

Syntheses, Structure, and Molecular Cubic Hyperpolarizabilities of Systematically Varied Ethynylgold(I) Complexes

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The reactions of $Q[Au(acac)_2]$ ($Q = N(PPh_3)_2$ (PPN; **a**), NPr_4 (**b**); acac = acetylacetonato) with terminal alkynes of the type $HC\equiv CC_6H_4R-4$ in a 1:2 molar ratio affords the complexes $Q[Au(C\equiv CC_6H_4R-4)_2]$ ($R = NO_2$ (**1**), $C_6H_4NO_2-4$ (**2**), (*E*)- $CH=CHC_6H_4NO_2-4$ (**3**)). The same alkynes react with $[AuCl(CNBU^t)]$ in NEt_3 to give the complexes $[Au(C\equiv CC_6H_4R-4)(CNBU^t)]$ ($R = NO_2$ (**4**), $C_6H_4NO_2-4$ (**5**), (*E*)- $CH=CHC_6H_4NO_2-4$ (**6**)). When $NHET_2$ is used instead of NEt_3 , attack of the secondary amine at the isonitrile ligand takes place and alkynyl carbene complexes of the type $[Au(C\equiv CC_6H_4R-4)\{C(NHBU^t)(NEt_2)\}]$ ($R = NO_2$ (**7**), $C_6H_4NO_2-4$ (**8**), (*E*)- $CH=CHC_6H_4NO_2-4$ (**9**)) are obtained. The crystal structures of **1a**, **4**, **7**, and **9** have been determined. The cubic hyperpolarizabilities of **1a**, **b**, **4–6**, **8**, **9**, and the related complexes $[Au(C\equiv CC_6H_4R-4)(PPh_3)]$ ($R = H$ (**10**), NO_2 (**11**), $4-C_6H_4NO_2$ (**12**), (*E*)- $CH=CHC_6H_4NO_2-4$ (**13**), $C\equiv CC_6H_4NO_2-4$ (**14**), (*Z*)- $CH=CHC_6H_4NO_2-4$ (**15**), (*E*)- $N=CHC_6H_4NO_2-4$ (**16**)) have been determined by Z-scans at 800 nm. An increase in γ_{real} is observed on replacing the coligand BU^tNC by PPh_3 (proceeding from **5** to **12** and from **6** to **13**), introduction of the NO_2 group (proceeding from **10** to **11**), extending the arylalkynyl π -bridge (proceeding from **11** to **12–15**), and replacing (*Z*)- $CH=CH$ by the (*E*)- $CH=CH$ linking unit (proceeding from **15** to **13**).

Introduction

The materials properties of alkynylmetal complexes have attracted significant interest recently,^{1–3} with particular focus on nonlinear optical (NLO) behavior,^{4–15}

liquid crystalline properties,^{16,17} and photophysical properties.^{1,2,18–20} Prominent among the complexes studied have been alkynylgold(I) examples. However, most

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of the alkynylgold(I) complexes reported so far are neutral and correspond to the types $[\text{Au}(\text{C}\equiv\text{CR})(\text{L})]$ and $[\text{Au}_2(\mu\text{-C}\equiv\text{C})\text{L}_2]$.²¹ In many of these cases L is a phosphine (or L₂ a diphosphine),^{1-3,18,19,22-24} although complexes with isocyanide,^{16,17,20,25,26} amine,^{27,28} or ylide ligands²⁹ have also been reported. It is of interest to us to widen the scope of available alkynylgold(I) complexes to permit wider ranging structure-activity materials investigations, and with this in mind, this paper reports the syntheses, spectroscopic properties, and structures of some new alkynylgold(I) complexes of the types $\text{Q}[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}-4)_2]$ and $[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R}-4)\text{L}]$ (Q = PPN, NPr₄; R = NO₂, C₆H₄NO₂-4, (E)-CH=CHC₆H₄NO₂-4; L = Bu^tNC, C(NHBU^t)(NEt₂)).

Studies addressing the quadratic NLO performance of organometallic complexes are significantly more numerous than those probing cubic NLO merit.^{5,30} This is despite the fact that new materials with enhanced cubic NLO properties are required for a range of photonics applications.⁵ We previously reported the cubic molecular optical nonlinearities of alkynylruthenium(II)^{9,10,31} and alkynylnickel(II)¹² complexes. The negative real components and significant imaginary components of the cubic NLO data for these complexes at 800 nm are indicative of two-photon absorption contributions, which renders development of structure-cubic NLO activity relationships very problematic. Alkynylgold(I) complexes such as those examined in the current study can have optical absorption maxima significantly blue-shifted compared to those of the

analogous ruthenium and nickel complexes,³² raising the expectation that the significance of two-photon effects on measured cubic nonlinearities at 800 nm could be greatly diminished. Indeed, we recently reported cubic NLO data for a range of 1,1-ethylenedithiolato complexes of gold, which have absorption maxima at short wavelengths (310–390 nm) together with positive real and small imaginary components of third-order nonlinearities.³³ We have therefore carried out a comprehensive study of the cubic NLO merit of a range of systematically varied alkynylgold complexes, which includes both the new examples prepared in the current study and related complexes we have prepared in earlier work. Some of the cubic NLO results have been the subject of a preliminary communication.⁴

Experimental Section

The acetylenes $\text{HC}\equiv\text{CC}_6\text{H}_4\text{NO}_2-4$,³⁴ $\text{HC}\equiv\text{CC}_6\text{H}_4-4-\text{C}_6\text{H}_4\text{NO}_2-4$,¹⁰ and $\text{HC}\equiv\text{CC}_6\text{H}_4-4-(E)\text{-CH=CHC}_6\text{H}_4\text{NO}_2-4$ ³⁵ and PPN[Au(acac)₂]³⁶ (acac = acetylacetonate) were prepared by literature procedures. NPr₄[Au(acac)₂] was prepared from NPr₄[AuCl₂] using the same procedure as for the PPN⁺ salt³⁶ and was used "in situ". NPr₄[AuCl₂] was prepared following the procedure described for PPN[AuCl₂].³⁶ The alkynylgold complexes [Au(C≡CC₆H₄R-4)(PPh₃)] (R = H (**10**), NO₂ (**11**), C₆H₄NO₂-4 (**12**), (E)-CH=CHC₆H₄NO₂-4 (**13**), C≡CC₆H₄NO₂-4 (**14**), (Z)-CH=CHC₆H₄NO₂-4 (**15**), (E)-N=CHC₆H₄NO₂-4 (**16**)) were prepared as reported previously.³²

Unless otherwise stated, NMR spectra were recorded in CDCl₃ on a Varian Unity 300 instrument at room temperature. Chemical shifts are referenced to TMS (¹H, ¹³C) or H₃PO₄ (³¹P). The ¹³C resonances of PPN (PPN = N(PPh₃)₂) in complexes **1a** and **2a** appear, with very small differences, at 127 (m, *i*-C), 130 (m, *o*-C), 132 (m, *m*-C), and 134 (s, *p*-C) ppm and the ¹H resonances at 7.3–7.7 (m) ppm. IR absorptions due to PPN appear around 1581 (m), 1320–1220 (s, br), 544 (s), 527 (s), and 491 (s) cm⁻¹. Similarly, the NPr₄ cations in complexes **1b** and **2b** show ¹³C resonances at 10.9 (s, Me), 16.0 (s, CH₂), and 61.1 (s, NCH₂) ppm and ¹H resonances at 1.0 (t, Me, 12H, ³J_{HH} = 7 Hz), 1.7–2.2 (m, CH₂, 8H), and 3.2–3.3 (m, NCH₂, 8H) ppm, while the IR spectra show a characteristic absorption at 970 (m) cm⁻¹. All these data are not given below. Most C resonances have not been assigned, but signals corresponding to quaternary carbons are indicated as C and the others as CH. Molar conductivities (Λ_M) were measured with a Philips conductimeter on ca. 5 × 10⁻⁴ M acetone solutions and gave values in the ranges 82–102 (**1–3**) and 0–2 cm² Ω⁻¹ mol⁻¹ (**4–9**).

Nonlinear Optical 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 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. CH₂Cl₂ and thf solutions were examined in a glass cell with a 0.1 cm path length (complexes **2b** and **3** were insufficiently soluble to afford useful data). The Z-scans were recorded at two concentrations for each compound and the real and imaginary parts of the

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Table 1. Summary of X-ray Data for Compounds **1a**, **4**, **7**, and **9**

	1a	4	7	9
formula	C ₅₂ H ₃₈ AuN ₃ O ₄ P ₂	C ₁₃ H ₁₃ AuN ₂ O ₂	C ₁₇ H ₂₄ AuN ₃ O ₂	C ₂₅ H ₃₀ AuN ₃ O ₂
<i>M_r</i>	1027.76	426.22	499.36	601.49
habit	pale yellow block	amber tablet	pale yellow prism	yellow prism
cryst size (mm)	0.4 × 0.3 × 0.3	0.5 × 0.6 × 0.2	0.5 × 0.2 × 0.15	0.5 × 0.2 × 0.2
cryst syst	monoclinic	triclinic	monoclinic	monoclinic
space group	<i>C2/c</i>	<i>P1</i>	<i>P2₁/c</i>	<i>P2₁/c</i>
cell constants				
<i>a</i> (Å)	17.523(3)	10.341(2)	10.0831(10)	11.519(3)
<i>b</i> (Å)	17.854(2)	10.519(2)	12.4398(14)	13.473(3)
<i>c</i> (Å)	15.147(2)	13.841(3)	15.568(2)	16.083(4)
α (deg)	90	81.391(12)	90	90
β (deg)	114.252(10)	73.339(14)	108.353(8)	108.58(2)
γ (deg)	90	75.650(8)	90	90
<i>V</i> (Å ³)	4320.7	1392.3	1853.4	2365.9
<i>Z</i>	4	4	4	4
<i>D</i> _{exptl} (Mg m ⁻³)	1.580	2.033	1.790	1.689
μ (mm ⁻¹)	3.5	10.6	8.0	6.2
transmissions	0.363–0.438	0.271–0.999	0.716–0.988	0.614–0.862
<i>F</i> (000)	2048	800	968	1184
<i>T</i> (°C)	–100	–100	–100	–130
no. of rflns				
measd	8140	5119	4720	4435
indep	3752	4899	3223	4158
<i>R</i> _{int}	0.021	0.016	0.025	0.017
no. of params	281	331	218	289
no. of restraints	241	266	43	245
w <i>R</i> 2 ^a	0.040	0.067	0.049	0.074
<i>R</i> 1 ^b	0.017	0.031	0.025	0.034
<i>S</i>	0.94	0.89	0.92	1.07
max Δρ (e Å ⁻³)	0.3	1.5	1.0	0.8

^a $R1 = \sum ||F_o| - |F_c|| / \sum |F_o|$ for reflections with $I > 2\sigma(I)$. ^b $wR2 = [\sum [w(F_o^2 - F_c^2)] / \sum [w(F_o^2)]]^{0.5}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and *a* and *b* are constants set by the program.

nonlinear phase change determined by numerical fitting. The real and imaginary parts of the hyperpolarizability of the solute were then calculated assuming linear concentration dependencies of the nonlinear phase change. The nonlinearities and light intensities were calibrated using Z-scan measurements of a 1 mm thick silica plate for which the nonlinear refractive index $n_2 = 3 \times 10^{-16}$ cm² W⁻¹ was assumed.

X-ray Structure Determinations. Crystals were mounted in inert oil on glass fibers and transferred to the cold gas stream of the diffractometer (**1a**, **4**, and **7**, Siemens P4; **9**, Stoe STADI-4; each with Siemens LT-2 low-temperature attachment). Cell constants were refined from $\pm\omega$ (Stoe) or setting angles (Siemens) of ca. 60 reflections to $2\theta = 25^\circ$. Data were registered to $2\theta = 50^\circ$ (Mo K α radiation, $\lambda = 0.71073$ Å); scan mode ω/θ (Stoe) or ω (Siemens). Absorption corrections were based on ψ scans. The structures were solved by the heavy-atom method and refined anisotropically against F^2 (program SHELXL-97, G. M. Sheldrick, University of Göttingen). Hydrogen atoms of NH functions were refined freely; other H atoms were included using a riding model or rigid methyl groups. Crystal data are summarized in Table 1.

Q[Au(C≡CC₆H₄R-4)] (**R** = NO₂, **Q** = PPN (**1a**), NPr₄ (**1b**); **R** = C₆H₄NO₂-4, **Q** = PPN (**2a**), NPr₄ (**2b**); **R** = (E)-CH=CHC₆H₄NO₂-4, **Q** = NPr₄ (**3**)). Solid Q[Au(acac)₂] (0.2–0.3 mmol) was added to a solution containing 2 equiv of the corresponding alkyne in dichloromethane (10 mL). After 1 h of stirring under a nitrogen atmosphere, the resulting suspension was filtered through anhydrous MgSO₄, the solution concentrated under vacuum (2 mL), and diethyl ether (20 mL) added to precipitate yellow complexes **1a,b** and **2a**, which were recrystallized from dichloromethane and diethyl ether. Complexes **2b** and **3** are insoluble in dichloromethane and were isolated from the reaction mixture by filtration. Concentration of the mother liquor (1 mL) and addition of diethyl ether (15 mL) gave a second crop of the same product. The yellow solid was washed with diethyl ether (2 × 5 mL) and dried in vacuo.

1a: yield 75%; mp 180 °C dec. Anal. Calcd for C₅₂H₃₈-AuN₃O₄P₂: C, 60.77; H, 3.73; N, 4.09. Found: C, 60.60; H, 3.69;

N, 3.98. IR (cm⁻¹): ν (C≡C), 2096 (m); $\nu_{\text{asym}}(\text{NO}_2)$, 1506 (s). ¹H NMR: δ 7.40–7.70 (m, 34 H, PPN + C₆H₄), 7.97 (d, 4 H, *m*-C₆H₄, ³*J*_{HH} = 9 Hz). ¹³C{¹H} NMR (50 MHz): δ 102.38 (C), 123.04 (CH), 132.56 (CH), 134.99 (C), 144.03 (C), 144.57 (C). Single crystals of **1a** were obtained by slow diffusion of diethyl ether into a solution of **1a** in dichloromethane.

1b: yield 71%; mp 113 °C dec. Anal. Calcd for C₂₈H₃₆-AuN₃O₄: C, 49.78; H, 5.37; N, 6.22. Found: C, 49.83; H, 5.35; N, 6.23. IR (cm⁻¹): ν (C≡C), 2100 (s); $\nu_{\text{asym}}(\text{NO}_2)$, 1508 (s), $\nu_{\text{sym}}(\text{NO}_2)$, 1346 (s). ¹H NMR: δ 7.45, 8.06 (AB system, 8 H, C₆H₄, ³*J*_{HH} = 9 Hz). ¹³C{¹H} NMR (50 MHz): δ 102.64 (C), 123.39 (CH), 132.28 (CH), 134.37 (C), 143.13 (C), 145.01 (C).

2a: yield 91%; mp 125 °C dec. Anal. Calcd for C₆₄H₄₆-AuN₃O₄P₂-^{2/3}CH₂Cl₂: C, 62.81; H, 3.86; N, 3.40. Found: C, 62.65; H, 3.98; N, 3.12. IR (cm⁻¹): ν (C≡C), 2098 (s); $\nu_{\text{asym}}(\text{NO}_2)$, 1510 (s). ¹H NMR (200 MHz): δ 7.39–7.70 (m, 42 H, PPN + C₆H₄ + C₆H₄NO₂), 8.23 (d, 4 H, *m*-C₆H₄NO₂, ³*J*_{HH} = 9 Hz), 5.30 (s, ^{4/3}H, CH₂Cl₂). ¹³C{¹H} NMR: δ 102.39 (C), 124.01 (CH), 126.43 (CH), 127.14 (CH), 128.92 (C), 132.97 (CH), 134.54 (C), 137.94 (C), 146.51 (C), 147.67 (C).

2b: yield 65%; mp 236 °C. Anal. Calcd for C₄₀H₄₄AuN₃O₄: C, 58.04; H, 5.36; N, 5.08. Found: C, 57.98; H, 5.68; N, 5.08. IR (cm⁻¹): ν (C≡C), 2100 (s); $\nu_{\text{asym}}(\text{NO}_2)$, 1510 (s), $\nu_{\text{sym}}(\text{NO}_2)$, 1342 (s). ¹H NMR (200 MHz): δ 7.61 (s, 8 H, C₆H₄), 7.74, 8.32, (AB system, 8 H, C₆H₄NO₂, ³*J*_{HH} = 13 Hz).

3: yield 63%; mp 143 °C dec. Anal. Calcd for C₄₄H₄₈-AuN₃O₄: C, 60.07; H, 5.50; N, 4.78. Found: C, 60.01; H, 5.74; N, 4.91. IR (cm⁻¹): ν (C≡C), 2102 (s); ν (C=C), 1626 (w); $\nu_{\text{asym}}(\text{NO}_2)$, 1514 (s), $\nu_{\text{sym}}(\text{NO}_2)$, 1338 (s). ¹H NMR (DMSO-*d*₆): δ 7.35, 7.64 (AB system, 8 H, C₆H₄, ³*J*_{HH} = 9 Hz), 7.47, 7.59 (AB system, 4 H, CH, ³*J*_{HH} = 16 Hz), 7.95, 8.33 (AB system, 8 H, C₆H₄NO₂, ³*J*_{HH} = 9 Hz).

[Au(C≡CC₆H₄R-4)(CNBu^t)] (**R** = NO₂ (**4**), C₆H₄NO₂-4 (**5**), (E)-CH=CHC₆H₄NO₂-4 (**6**)). To a solution of [AuCl(CNBu^t)] (0.3–0.5 mmol) in dichloromethane (15 mL) were added equimolar amounts of the corresponding alkyne and triethylamine (5 mL). After 24 h of stirring, the solvent was removed under vacuum. The residue was dissolved in dichloromethane

(2 mL), and diethyl ether (20 mL) was added to precipitate a pale yellow solid, which was filtered and washed with water (2×5 mL) to remove $(\text{NH}_4\text{Et}_3)\text{Cl}$. The solid residue was dissolved in dichloromethane (20 mL), the solution was filtered through anhydrous MgSO_4 and concentrated (1 mL), and *n*-hexane (20 mL) was added to precipitate complexes **4–6** as pale yellow solids.

4: yield 56%; mp 118 °C dec. Anal. Calcd for $\text{C}_{13}\text{H}_{13}\text{-AuN}_2\text{O}_2$: C, 36.63; H, 3.07; N, 6.57. Found: C, 36.53; H, 2.95; N, 6.45. IR (cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2230 (s); $\nu(\text{C}\equiv\text{C})$, 2122 (s); $\nu_{\text{asym}}(\text{NO}_2)$, 1504 (s), $\nu_{\text{sym}}(\text{NO}_2)$, 1336 (s). ^1H NMR: δ 1.59 (s, 9 H, Bu^t), 7.55, 8.12 (AB system, 4 H, C_6H_4 , $^3J_{\text{HH}} = 9$ H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 29.76 (Me), 58.80 (CMe_3), 101.60 (C), 123.33 (CH), 130.18 (C), 132.08 (C), 132.92 (CH), 145.93 (C), 146.59 (t, AuCN , $^1J_{\text{CN}} = 19$ Hz). Single crystals of **4** were obtained by slow diffusion of *n*-hexane into a solution of **4** in dichloromethane.

5: yield 66%; mp 152 °C dec. Anal. Calcd for $\text{C}_{19}\text{H}_{17}\text{-AuN}_2\text{O}_2$: C, 45.43; H, 3.41; N, 5.58. Found: C, 45.33; H, 3.29; N, 5.44. IR (cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2224 (s); $\nu(\text{C}\equiv\text{C})$, 2120 (w); $\nu_{\text{asym}}(\text{NO}_2)$, 1512 (s), $\nu_{\text{sym}}(\text{NO}_2)$, 1342 (s). ^1H NMR: δ 1.59 (s, 9 H, Bu^t), 7.53, 7.58 (AB system, 4 H, C_6H_4 , $^3J_{\text{HH}} = 9$ H), 7.73, 8.28 (AB system, 4 H, $\text{C}_6\text{H}_4\text{NO}_2$, $^3J_{\text{HH}} = 9$ H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 29.79 (Me), 58.67 (CMe_3), 102.68 (C), 124.01 (CH), 124.61 (C), 125.69 (C), 126.91 (CH), 127.51 (CH), 133.17 (CH), 136.81 (C), 146.98 (C), 147.14 (C).

6: yield 69%; mp 168 °C dec. Anal. Calcd for $\text{C}_{21}\text{H}_{19}\text{-AuN}_2\text{O}_2$: C, 47.74; H, 3.62; N, 5.30. Found: C, 47.70; H, 3.43; N, 5.16. IR (cm^{-1}): $\nu(\text{C}\equiv\text{N})$, 2232 (s); $\nu(\text{C}\equiv\text{C})$, 2122 (w); $\nu(\text{C}=\text{N})$, 1626 (w), $\nu_{\text{asym}}(\text{NO}_2)$, 1504 (s); $\nu_{\text{sym}}(\text{NO}_2)$, 1342 (s). ^1H NMR: δ 1.59 (s, 9 H, Bu^t), 7.10, 7.22 (AB system, 2 H, CH, $^3J_{\text{HH}} = 16$ Hz), 7.43, 7.48 (AB system, 4 H, C_6H_4 , $^3J_{\text{HH}} = 9$ H), 7.64, 8.22 (AB system, 4 H, $\text{C}_6\text{H}_4\text{NO}_2$, $^3J_{\text{HH}} = 9$ H).

[Au(C \equiv CC $_6$ H $_4$ R-4){C(NHBu t)(NET $_2$)] (**R** = NO_2 (**7**), $\text{C}_6\text{H}_4\text{NO}_2$ -4 (**8**), (*E*)-CH=CHC $_6$ H $_4$ NO $_2$ -4 (**9**)). To a solution of $[\text{AuCl}(\text{CNBu}^t)]$ (0.2–0.6 mmol) in diethylamine (10 mL) was added an equimolar amount of the corresponding alkyne, and the mixture was stirred for 24 h (**7**, **9**) or 2 h (**8**). The resulting suspension was filtered and washed with water (2×5 mL) to remove $(\text{NH}_2\text{Et}_2)\text{Cl}$. The solid residue was extracted with dichloromethane (20 mL) and the extract filtered through anhydrous MgSO_4 . The solution was concentrated (1 mL), and diethyl ether (**8**, **9**) or *n*-hexane (**7**) (20 mL) was added to give a yellow solid, which was filtered off and air-dried.

7: yield 73%; mp 123 °C dec. Anal. Calcd for $\text{C}_{17}\text{H}_{24}\text{-AuN}_3\text{O}_2$: C, 40.89; H, 4.84; N, 8.41. Found: C, 40.47; H, 5.04; N, 8.31. IR (cm^{-1}): $\nu(\text{NH})$, 3339 (w); $\nu(\text{C}\equiv\text{C})$, 2104 (w); $\nu(\text{C}=\text{N})$, 1530 (s), $\nu_{\text{asym}}(\text{NO}_2)$, 1496 (s); $\nu_{\text{sym}}(\text{NO}_2)$, 1351, 1339 (s). ^1H NMR: δ 1.16 (t, 3 H, Me, $^3J_{\text{HH}} = 7$ Hz), 1.28 (t, 3 H, Me, $^3J_{\text{HH}} = 6$ Hz), 1.62 (s, 9 H, Bu^t), 3.24 (q, 2 H, CH_2 , $^3J_{\text{HH}} = 7$ Hz), 3.99 (q, 2 H, CH_2 , $^3J_{\text{HH}} = 6$ Hz), 5.87 (s, 1 H, NH), 7.524, 8.06 (AB system, 4 H, C_6H_4 , $^3J_{\text{HH}} = 9$ H). $^{13}\text{C}\{^1\text{H}\}$ NMR (50 MHz): δ 11.81 (Me), 14.89 (Me), 31.95 (CMe_3), 40.10 (CH_2), 53.98 (CMe_3), 54.21 (CH_2), 104.02 (C), 123.16 (CH), 132.66 (CH), 133.46 (C), 136.16 (C), 145.30 (C), 204.70 (AuCN_2). Single crystals of **7** were obtained by slow diffusion of *n*-hexane into a dichloromethane solution.

8: yield 76%; mp 140 °C dec. Anal. Calcd for $\text{C}_{23}\text{H}_{28}\text{-AuN}_3\text{O}_2$: C, 48.01; H, 4.90; N, 7.30. Found: C, 48.31; H, 4.89; N, 7.12. IR (cm^{-1}): $\nu(\text{NH})$, 3346 (w); $\nu(\text{C}\equiv\text{C})$, 2108 (m); $\nu(\text{C}=\text{N})$, 1544 (s); $\nu_{\text{asym}}(\text{NO}_2)$, 1508 (s); $\nu_{\text{sym}}(\text{NO}_2)$, 1340 (s). ^1H NMR: δ 1.19 (t, 3 H, Me, $^3J_{\text{HH}} = 7$ Hz), 1.31 (t, 3 H, Me, $^3J_{\text{HH}} = 7$ Hz), 1.66 (s, 9 H, Bu^t), 3.26 (q, 2 H, CH_2 , $^3J_{\text{HH}} = 7$ Hz), 4.04 (q, 2 H, CH_2 , $^3J_{\text{HH}} = 7$ Hz), 5.86 (s, 1 H, NH), 7.51, 7.60 (AB system, 4 H, C_6H_4 , $^3J_{\text{HH}} = 9$ H), 7.73, 8.27 (AB system, 4 H, $\text{C}_6\text{H}_4\text{NO}_2$, $^3J_{\text{HH}} = 9$ H). $^{13}\text{C}\{^1\text{H}\}$ NMR: δ 11.86 (Me), 14.92 (Me), 32.00 (CMe_3), 40.05 (CH_2), 54.01 (CMe_3), 54.23 (CH_2), 104.89 (C), 124.04 (CH), 126.70 (CH), 127.36 (CH), 127.01 (C), 129.54 (C), 133.01 (CH), 135.83 (C), 146.75 (C), 147.34 (C), 205.26 (AuCN_2).

9: yield 82%; mp 127 °C dec. Anal. Calcd for $\text{C}_{25}\text{H}_{30}\text{-AuN}_3\text{O}_2$: C, 49.92; H, 5.03; N, 6.98. Found: C, 49.80; H, 5.08; N, 6.79. IR (cm^{-1}): $\nu(\text{NH})$, 3340 (w); $\nu(\text{C}\equiv\text{C})$, 2104 (m); $\nu(\text{C}=\text{C})$, 1632 (m); $\nu(\text{C}=\text{N})$, 1540 (s); $\nu_{\text{asym}}(\text{NO}_2)$, 1512, 1504 (s); $\nu_{\text{sym}}(\text{NO}_2)$, 1340 (s). ^1H NMR (200 MHz): δ 1.19 (t, 3 H, Me, $^3J_{\text{HH}} = 7$ Hz), 1.30 (t, 3 H, Me, $^3J_{\text{HH}} = 7$ Hz), 1.65 (s, 9 H, Bu^t), 3.25 (q, 2 H, CH_2 , $^3J_{\text{HH}} = 7$ Hz), 4.04 (q, 2 H, CH_2 , $^3J_{\text{HH}} = 7$ Hz), 5.86 (s, 1 H, NH), 7.09, 7.22 (AB system, 2 H, $\text{CH}=\text{CH}$, $^3J_{\text{HH}} = 16$ Hz), 7.41, 7.51 (AB system, 4 H, C_6H_4 , $^3J_{\text{HH}} = 15$ H), 7.61, 8.21 (AB system, 4 H, $\text{C}_6\text{H}_4\text{NO}_2$, $^3J_{\text{HH}} = 15$ H). Single crystals of **9** were obtained by slow diffusion of *n*-hexane into a solution of **9** in dichloromethane.

Results and Discussion

Synthesis. The reaction of (acetylacetonato)gold(I) complexes with species containing even weakly acidic hydrogen atoms has proved to be a versatile and efficient method for the synthesis of a variety of gold(I) complexes, including hydrosulfide, thiolato, phosphide, bis(diphenylphosphino)methanide, alkyl, and alkynyl derivatives.^{37–45} The reactions in dichloromethane between $\text{Q}[\text{Au}(\text{acac})_2]$ ($\text{Q} = \text{PPN}$, NPr_4 ; acac = acetylacetonato) and 2 equiv of different terminal alkynes allowed us to prepare the new bis(alkynyl)aurate(I) complexes $\text{Q}[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R-4})_2]$ ($\text{R} = \text{NO}_2$ (**R**¹), $\text{Q} = \text{PPN}$ (**1a**), NPr_4 (**1b**); $\text{R} = \text{C}_6\text{H}_4\text{NO}_2$ -4 (**R**²), $\text{Q} = \text{PPN}$ (**2a**), NPr_4 (**2b**); $\text{R} = (\text{E})\text{-CH}=\text{CHC}_6\text{H}_4\text{NO}_2$ -4 (**R**³), $\text{Q} = \text{NPr}_4$ (**3**)) in good to excellent yields (Scheme 1). Deprotonation of the alkyne by the basic acetylacetonato ligands present in $[\text{Au}(\text{acac})_2]^-$ produces acetylacetonato and two alkynyl ligands that occupy the coordinative vacancies generated around the gold center.^{37–46}

The same alkynes react with equimolar amounts of $[\text{AuCl}(\text{CNBu}^t)]$ in triethylamine to give the complexes $[\text{Au}(\text{C}\equiv\text{CC}_6\text{H}_4\text{R-4})(\text{CNBu}^t)]$ ($\text{R} = \text{R}^1$ (**4**), R^2 (**5**), R^3 (**6**)) in moderate yields (see Scheme 1). After replacement of the chloro ligand by alkynyl, the desired complexes form along with $(\text{NH}_4\text{Et}_3)\text{Cl}$. Concentration of the resulting suspensions to dryness, washing the residue with water to remove the ammonium salt, and recrystallization from dichloromethane and *n*-hexane are required in order to isolate pure **4–6**. We have previously used this method for the synthesis of $[\text{Au}(\text{C}\equiv\text{CR})(\text{CNBu}^t)]$ ($\text{R} = \text{SiMe}_3$, Bu^t).³⁷ It is well-known that primary or secondary amines add to (isocyanide)gold(I) complexes to give the corresponding carbene derivatives,^{47–50} and

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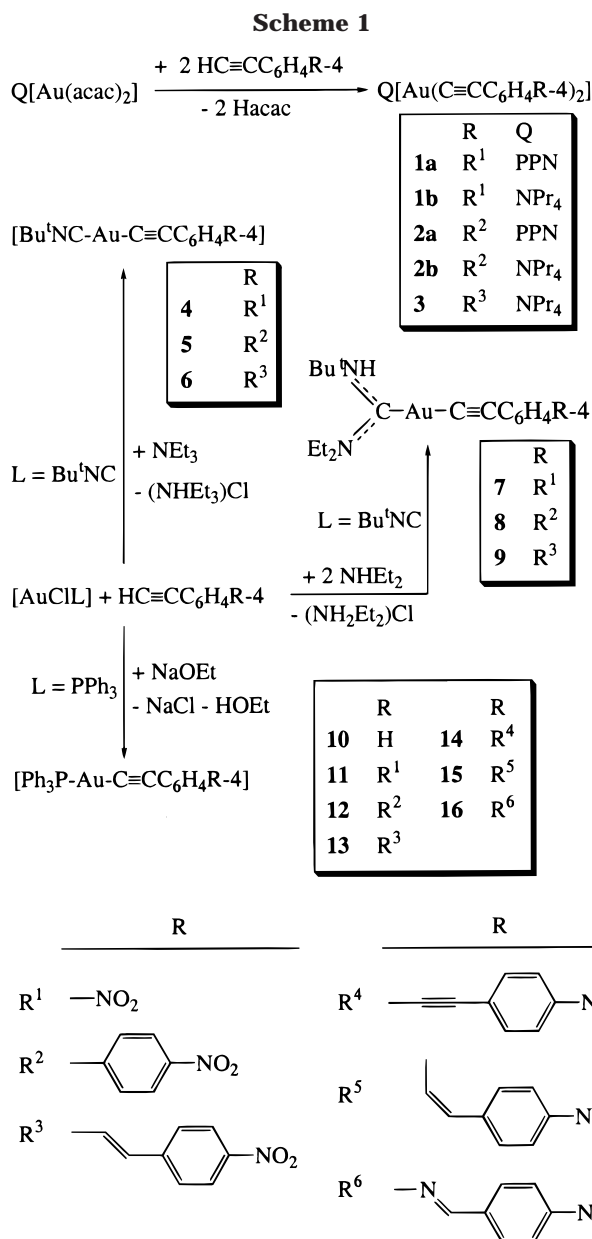
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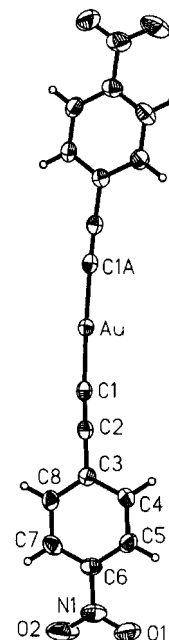
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their use has to be avoided in order to prepare complexes **4–6**. In fact, when NHET₂ is used instead of NEt₃, the reactions of the same alkynes with equimolar amounts of [AuCl(CNBu^t)] produce good yields of the alkynyl carbene complexes [Au(C≡CC₆H₄R-4){C(NH-Bu^t)(NET₂)}] (R = R¹ (**7**), R² (**8**), R³ (**9**)) (see Scheme 1), which result from the double role of the amine as a base toward the alkyne and as a nucleophile that attacks the isocyanide ligand. Complexes [Au(C≡CC₆H₄R-4)(PPh₃)] (R = H (**10**), R¹ (**11**), R² (**12**), R³ (**13**), R⁴ (**14**), R⁵ (**15**), R⁶ (**16**)) (see Scheme 1) were prepared by stirring methanol solutions of [AuCl(PPh₃)], the corresponding alkynes, and sodium methoxide.³²

Structure of Complexes: Crystal Structures of 1a, 4, 7, and 9. Figures 1–4 show the crystal structures of complexes **1a**, **4**, **7**, and **9**, respectively. In all cases, the gold atoms are in essentially linear environments, with CAuC angles of 177.7(1)° (**1a**), 176.3(3) and 172.5(3)° (**4**), 176.2(2)° (**7**), and 176.3(2)° (**9**). The Au–C and C≡C bond distances, in the ranges 1.972(8)–2.002(6) and 1.179(8)–1.211(5) Å, respectively, are similar to those found in other alkynylgold(I) complexes.^{3,22,24,32,51–57}



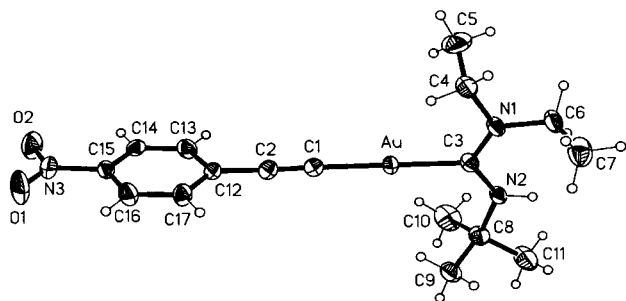


Figure 3. Thermal ellipsoid plot of **7** (50% probability levels) with the labeling scheme. Selected bond lengths (Å) and angles (deg): Au–C(1) = 1.999(5), Au–C(3) = 2.044(5), C(1)–C(2) = 1.193(6), N(1)–C(3) = 1.340(6), N(1)–C(6) = 1.464(6), N(1)–C(4) = 1.467(6), N(2)–C(3) = 1.344(6), N(2)–C(8) = 1.495(6), O(1)–N(3) = 1.218(5), O(2)–N(3) = 1.225(5); C(1)–Au–C(3) = 176.2(2), C(2)–C(1)–Au = 176.6(4), N(1)–C(3)–N(2) = 116.7(4), N(1)–C(3)–Au = 119.5(3), N(2)–C(3)–Au = 123.8(3), C(3)–N(1)–C(6) = 125.0(4), C(3)–N(1)–C(4) = 120.4(4), C(6)–N(1)–C(4) = 114.6(4), C(3)–N(2)–C(8) = 127.1(4), O(1)–N(3)–O(2) = 123.3(4).

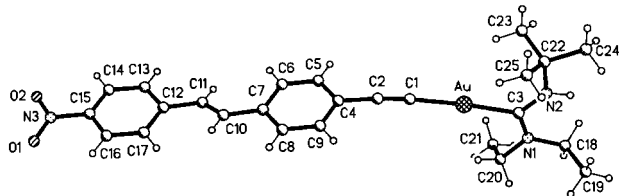


Figure 4. Molecule of complex **9** in the crystal with the labeling scheme. Radii are arbitrary. Selected bond lengths (Å) and angles (deg): Au–C(1) = 2.002(6), Au–C(3) = 2.052(6), C(1)–C(2) = 1.179(8), C(10)–C(11) = 1.315(8), N(1)–C(3) = 1.332(7), N(1)–C(18) = 1.470(7), N(1)–C(20) = 1.481(8), N(2)–C(3) = 1.318(8), N(2)–C(22) = 1.494(7), N(3)–O(2) = 1.213(7), N(3)–O(1) = 1.223(7); C(1)–Au–C(3) = 176.3(2), C(2)–C(1)–Au = 174.8(6), N(2)–C(3)–N(1) = 116.6(5), N(2)–C(3)–Au = 123.8(4), N(1)–C(3)–Au = 119.5(4), C(3)–N(1)–C(18) = 124.9(5), C(3)–N(1)–C(20) = 121.7(5), C(18)–N(1)–C(20) = 113.4(5), C(3)–N(2)–C(22) = 128.1(5), O(2)–N(3)–O(1) = 123.8(6).

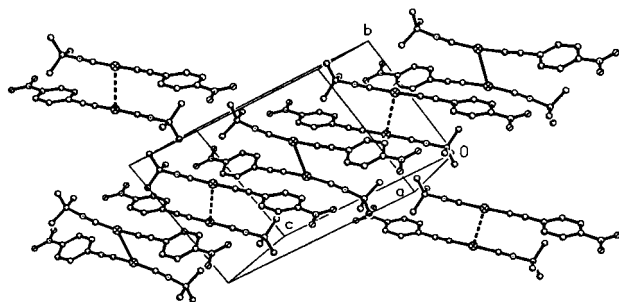


Figure 5. Packing diagram showing Au...Au interactions in complex **4**.

infinite sequence. While the Au–C and C≡C bond distances are similar in both molecules, they differ mainly in the C(2)≡C(1)–Au(1) and Au(1)–C(3)≡N(1) bond angles, which are closer to linearity in **A** (178.5(7) and 176.0(7)°, respectively) than in **A'** (175.7(6) and 172.5(7)°, respectively). This increase in deviation from idealized linearity is possibly correlated with the aurophilic Au'...Au' short contacts (3.144(1) Å) in **A'** molecules, because the Au–Au distance between **A** molecules is 4.085(1) Å. The nitro groups are almost coplanar with the adjacent phenyl rings (torsion angle

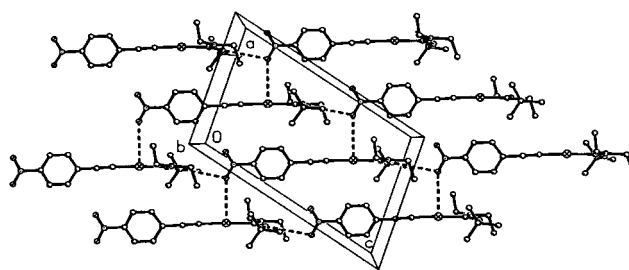


Figure 6. Packing diagram showing O...Au and hydrogen bond interactions in **7**.

5.2°). To avoid repulsion between the bulky Bu^t groups, the alkyne and isocyanide ligands alternate their positions along the chain.

The crystal structures of complexes **7** and **9** (see Figures 3 and 4) are the first of gold complexes containing both carbene and alkyne ligands. Their crystal structures show Au–CN and C–N bond distances and Au–C–N bond angles similar to those found in **7** and **9**. The carbene C(3)–N(1) and C(3)–N(2) bond distances (**7**, 1.340(6) and 1.344(6) Å; **9**, 1.332(7) and 1.318(8) Å) are intermediate between those corresponding to single and double C–N bonds (1.47 and 1.29 Å, respectively),⁵⁸ suggesting that there is significant electron delocalization in the CN₂ moiety. The packing diagram of **7** (see Figure 6) shows that linear chains form due to hydrogen bonding between NH and NO₂ groups of neighboring molecules (N...O, 3.449(6) Å, O...H, 2.55(6) Å; N–H...O, 169(5)°). The chains are aligned parallel, with alternating alkyne and carbene ligands minimizing the repulsion. A similar structural motif has been noted in earlier work; the hydrogen bonding between a carbene NH and a BF₄[−] anion in [{*trans, trans*, *p*-MeC₆H₄-NH)₂C₂Au}BF₄] has been reported.⁵⁹ A weak Au...O interaction (3.624 Å) is also observed between chains.

IR Spectroscopy. The bands assignable to ν(C≡C) appear in the 2096–2122 cm^{−1} range. For the same R, the energy of this band follows the sequence [Au(C≡CC₆H₄R-4)(CNBu^t)] (2120–2122 cm^{−1}) > [Au(C≡CC₆H₄R-4)(PPh₃)] (2112–2116 cm^{−1})³² > [Au(C≡CC₆H₄R-4){C(NHBU^t)(NEt₂)}] (2104–2108 cm^{−1}) > [Au(C≡CC₆H₄R-4)₂][−] (2096–2102 cm^{−1}). We have previously observed similar trends in other alkynylgold(I) complexes.³⁵ The Bu^tNC complexes **4–6** show the ν(CN) band in the 2224–2232 cm^{−1} region, intermediate between those in the free ligand and in [AuCl(CNBU^t)] (2143 and 2252 cm^{−1}, respectively), suggesting that the isocyanide ligand acts preferentially as a σ-donor.⁶⁰ Complexes with carbene ligands (**7–9**) show the corresponding ν(NH) bands in the 3339–3346 cm^{−1} range. They also show a strong band in the 1530–1544 cm^{−1} region, assignable to the asymmetric N=C=N stretching mode.^{50,59,61–63}

Cubic Hyperpolarizabilities. Third-order nonlinearities of the new complexes **1a,b**, **4–6**, **8**, **9**, and the

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Table 2. Linear Optical and Cubic Nonlinear Optical Response Parameters for Alkynylgold(I) Complexes^a

	λ (nm) [ϵ (10^4 M ⁻¹ cm ⁻¹)]	γ_{800} (10^{-36} esu)	
		real	imaginary
PPN[Au(C \equiv CC ₆ H ₄ NO ₂ -4) ₂] (1a) ^b	376 [5.4]	-800 \pm 400	115 \pm 50
NPr ₄ [Au(C \equiv CC ₆ H ₄ NO ₂ -4) ₂] (1b) ^b	374 [3.1]	90 \pm 150	190 \pm 50
[Au(C \equiv CC ₆ H ₄ NO ₂ -4)(CNBu ^t)] (4) ^b	332 [2.6]	\leq 130	\leq 50
[Au(C \equiv CC ₆ H ₄ -4-C ₆ H ₄ NO ₂ -4)(CNBu ^t)] (5) ^b	343 [3.1]	20 \pm 100	70 \pm 50
[Au(C \equiv CC ₆ H ₄ -4-(<i>E</i>)-CH=CHC ₆ H ₄ NO ₂ -4)(CNBu ^t)] (6) ^b	381 [4.1]	390 \pm 200	1050 \pm 300
[Au(C \equiv CC ₆ H ₄ -4-C ₆ H ₄ NO ₂ -4){C(NHBu ^t)(NEt ₂)}] (8) ^b	354 [0.4]	10 \pm 100	160 \pm 40
[Au(C \equiv CC ₆ H ₄ -4-(<i>E</i>)-CH=CHC ₆ H ₄ NO ₂ -4){C(NHBu ^t)(NEt ₂)}] (9) ^b	389 [0.6]	-200 \pm 80	610 \pm 200
[Au(C \equiv CPh)(PPh ₃)] (10) ^c	296 [1.3]	39 \pm 20	
[Au(C \equiv CC ₆ H ₄ NO ₂ -4)(PPh ₃)] (11) ^c	338 [2.5]	120 \pm 40	20 \pm 50
[Au(C \equiv CC ₆ H ₄ -4-C ₆ H ₄ NO ₂ -4)(PPh ₃)] (12) ^c	350 [2.9]	540 \pm 150	120 \pm 50
[Au(C \equiv CC ₆ H ₄ C \equiv C-4-C ₆ H ₄ NO ₂ -4)(PPh ₃)] (13) ^c	362 [3.6]	1300 \pm 400	560 \pm 150
[Au(C \equiv CC ₆ H ₄ -4-(<i>E</i>)-CH=CHC ₆ H ₄ NO ₂ -4)(PPh ₃)] (14) ^c	386 [3.8]	1200 \pm 200	470 \pm 150
[Au(C \equiv CC ₆ H ₄ -4-(<i>Z</i>)-CH=CHC ₆ H ₄ NO ₂ -4)(PPh ₃)] (15) ^c	362 [2.0]	420 \pm 150	92 \pm 30
[Au(C \equiv CC ₆ H ₄ -4-(<i>E</i>)-N=CHC ₆ H ₄ NO ₂ -4)(PPh ₃)] (16) ^c	392 [2.1]	130 \pm 30	330 \pm 60

^a All complexes are optically transparent at 800 nm. ^b Measurements in CH₂Cl₂. ^c Measurements in thf.⁴

previously reported complexes **10**–**16** (see Scheme 1) were evaluated by the Z-scan technique;⁶⁴ the results of these measurements, together with important linear optical absorption data, are given in Table 2. Complexes **2b** and **3** were insufficiently soluble to afford useful data.

Inspection of tabulated data reveals that not all of the real components of the hyperpolarizabilities are positive, and some of the imaginary components are significant. Comparison of magnitude and sign of real and imaginary components of cubic nonlinearities with those of related ruthenium⁹ and nickel¹² alkynyl complexes confirms that two-photon effects are reduced for the present series of complexes, but it is likely that two-photon states contribute to the observed responses; comment on the effect of structural variation on refractive NLO merit is therefore cautious. An increase in γ_{real} is observed on introduction of the strongly electron-withdrawing (and therefore polarizing) NO₂ group (proceeding from **10** to **11**). π -System lengthening is a well-established procedure to increase cubic NLO response in organic compounds, and extending the aryl-alkynyl π -bridge for the gold complexes (proceeding from **11** to **12**–**15**) also leads to an increase in γ_{real} . Modification of bridge stereochemistry (replacing (*Z*)-CH=CH by (*E*)-CH=CH linking unit in proceeding from **15** to **13**) leads to an enhancement of the real component of the cubic nonlinearity. These three molecular modifications directed at the organic alkyne residue also lead to an increase in quadratic optical nonlinearity in these complexes.³²

Assessment of the effect on cubic nonlinearity of counterion replacement (in proceeding from **1a** to **1b**)

or π -system lengthening through the metal (in proceeding from **4** or **11** to **1a** or **1b**) is precluded by the significant error margins. We can comment cautiously on the effect of ligand replacement (being mindful that errors associated with the isocyanide and carbene complex data are significantly larger than those of the phosphine-containing complexes). Replacing the co-ligand Bu^tNC by PPh₃ (in proceeding from **5** and **6** to **12** and **13**) results in a large increase in γ_{real} , with no significant variation in λ_{max} or ϵ . The carbene analogues **8** and **9** have optical absorption maxima similar to those of the isocyanide examples, but with significantly weaker extinction coefficients; cubic nonlinearities of the carbene complexes have similarly large error margins to the isocyanide complexes, precluding further comment. Data at a wavelength minimizing electronic resonance enhancement are required for further comment concerning the effect of structural modification on nonlinear refractive merit.

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Supporting Information Available: X-ray crystallographic files, in CIF format, for **1a**, **4**, **7**, and **9**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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