPh$_3$) provide strong support for the importance of valence electron count and ease of oxidation in enhancing quadratic NLO merit. In contrast, these variables do not influence cubic NLO response in a rational fashion. Data for the nickel complexes are, within the error margins, equivalent to those of the ruthenium complexes, although the ruthenium complexes possess a more easily oxidizable metal and greater delocalization possibilities with the second triphenylphosphine ligand. Data for Au(4,4′-C≡CC$_6$-H$_4$C≡CC$_6$H$_4$NO$_2$)(PPh$_3$) and Au((E)-4,4′-C≡CC$_6$H$_4$-CH=CHC$_6$H$_4$NO$_2$)(PPh$_3$) are substantially larger than those for the nickel and ruthenium analogues (and indeed are the largest values thus far for monomeric organometallic complexes), despite the lower valence electron count, decreased co-ligand delocalization possibilities, and less easily oxidizable metal. Further

studies with systematically varied molecules are currently underway.

OM961066Z