Syntheses and Second-Order Optical Nonlinearity of Ruthenium σ-Acetylides with an End-Capping Organic Electron Acceptor and Thienyl Entity in the Conjugation Chain

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Ruthenium σ-acetylides with an end-capping organic electron acceptor and thienyl entity in the conjugation chain, Ru(C≡C−Y)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (Y = th-CHO, th-CH=C$(CN)_2$, th-(*E*)-CH=CH-th-CHO, th-(*E*)-CH=CH-th-CH=C$(CN)_2$, C_6H_4-(*E*)-CH=CH-th-NO_2, th-(*E*)-CH=CHC_6H_4-4-NO_2, C_6H_4C≡C-th-NO_2, th-(*E*)-CH=CH-th-CH=CHC_6H_4-4-NO_2, C_6H_4N=C(H)-th-NO_2, th-(*E*)-CH=C$HC_5H_4N^+$Me, th-C≡C$C_5H_4N^+$Me, th-(*E*)-CH=CH-th-NO_2, th-C≡C-th-NO_2) (th = 2,5-disubstituted thiophene), were synthesized. These complexes exhibit intense charge transfer from the ruthenium donor to the organic acceptor. The quadratic hyperpolarizabilities of the selected complexes were determined using the hyper Rayleigh scattering method. Single-crystal X-ray analysis was employed to examine the structures of Ru(C≡CC_6H_4-(*E*)-CH=CH-th-NO_2)$(PPh_3)_2(\eta^5$-$C_5H_5)$ and Ru(C≡C-th-CH=C$(CN)_2$)$(PPh_3)_2(\eta^5$-$C_5H_5)$.

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Introduction

There are growing interests in organometallic nonlinear optics[1] since the first report in this area by Green.[2] Organometallic complexes are attractive because of the facile modification of their properties by either altering the metals themselves or their bystander ligands. Organometallic fragments have been demonstrated to be able to act as potential electron donors or electron acceptors in second-order nonlinear optical chromophores.[3] Among organometallic electron donors, ferrocenyl[4] and $CpRu(L)_2$ (L = phosphine)[5] moieties seem to be promising candidates. Coplanarity of the metals and the π-electrons was suggested to be beneficial for optical nonlinearity;[6] accordingly, $CpRu(L)_2$ σ-acetylide complexes with appropriate electron acceptor are expected to have reasonable optical nonlinearity. Recently we[7] and others[8] synthesized several series of such ruthenium complexes which exhibited good quadratic hyperpolarizability. In our continuation of desiging second-order nonlinear optical materials, we turned our attention to thiophene moiety which has been successfully used in organic chromophores.[9] The reduced aromaticity of thiophene as compared to benzene (stabilization energy: thiophene, 29 kcal mol^{-1}; benzene, 36 kcal mol^{-1}) would allow better electron delocalization.[10] In this report, we describe the syntheses of a series of $CpRu(L)_2$ σ-acetylide complexes incorporating one or two thienyl entity in the conjugation chain. A preliminary study on second-order optical nonlinearity is also presented.

Experimental Section

The general procedures and physical measurements resemble those described in an earlier report.[7] Compounds

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$RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)$,[11] $[Ph_3PCH_2C_6H_4NO_2\text{-}4][Br]$,[8b] 4-ethynylaniline,[12] 4-ethynylpyridine,[13] 5-bromo-2-iodothiophene,[14] 2,5-diethynylthiophene,[15] and (2-thienylmethyl)triphenylphosphonium chloride[16] were prepared by following published methods. (*E*)-1-(5-bromo-2-thienyl)-2-(5-formyl-2-thienyl)ethylene and (*E*)-1-(5-bromo-2-thienyl)-2-(5-nitro-2-thienyl)ethylene were prepared by published procedures with modifications.[17]

5-Ethynyl-2-formylthiophene (1). To a flask containing 5-bromo-2-thiophenecarboxaldehyde (9.55 g, 50.0 mmol), $PdCl_2(PPh_3)_2$ (0.701 g, 1.00 mmol), CuI (0.096 g, 0.50 mmol), and Et_2NH (150 mL) was added (trimethylsilyl)acetylene (7.7 mL, 54.6 mmol). The resulting mixture was stirred at 0 °C for 30 min, allowed to warm to room temperature, and stirred for 12 h. The solvent was removed under vacuum, and the residue was extracted with Et_2O. Removal of Et_2O provided a brown-black oil, which was then chromatographed. Elution with CH_2Cl_2/hexane (1:1) gave a yellow band from which powdery 2-formyl-5-((trimethylsilyl)ethynyl)thiophene (**1a**) was isolated in 86% yield (8.96 g) after removal of solvent. ^{1}H NMR ($CDCl_3$): δ 9.82 (s, 1 H, C*H*O), 7.59 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.23 (d, 1 H, SCC*H*), 0.24 (s, 9 H, CH_3).

Powdery KOH (1.50 g, 26.8 mmol) was added to a solution of **1a** (4.17 g, 20.0 mmol) in 80 mL of MeOH, and the resulting solution was stirred at room temperature for 40 min. The addition of a mixture of H_2O (100 mL) and CH_2Cl_2 (100 mL) resulted in two layers. The aqueous layer was further washed with CH_2Cl_2 (2 × 50 mL), and the CH_2Cl_2 washings were combined with the organic layer and dried over $MgSO_4$. The solution was filtered, and the filtrate was pumped dry. The crude product was chromatographed using CH_2Cl_2/hexane (1:4) as eluent to afford **1** as a colorless powder in 92% yield (2.51 g). ^{1}H NMR ($CDCl_3$): δ 9.85 (s, 1 H, C*H*O), 7.62 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.29 (d, 1 H, SCC*H*), 3.56 (s, 1 H, ≡C*H*). Anal. Calcd for C_7H_4OS: C, 61.74; H, 2.96. Found: C, 61.49; H, 2.78.

Ru(C≡C-th-CHO)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (2; th = 2,5-Substituted Thiophene). To a mixture of $RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)$ (726 mg, 1.00 mmol) and 2-ethynyl-5-nitrothiophene (163 mg, 1.20 mmol) was added 50 mL of MeOH. The resulting mixture was heated at 50 °C for 30 min. The dark green solution formed was cooled to room temperature, and a solution of NaOMe, prepared in situ from Na (40 mg, 1.74 mmol) and MeOH (10 mL), was added. The resulting yellow solution was pumped dry, and the residue was chromatographed using CH_2Cl_2 as eluent to afford **2** as a yellow powder (560 mg, 68%). MS (FAB): *m/e* 826 (M^+, ^{102}Ru). IR (KBr, cm^{-1}): 2037 (s), ν(C≡C); 1644 (s), ν(CO). ^{13}C NMR (CD_2Cl_2): δ 181.0 (s, *C*HO), 145.8 (t, J_{C-P} = 24.5, Ru−*C*≡C), 141.5 (s, =*C*S), 138.3 (t, J_{C-P} = 21.6, C_{ipso} of PPh_3), 138.2 (s, =*C*H), 136.7 (s, =*C*S), 133.6 (t, J_{C-P} = 4.7, C_{ortho} of PPh_3), 128.7 (s, C_{para} of PPh_3), 127.4 (t, J_{C-P} = 4.1, C_{meta} of PPh_3), 126.5 (s, =*C*H), 109.6 (s, RuC≡*C*), 85.8 (s, C_5H_5). Anal. Calcd for $C_{48}H_{38}OP_2SRu$: C, 69.81; H, 4.64. Found: C, 69.96; H, 4.78.

***(E)*-1-(5-Formyl-2-thienyl)-2-(5-ethynyl-2-thienyl)ethylene (3).** (*E*)-1-(5-bromo-2-thienyl)-2-(5-formyl-2-thienyl)-ethylene was utilized to synthesize (*E*)-1-(5-formyl-2-thienyl)-2-(5-(trimethylsilyl)ethynyl-2-thienyl)ethylene (**3a**) by a procedure similar to that employed for **1a**, and the reaction proceeded at room temperature for 2.5 days. After removal of the solvent, the residue was extracted with CH_2Cl_2/H_2O (1:1). The organic layer was collected, dried over $MgSO_4$, filtered, and pumped dry. The residue was chromatographed using hexane as eluent to afford yellow powdery **3a** in 74% yield. IR (KBr, cm^{-1}): 2139 (s), ν(C≡C); 1662 (s), ν(CO). ^{1}H NMR ($CDCl_3$): δ 9.83 (s, 1 H, C*H*O), 7.63 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.13 (d, 1 H, $^3J_{H-H}$ = 16.0 Hz, C*H*=), 7.10 (d, 2 H, 3.9 Hz, SCC*H*), 6.96 (d, 1 H, C*H*=), 6.95 (d, 1 H, SCC*H*), 0.24 (s, 9 H, CH_3).

Powdery KOH (160 mg, 2.86 mmol) was added to a solution of **3a** (850 mg, 2.69 mmol) in 40 mL of MeOH, and the resulting solution was stirred at room temperature for 10 h. A 100 mL of H_2O was added, and the solution was filtered. The solid collected was recrystallized from CH_2Cl_2 to give an orange-yellow powdery **3** in 100% yield (590 mg). MS (EI): *m/e* 244 (M^+). IR (KBr, cm^{-1}): 1657 (s), ν(CO). ^{1}H NMR ($CDCl_3$): δ 9.84 (s, 1 H, C*H*O), 7.63 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.16 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.15 (d, 1 H, $^3J_{H-H}$ = 15.9 Hz, C*H*=), 7.11 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 6.98 (d, 1 H, C*H*=), 6.97 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 3.43 (s, 1 H, C*H*≡). Anal. Calcd for $C_{13}H_8OS_2$: C, 63.90; H, 3.30. Found: C, 64.26; H, 3.19.

Ru(C≡C-th-(*E*)-CH=CH-th-CHO)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (4). To a mixture of $RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)$ (605 mg, 0.83 mmol), $NH_4^+PF_6^-$ (163 mg, 1.00 mmol), and **3** (244 mg, 1.00 mmol) was added 50 mL of CH_2Cl_2 and 25 mL of MeOH. The resulting mixture was stirred at room temperature for 14 h. The solvent was removed under vacuum, and the residue was extracted with CH_2Cl_2 (30 mL). The CH_2Cl_2 solution was filtered through Celite, and the solid was further washed with CH_2Cl_2 (2 × 10 mL). The filtrate was then slowly added to a mixture of Et_2O and hexane (1:5 by volume, 350 mL) with rapid stirring. The solution was filtered, and the solid was dissolved in a mixture of acetone and MeOH (1:1 by volume, 50 mL). A solution of NaOMe (23 mg, 1.00 mmol) in 5 mL of MeOH was added, and the solution was stirred at room temperature for 5 min. After addition of 25 mL of H_2O the solution was filtered. The collected precipitate was washed with cold MeOH (2 × 5 mL) and dried to provide **4** as a dark purple powder (600 mg, 78%). MS (FAB): *m/e* 934 (M^+, ^{102}Ru). IR (KBr, cm^{-1}): 2043 (s), ν(C≡C); 1657 (s), ν(CO). ^{13}C NMR (CD_2Cl_2): δ 182.1 (s, *C*HO), 153.1 (s, =*C*S), 140.4 (s, =*C*S), 138.6 (t, J_{C-P} = 21.6, C_{ipso} of PPh_3), 137.5 (s, =*C*H), 135.6 (t, J_{C-P} = 24.6, Ru−*C*≡C), 135.2 (s, =*C*S), 133.7 (t, J_{C-P} = 4.7, C_{ortho} of PPh_3), 133.2 (s, =*C*S), 129.6 (s, =*C*H), 128.6 (s, C_{para} of PPh_3), 127.4 (t, J_{C-P} = 4.1, C_{meta} of PPh_3), 126.7 (s, =*C*H), 126.1 (s, =*C*H), 125.4 (s, =*C*H), 116.7 (s, =*C*H), 108.4 (s, RuC≡*C*), 85.6 (s, C_5H_5). Anal. Calcd for $C_{54}H_{42}OP_2S_2Ru$: C, 69.44; H, 4.53. Found: C, 69.62; H, 4.68.

***(E)*-1-(5-Nitro-2-thienyl))-2-(4-ethynylphenyl)ethylene (5).** THF (100 mL) was added to a flask containing a mixture of $[Ph_3PCH_2C_6H_4Br\text{-}4][Br]$ (5.80 g, 11.3 mmol), 5-nitro-2-thiophenecarboxaldehyde (2.00 g, 12.4 mmol), and NaH (388 mg, 16.2 mmol). The resulting mixture was stirred at room temperature for 48 h, and the solvent was removed in vacuo. The residue was dissolved in CH_2Cl_2 and filtered. MeOH was slowly added to the filtrate until effervescence ceased. After the solvent was removed, the residue was chromatographed using CH_2Cl_2/hexane (2:3) as eluent. The yellow powdery (*E*)-1-(4-bromophenyl)-2-(5-nitro-2-thienyl)ethylene (**5a**) was isolated in 36% yield (1.26 g) from the second band. ^{1}H NMR ($CDCl_3$): δ 7.81 (d, 1 H, $^3J_{H-H}$ = 4.5 Hz, SCC*H*), 6.98 (d, 1 H, SCC*H*), 7.49 (d, 2 H, $^3J_{H-H}$ = 8.7 Hz, C_6H_4), 7.34 (d, 2 H, C_6H_4), 7.10 (d, 1 H, $^3J_{H-H}$ = 17.2 Hz, C*H*=), 7.03 (d, 1 H, C*H*=).

Compound **5a** was converted to (*E*)-1-(5-nitro-2-thienyl)-2-(4-(trimethylsilyl)ethynylphenyl)ethylene (**5b**) by the same procedures as employed for **1**, except that the reaction proceeded at 60 °C for 48 h. After the solvent was removed, the residue was chromatographed using CH_2Cl_2/hexane (1:1) as eluent to afford the bright yellow powdery **5b** in 76% yield. ^{1}H NMR ($CDCl_3$): δ 7.81 (d, 1 H, $^3J_{H-H}$ = 4.5 Hz, SCC*H*), 7.45

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(d, 2 H, $^3J_{H-H}$ = 8.7 Hz, C_6H_4), 7.41 (d, 2 H, C_6H_4), 7.12 (d, 1 H, $^3J_{H-H}$ = 16.2 Hz, C*H*═), 7.06 (d, 1 H, C*H*═), 6.98 (d, 1 H, SCC*H*), 0.24 (s, 9 H, CH_3).

A solution of **5b** (800 mg, 2.40 mmol) in 50 mL of THF was added a solution of (n-Bu)$_4$N$^+$F$^-$ (770 mg, 2.80 mmol) in 10 mL of THF, and the resulting solution was stirred at room temperature for 20 min. The solvent was removed, and the residue was chromatographed using CH_2Cl_2/hexane (2:3) as eluent. The orange-yellow powdery **5** was isolated in 77% yield (477 mg) from the first band. ^{1}H NMR ($CDCl_3$): δ 7.82 (d, 1 H, $^3J_{H-H}$ = 4.5 Hz, SCC*H*), 7.48 (d, 2 H, $^3J_{H-H}$ = 8.7 Hz, C_6H_4), 7.43 (d, 2 H, C_6H_4), 7.13 (d, 1 H, $^3J_{H-H}$ = 16.2 Hz, C*H*═), 7.07 (d, 1 H, C*H*═), 6.99 (d, 1 H, SCC*H*), 3.16 (s, 1 H, C*H*≡). Anal. Calcd for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 65.66; H, 3.40; N, 5.39.

[Ru(═C═C(H)C$_6$H$_5$-(*E*)-CH═CH-th-NO$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$)]-[PF$_6$] (6). To a mixture of RuCl(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (200 mg, 0.27 mmol), $NH_4^+PF_6^-$ (56 mg, 0.32 mmol), and **5** (73 mg, 0.27 mmol) was added 80 mL of CH_2Cl_2 and 20 mL of MeOH. The resulting mixture was stirred at room temperature for 10 h. The solvent was removed under vacuum, and the residue was recrystallized from CH_2Cl_2/hexane to afford dark red powdery **6** in 93% yield (280 mg). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, 1 H, $^3J_{H-H}$ = 4.5 Hz, SCC*H*), 7.41−7.69 (m, 37 H, Ph, SCC*H*, and C*H*═), 5.37 (t, 1 H, $^4J_{H-P}$ = 2.4 Hz, Ru═C═C*H*), 5.29 (s, 5 H, C_5H_5). ^{31}P{H} NMR ($CDCl_3$): δ 42.7 (s, 2 P, Ru*P*), −145 (heptet, 1 P, $^1J_{P-F}$ = 702 Hz, *P*F$_6$). Anal. Calcd for $C_{55}H_{44}F_6NO_2P_3SRu$: C, 60.55; H, 4.06; N, 1.28. Found: C, 60.11; H, 4.50; N, 1.01.

Ru(C≡CC$_6$H$_5$-(*E*)-CH═CH-th-NO$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (7). A solution of Et_3N (2 mL) in 50 mL of CH_2Cl_2 was added to a flask containing **6** (280 mg, 0.26 mmol), and the resulting solution was stirred at room temperature for 10 min. After the solvent was removed, the residue was chromatographed using THF/hexane (1:4) as eluent to afford the dark purple powdery **7** in 78% yield (190 mg). IR (KBr, cm^{-1}): 2061 (s), ν(C≡C). ^{13}C NMR (CD_2Cl_2): δ 151.8 (s, ═*C*S), 148.3 (s, ═*C*S), 138.8 (t, J_{C-P} = 21.6, C_{ipso} of PPh$_3$), 135.9 (s, ═*C*S), 135.8 (s, ═*C*S), 134.3 (s, ═*C*H), 133.8 (t, J_{C-P} = 4.7, C_{ortho} of PPh$_3$), 130.8 (s, ═*C*H), 129.9 (s, ═*C*H), 128.6 (s, C_{para} of PPh$_3$), 127.3 (t, J_{C-P} = 4.1, C_{meta} of PPh$_3$), 126.3 (t, J_{C-P} = 24.6, Ru−*C*≡C), 126.3 (s, ═*C*H), 124.0 (s, ═*C*H), 117.5 (s, ═*C*H), 116.3 (s, RuC≡*C*), 85.4 (s, C_5H_5). Anal. Calcd for $C_{55}H_{43}NO_2P_2SRu$: C, 69.90; H, 4.59; N, 1.48. Found: C, 69.82; H, 4.44; N, 1.42.

(*E*)-1-(5-Ethynyl-2-thienyl)-2-(4-nitrophenyl)ethylene (8). A solution of NaOMe, prepared in situ from Na (303 mg, 13.2 mmol) and MeOH (30 mL), was added to a mixture of **1a** (1.25 g, 6.00 mmol) and [Ph$_3$PCH$_2$C$_6$H$_4$NO$_2$-4][Br] (2.63 g, 5.50 mmol) in 40 mL of MeOH, and the resulting mixture was stirred at room temperature for 2.5 h. A 20 mL volume of H_2O was added and the solution filtered. The solid was collected and chromatographed using CH_2Cl_2/hexane (1:3) as eluent. The orange yellow powdery **8** was isolated in 45% yield (630 mg). MS (EI): *m*/*e* 255 (M$^+$). ^{1}H NMR ($CDCl_3$): δ 8.17 (d, 2 H, $^3J_{H-H}$ = 8.9 Hz, C_6H_4), 7.54 (d, 2 H, C_6H_4), 7.26 (d, 1 H, $^3J_{H-H}$ = 16.1 Hz, C*H*═), 7.17 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 6.99 (d, 1 H, SCC*H*), 6.90 (d, 1 H, C*H*═), 3.43 (s, 1 H, C*H*≡). Anal. Calcd for $C_{14}H_9NO_2S$: C, 65.87; H, 3.55; N, 5.49. Found: C, 65.84; H, 3.44; N, 5.66.

Ru(C≡C-th-(*E*)-CH═CHC$_6$H$_4$NO$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (9). To a mixture of RuCl(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (726 mg, 1.00 mmol) and **8** (306 mg, 1.20 mmol) was added 25 mL of MeOH. The resulting mixture was refluxed for 2 h and then allowed to cool to room temperature. A solution of NaOMe, prepared in situ from Na (28 mg, 1.22 mmol) and MeOH (5 mL), was added, and the resulting mixture was stirred at room temperature for 5 min. The volume of the solution was reduced to 10 mL and filtered. The solid was washed with cold MeOH (2 × 3 mL) and dried to provide the dark purple powdery **9** in 71% yield (670 mg). MS (FAB): *m*/*e* 947 (M$^+$, ^{104}Ru). IR (KBr, cm^{-1}): 2044 (vs), ν(C≡C); 1614 (m), ν(C═C). ^{13}C NMR (CD_2Cl_2): δ 145.7 (s, *C*NO$_2$), 144.6 (s, *C*CCCNO$_2$), 138.4 (t, J_{C-P} = 21.2, C_{ipso} of PPh$_3$), 135.6 (s, ═*C*S), 135.0 (t, J_{C-P} = 24.9, Ru−*C*≡C), 133.7 (t, J_{C-P} = 4.6, C_{ortho} of PPh$_3$), 133.3 (s, ═*C*S), 129.6 (s, ═*C*H), 128.6 (s, C_{para} of PPh$_3$), 127.3 (t, J_{C-P} = 4.0, C_{meta} of PPh$_3$), 127.2 (s, ═*C*H), 126.2 (s, ═*C*H), 125.9 (s, C_6H_4), 124.2 (s, C_6H_4), 122.0 (s, ═*C*H), 108.3 (s, RuC≡*C*), 85.5 (s, C_5H_5). Anal. Calcd for $C_{55}H_{43}NO_2P_2SRu$: C, 69.90; H, 4.59; N, 1.48. Found: C, 69.69; H, 4.71; N, 1.47.

(4-Ethynylphenyl)(5-nitro-2-thienyl)acetylene (10). To a mixture of 4-bromophenylacetylene (2.00 g, 11.0 mmol), 2-bromo-5-nitrothiophene (2.29 g, 11.0 mmol), PdCl$_2$(PPh$_3$)$_2$ (150 mg, 0.21 mmol), and CuI (40 mg, 0.21 mmol) was added 100 mL of Et_3N, and the resulting mixture stirred at room temperature for 10 h. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2/hexane (1:1). The organic layer was pumped dry, and the residual solid was chromatographed. The bright yellow powdery (4-bromophenyl)(5-nitro-2-thienyl)acetylene (**10a**) was isolated in 62% yield (2.11 g) from the second band. ^{1}H NMR ($CDCl_3$): δ 7.81 (d, 1 H, $^3J_{H-H}$ = 4.2 Hz, SCC*H*), 7.51 (d, 2 H, $^3J_{H-H}$ = 8.4 Hz, C_6H_4), 7.38 (d, 2 H, C_6H_4), 7.14 (d, 1 H, SCC*H*).

Compound **10a** was then converted to (5-nitro-2-thienyl)-(4-(trimethylsilyl)ethynylphenyl)acetylene (**10b**) by the procedure described for the synthesis of **5b**, except that NEt_3 was used instead of Et_2NH. After the solvent was removed in vacuo, the residue extracted with CH_2Cl_2/H_2O (1:1). The organic layer was pumped dry and the residue chromatographed using CH_2Cl_2/hexane (1:4) as eluent. The yellow powdery **10b** was isolated in 77% yield from the second band. ^{1}H NMR ($CDCl_3$): δ 7.81 (d, 1 H, $^3J_{H-H}$ = 4.2 Hz, SCC*H*), 7.51 (d, 2 H, $^3J_{H-H}$ = 8.4 Hz, C_6H_4), 7.30 (d, 2 H, C_6H_4), 7.14 (d, 1 H, SCC*H*), 0.24 (s, 9 H, CH_3).

Compound **10b** was converted to **10** by the same procedures as employed for the synthesis of **5** from **5b**. The yellow powdery **10** was eluted by CH_2Cl_2/hexane (1:1) and isolated in 64% yield from the first band. MS (EI): *m*/*e* 253 (M$^+$). ^{1}H NMR ($CDCl_3$): δ 7.81 (d, 1 H, $^3J_{H-H}$ = 4.2 Hz, SCC*H*), 7.48 (s, 4 H, C_6H_4), 7.14 (d, 1 H, SCC*H*), 3.20 (s, 1 H, C*H*≡). Anal. Calcd for $C_{14}H_7NO_2S$: C, 66.39; H, 2.79; N, 5.53. Found: C, 66.19; H, 2.75; N, 5.30.

Ru(C≡CC$_6$H$_5$C≡C-th-NO$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (11). Compound **11** was synthesized by the same procedures as employed for **9**, except that **10** was utilized instead of **8**. The crude product was chromatographed using THF/hexane (1:4) as eluent. The dark brown **11** was isolated in 64% yield from the second band. MS (FAB): *m*/*e* 943 (M$^+$). IR (KBr, cm^{-1}): 2195 (m), 2061 (s), ν(C≡C). Anal. Calcd for $C_{55}H_{41}NO_2P_2SRu$: C, 70.05; H, 4.38; N, 1.49. Found: C, 70.10; H, 4.30; N, 1.25.

2-(2-(5-Ethynyl-2-thienyl)-(*E*)-ethenyl)-5-(2-(4-nitrophenyl-(*E*)-ethenyl)thiophene (12). A solution of NaOMe, prepared in situ from Na (248 mg, 10.8 mmol) and MeOH (30 mL), was added to a mixture of **3a** (950 mg, 3.00 mmol) and [Ph$_3$PCH$_2$C$_6$H$_4$NO$_2$-4][Br] (1.44 g, 3.01 mmol) in 25 mL of MeOH. The resulting mixture was stirred at room temperature for 2 h and then kept in a refrigerator overnight. The purple-red precipitate formed was collected by filtration and washed with cold MeOH (2 × 3 mL) and subsequently dried to afford **12** in 49% yield (530 mg). ^{1}H NMR ($CDCl_3$): δ 8.19 (d, 2 H, $^3J_{H-H}$ = 8.7 Hz, C_6H_4), 7.55 (d, 2 H, C_6H_4), 7.30 (d, 1 H, $^3J_{H-H}$ = 16.0 Hz, C*H*═), 7.14 (d, 1 H, $^3J_{H-H}$ = 3.7 Hz, SCC*H*), 7.03 (d, 1 H, $^3J_{H-H}$ = 3.7 Hz, SCC*H*), 6.96 (d, 1 H, $^3J_{H-H}$ = 3.7 Hz, SCC*H*), 6.96 (s, 2 H, C*H*═), 6.89 (d, 1 H, $^3J_{H-H}$ = 3.7 Hz, SCC*H*), 6.88 (d, 1 H, $^3J_{H-H}$ = 16.0 Hz, C*H*═), 3.41 (s, 1 H, C*H*≡). Anal. Calcd for $C_{20}H_{13}NO_2S_2$: C, 66.09; H, 3.61; N, 3.85. Found: C, 65.97; H, 3.55; N, 3.73.

Ru(C≡C-th-(*E*)-CH═CH-th-CH═CH-th-NO$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (13). Complex **13** was synthesized in the same manner as **2**, except that **12** was used instead of **1**. A dark purple powdery **13** was isolated in 72% yield. MS (FAB): *m*/*e* 1055 (M$^+$, ^{104}Ru). IR (KBr, cm^{-1}): 2046 (s). ^{13}C NMR (CD_2Cl_2): δ

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146.3 (s, *C*NO$_2$), 144.7 (s, *C*CCCNO$_2$), 143.8 (s, =*C*S), 139.2 (s, =*C*S), 138.5 (t, J_{C-P} = 21.2, C_{ipso} of PPh$_3$), 136.0 (s, =*C*S), 133.7 (t, J_{C-P} = 5.2, C_{ortho} of PPh$_3$), 132.5 (t, J_{C-P} = 24.4, Ru−*C*≡C), 132.0 (s, =*C*S), 129.6 (s, =*C*H), 128.5 (s, C_{para} of PPh$_3$), 127.8 (s, =*C*H), 127.3 (t, J_{C-P} = 4.7, C_{meta} of PPh$_3$), 126.4 (s, =*C*H), 126.3 (s, *C*$_6$H$_4$), 126.0 (s, =*C*H), 125.8 (s, =*C*H), 124.8 (s, =*C*H), 124.2 (s, *C*$_6$H$_4$), 123.9 (s, =*C*H), 117.8 (s, =*C*H), 108.1 (s, RuC≡*C*), 85.5 (s, *C*$_5$H$_5$). Anal. Calcd for $C_{61}H_{47}NO_2P_2S_2$Ru: C, 69.57; H, 4.50; N, 1.33. Found: C, 69.22; H, 4.83; N, 1.30.

(*E*)-*N*-(4-Ethynylphenyl)-*C*-(5-nitro-2-thienyl)imine (14). A 50 mL amount of benzene was added to a flask containing a mixture of 5-nitro-2-thiophenecarboxaldehyde (157 mg, 1.00 mmol) and 4-ethynylaniline (150 mg, 1.28 mmol) and equipped with a Dean−Stark trap. The solution was refluxed for ca. 3 h. The solvent was removed and the residue chromatographed. The orange powdery **14** was eluted by CH_2Cl_2/hexane (1:5) and isolated in 78% yield (195 mg). MS (EI): *m/e* 255 ((M − 1)$^+$). ^{1}H NMR (acetone-d_6): δ 8.51 (s, 1 H, N=C*H*), 7.90 (d, 1 H, $^3J_{H-H}$ = 4.1 Hz, SCC*H*), 7.52 (d, 2 H, $^3J_{H-H}$ = 8.6 Hz, C$_6H_4$), 7.37 (d, 1 H, SCC*H*), 7.19 (d, 2 H, C$_6H_4$). Anal. Calcd for $C_{13}H_8N_2O_2S$: C, 60.93; H, 3.15; N, 10.93. Found: C, 60.76; H, 3.03; N, 10.82.

Ru(C≡CC$_6$H$_5$N=C(H)-th-NO$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (15). Compound **15** was synthesized by the same procedure as employed for **7**, except that **14** was utilized instead of **5**. After the solvent was removed, the residue chromatographed using CH_2Cl_2/hexane (1:1) as eluent to afford the blue powdery **15** in 57% yield. Anal. Calcd for $C_{54}H_{42}N_2O_2P_2SRu$: C, 68.56; H, 4.48; N, 2.96. Found: C, 68.62; H, 4.38; N, 2.92.

(*E*)-1-(5-Ethynyl-2-thienyl)-2-(4-pyridyl)ethylene (16). A 10 mL amount of Ac_2O was added to a mixture of 4-picoline (1.12 mL, 11.5 mmol) and 5-bromo-2-thiophenecarboxaldehyde (2.00 g, 10.5 mmol), and the resulting solution was heated at 140 °C for 48 h. After addition of 200 mL of iced water, the solution was extracted with CH_2Cl_2. The organic layer was dried over $MgSO_4$, filtered, and pumped dry. The residue was chromatographed using THF/hexane (2:3) as eluent to afford the yellow powdery (*E*)-1-(5-bromo-2-thienyl)-2-(4-pyridyl)-ethylene (**16a**) in 76% yield (980 mg). ^{1}H NMR (acetone-d_6): δ 8.51 (d, 2 H, $^3J_{H-H}$ = 6.3 Hz, NC*H*), 7.61 (d, 1 H, $^3J_{H-H}$ = 16.2 Hz, C*H*=), 7.46 (d, 2 H, NCHC*H*), 7.13 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.09 (d, 1 H, SCC*H*), 6.90 (d, 1 H, C*H*=).

Compound **16a** was converted to (*E*)-1-(5-(trimethylsilyl)-ethynyl-2-thienyl)-2-(4-pyridyl)ethylene (**16b**) by the same procedure as employed for the synthesis of **5b**. Bright yellow powdery **16b** was isolated in 81% yield. ^{1}H NMR (acetone-d_6): δ 8.53 (br, 2 H, NC*H*), 7.64 (d, 1 H, $^3J_{H-H}$ = 16.2 Hz, C*H*=), 7.47 (br, 2 H, NCHC*H*), 7.22 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.19 (d, 1 H, SCC*H*), 6.98 (d, 1 H, C*H*=), 0.23 (s, 9 H, CH_3).

Compound **16** was synthesized from **16b** by the same procedures as employed for the synthesis of **5** from **5b**. The crude product was chromatographed using THF/hexane (1:1) as eluent to afford **16** as a light tan powder in 56% yield. MS (EI): *m/e* 211 (M$^+$). ^{1}H NMR (acetone-d_6): δ 8.52 (d, 2 H, $^3J_{H-H}$ = 6.0 Hz, NC*H*), 7.65 (d, 1 H, $^3J_{H-H}$ = 16.5 Hz, C*H*=), 7.48 (d, 2 H, NCHC*H*), 7.26 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.20 (d, 1 H, SCC*H*), 6.99 (d, 1 H, C*H*=), 4.10 (s, 1 H, C*H*≡). Anal. Calcd for $C_{13}H_9NS$: C, 79.90; H, 4.29; N, 6.63. Found: C, 79.82; H, 4.19; N, 6.53.

Ru(C≡C-th-(*E*)-CH=CHC$_5$H$_4$N)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (17). Compound **17** was synthesized by the same procedures as employed for **7**, except that **16** was utilized instead of **5**. After the solvent was removed, the residue chromatographed using THF/hexane (3:2) as eluent to afford the dark red powdery **17** in 75% yield. MS (FAB): *m/e* 901 (M$^+$, ^{102}Ru). IR (KBr, cm^{-1}): 2044 (s), ν(C≡C). Anal. Calcd for $C_{54}H_{43}NP_2SRu$: C, 71.98; H, 4.81; N, 1.55. Found: C, 71.46; H, 4.96; N, 1.22.

[Ru(C≡C-th-(*E*)-CH=CHC$_5$H$_4$NMe)(PPh$_3$)$_2$(η^5-C$_5$H$_5$)][PF$_6$] (18). To a flask containing **17** (500 mg, 0.55 mmol) and $Tl^+PF_6^-$ (290 mg, 0.83 mmol) was added 50 mL of THF and 0.070 mL (1.11 mmol) of MeI. The solution was stirred at room temperature in the dark for 10 h. After removal of the solvent, the residue was dissolved in CH_2Cl_2 and filtered. The filtrate was pumped dry and the residue recrystallized from CH_2Cl_2/hexane to give **18** as a dark blue powder (340 mg, 58%). MS (FAB): *m/e* 916 (M$^+$ − PF$_6$, ^{102}Ru). IR (KBr, cm^{-1}): 2032 (s), ν(C≡C). Anal. Calcd for $C_{55}H_{46}F_6NP_3SRu$: C, 62.26; H, 4.37; N, 1.32. Found: C, 61.90; H, 4.25; N, 1.24.

(5-Ethynyl-2-thienyl)(4-pyridyl)acetylene (19). To a mixture of 5-bromo-2-iodothiophene (3.90 g, 13.5 mmol), ethynylpyridine (1.40 g, 13.5 mmol), $PdCl_2(PPh_3)_2$ (170 mg, 0.24 mmol), and CuI (50 mg, 0.26 mmol) was added 50 mL of Et_2NH, and the resulting mixture was stirred at room temperature for 20 h. The solvent was removed under vacuum and the residue extracted with CH_2Cl_2/H_2O (3:5). The organic layer was pumped dry and the residue chromatographed using THF/hexane as eluent. The tan powdery (5-bromo-2-thienyl)-(4-pyridyl)acetylene (**19a**) was isolated in 75% yield (2.11 g). ^{1}H NMR (acetone-d_6): δ 8.61 (d, 2 H, $^3J_{H-H}$ = 6.0 Hz, NC*H*), 7.44 (d, 2 H, NCHC*H*), 7.27 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.20 (d, 1 H, SCC*H*).

Compound **19a** was converted to (4-pyridyl)(5-(trimethylsilyl)ethynyl-2-thienyl)acetylene (**19b**) by the same procedure as employed for the synthesis of **5b** from **5a**, except that the reaction proceeded at room temperature. The yellow powdery **19b** was isolated in 73% yield. ^{1}H NMR (acetone-d_6): δ 8.67 (d, 2 H, $^3J_{H-H}$ = 6.0 Hz, NC*H*), 7.46 (d, 2 H, NCHC*H*), 7.35 (d, 1 H, $^3J_{H-H}$ = 3.6 Hz, SCC*H*), 7.26 (d, 1 H, SCC*H*), 0.23 (s, 9 H, CH_3).

A solution of KOH (420 mg, 7.50 mmol) in 30 mL of MeOH was slowly added to a solution of **19b** (1.91 g, 6.80 mmol) in 50 mL of MeOH. The mixture was stirred at room temperature for 1 h. The solvent was removed in vacuo and the residue extracted with CH_2Cl_2/H_2O (3:5). The organic layer was chromatographed using CH_2Cl_2 as eluent. The compound **19** was obtained as an off-white powder in 70% yield (990 mg). MS (EI): *m/e* 209 (M$^+$). ^{1}H NMR (acetone-d_6): δ 8.62 (d, 2 H, $^3J_{H-H}$ = 6.3 Hz, NC*H*), 7.46 (d, 2 H, NCHC*H*), 7.36 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.31 (d, 1 H, SCC*H*), 4.15 (s, 1 H, C*H*≡). Anal. Calcd for $C_{13}H_7NS$: C, 74.61; H, 3.37; N, 6.69. Found: C, 74.44; H, 3.23; N, 6.50.

Ru(C≡C-th-C≡CC$_5$H$_4$N)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (20). Compound **20** was synthesized by the same procedure as employed for **7**, except that **19** was utilized instead of **5** and THF/hexane (2:3) used as eluent for chromatography. An orange yellow powdery **20** was isolated in 61% yield. MS (FAB): *m/e* 899 (M$^+$, ^{102}Ru). IR (KBr, cm^{-1}): 2194 (m), 2047 (s), ν(C≡C). Anal. Calcd for $C_{54}H_{41}NP_2SRu$: C, 72.14; H, 4.60; N, 1.56. Found: C, 71.89; H, 4.35; N, 1.42.

[Ru(C≡C-th-C≡CC$_5$H$_4$NMe)(PPh$_3$)$_2$(η^5-C$_5$H$_5$)][PF$_6$] (21). Compound **21** was synthesized by the same procedure as employed for **18**, except that **20** was utilized instead of **17**. A dark purple powdery **21** was isolated in 48% yield. MS (FAB): *m/e* 914 (M$^+$ − PF$_6$, ^{102}Ru). IR (KBr, cm^{-1}): 2160 (m), 2025 (s), ν(C≡C). Anal. Calcd for $C_{55}H_{44}F_6NP_3SRu$: C, 62.38; H, 4.19; N, 1.32. Found: C, 62.00; H, 3.98; N, 1.10.

(*E*)-1-(5-Ethynyl-2-thienyl)-2-(5-nitro-2-thienyl)ethylene (22). Triethylamine (100 mL) and (trimethylsilyl)acetylene (0.85 mL, 6.0 mmol) were added to a flask containing a mixture of (*E*)-1-(5-bromo-2-thienyl)-2-(5-nitro-2-thienyl)ethylene (1.42 g, 5.0 mmol), $PdCl_2(PPh_3)_2$ (70 mg, 0.10 mmol), and CuI (10 mg, 0.050 mmol). The resulting mixture was then stirred at room temperature for 16 h. The solvent was removed in vacuo and the residue extracted with Et_2O and H_2O. The organic layer was collected, dried over $MgSO_4$, and passed through a short Al_2O_3 column. Removal of the solvent gave red-brown crystalline (*E*)-1-(5-nitro-2-thienyl)-2-(5-(trimethylsilyl)ethynyl-2-thienyl)ethylene (**22a**). MS (EI): *m/e* 332 (M$^+$). ^{1}H NMR ($CDCl_3$): δ 7.80 (d, 1 H, $^3J_{H-H}$ = 4.3 Hz, SCC*H*), 7.14 (d, 1 H, $^3J_{H-H}$ = 15.8 Hz, C*H*=), 7.11 (d, 1 H, $^3J_{H-H}$ = 3.8 Hz, SCC*H*), 6.99 (d, 1 H, $^3J_{H-H}$ = 3.8 Hz, SCC*H*),

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6.95 (d, 1 H, $^3J_{H-H}$ = 4.3 Hz, SCC*H*), 6.86 (d, 1 H, C*H*═), 0.24 (s, 9 H, CH_3).

Compound **22a** was treated directly with a solution of KOH (0.28 g, 5.0 mmol) in 50 mL of MeOH and 5 mL of H_2O. The solution was stirred at room temperature for 1 h, and a mixture of CH_2Cl_2 (150 mL) and H_2O (150 mL) was added. The aqueous layer was further extracted with CH_2Cl_2 (2 × 50 mL). All organic extracts were combined and dried over $MgSO_4$. The solution was filtered and the filtrate evaporated to dryness. The residue was chromatographed using ethyl acetate/hexane (1:4) as eluent to afford **22** as a red-brown powder in 85% yield (1.11 g). MS (EI): *m/e* 260 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.81 (d, 1 H, $^3J_{H-H}$ = 4.3 Hz, SCC*H*), 7.17 (d, 1 H, $^3J_{H-H}$ = 3.8 Hz, SCC*H*), 7.15 (d, 1 H, $^3J_{H-H}$ = 15.9 Hz, C*H*═), 7.00 (d, 1 H, $^3J_{H-H}$ = 3.8 Hz, SCC*H*), 6.96 (d, 1 H, $^3J_{H-H}$ = 4.3 Hz, SCC*H*), 6.89 (d, 1 H, C*H*═), 3.45 (s, 1 H, C*H*≡). Anal. Calcd for $C_{13}H_7NS$: C, 74.61; H, 3.37; N, 6.69. Found: C, 74.44; H, 3.23; N, 6.50. Anal. Calcd for $C_{12}H_7NO_2S_2$: C, 55.16; H, 2.70; N, 5.36. Found: C, 54.98; H, 2.60; N, 5.27.

Ru(C≡C-th-(*E*)-CH═CH-th-NO$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (23). To a mixture of RuCl(PPh$_3$)$_2$(η^5-C_5H_5) (556 mg, 0.77 mmol), $NH_4^+PF_6^-$ (150 mg, 0.92 mmol), and **22** (200 mg, 0.77 mmol) was added 50 mL of CH_2Cl_2 and 20 mL of MeOH. The resulting mixture was stirred at room temperature for 18 h. The solvent was removed under vacuum and the residue extracted with 10 mL of CH_2Cl_2. The CH_2Cl_2 solution was filtered through Celite and the filtrate evaporated to dryness. To the residue was added CH_2Cl_2 (50 mL) and NEt_3 (10 mL), and the solution was stirred at room temperature for 20 min. The solvent was removed under vacuum and the residue chromatographed using CH_2Cl_2 as eluent to afford dark purple powdery **23** in 74% yield (536 mg). MS (FAB): *m/e* 951 (M^+, ^{102}Ru). IR (KBr, cm^{-1}): 2040 (s), ν(C≡C). ^{13}C NMR (CD_2Cl_2): δ 151.9 (s, ═*C*S), 147.5 (s, ═*C*S), 138.5 (t, J_{C-P} = 21.6, C_{ipso} of PPh$_3$), 138.2 (t, J_{C-P} = 24.1, Ru−*C*≡C), 134.7 (s, ═*C*S), 134.2 (s, ═*C*S), 133.7 (t, J_{C-P} = 4.7, C_{ortho} of PPh$_3$), 130.7 (s, ═*C*H), 130.1 (s, ═*C*H), 128.7 (s, C_{para} of PPh$_3$), 127.6 (s, ═*C*H), 127.4 (t, J_{C-P} = 4.1, C_{meta} of PPh$_3$), 126.3 (s, ═*C*H), 123.4 (s, ═*C*H), 115.8 (s, ═*C*H), 109.1 (s, RuC≡*C*), 85.7 (s, C_5H_5). Anal. Calcd for $C_{53}H_{41}NO_2P_2S_2Ru$: C, 66.93; H, 4.34; N, 1.43. Found: C, 66.73; H, 4.29; N, 1.40.

2-Ethynyl-5-((5-nitro-2-thienyl)ethynyl)thiophene (24). To a mixture of 2,5-diethynylthiophene (3.81 g, 28.9 mmol), 2-bromo-5-nitrothiophene (2.00 g, 9.62 mmol), $PdCl_2(PPh_3)_2$ (80 mg, 0.11 mmol), and CuI (40 mg, 0.21 mmol) was added 150 mL of $^iPr_2NH_2$, and the resulting mixture was stirred at room temperature for 18 h. The solvent was removed under vacuum and the residue chromatographed using CH_2Cl_2/hexane (1:4) as eluent. Orange-brown powdery **24** was isolated in 64% yield (1.60 g) from the first band. MS (EI): *m/e* 259 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.81 (d, 1 H, $^3J_{H-H}$ = 4.3 Hz, SCC*H*), 7.20 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.17 (d, 1 H, $^3J_{H-H}$ = 3.9 Hz, SCC*H*), 7.15 (d, 1 H, $^3J_{H-H}$ = 4.3 Hz, SCC*H*), 3.42 (s, 1 H, C*H*≡). 2,5-Bis(5-nitro-2-thienyl)ethynylthiophene was also obtained in 19% yield (700 mg). MS (EI): *m/e* 387 (M^+). ^{1}H NMR ($CDCl_3$): δ 7.82 (d, 2 H, $^3J_{H-H}$ = 4.3 Hz, SCC*H*), 7.17 (d, 1 H, SCC*H*). Anal. Calcd for $C_{12}H_5NO_2S_2$: C, 55.58; H, 1.94; N, 5.40. Found: C, 55.66; H, 1.99; N, 5.23.

Ru(C≡C-th-C≡C-th-NO$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (25). Complex **25** was synthesized by the same procedure as employed for **23**, except that **24** was utilized instead of **22**. Purple powdery **25** was isolated in 69% yield. MS (FAB): *m/e* 949 (M^+, ^{102}Ru). IR (KBr, cm^{-1}): 2174 (m), 2040 (s), ν(C≡C). Anal. Calcd for $C_{53}H_{39}NO_2P_2S_2Ru$: C, 67.08; H, 4.14; N, 1.48. Found: C, 67.21; H, 4.35; N, 1.41.

Ru(C≡C-th-CH═C(CN)$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (26). To a flask containing **2** (400 mg, 0.48 mmol) and $CH_2(CN)_2$ (40 mg, 0.60 mmol) was added 100 mL of ethanol and 0.10 mL of piperidine. The solution was refluxed for 2.5 h and the solvent removed under vacuum. The residue was chromatographed using CH_2Cl_2/EtOAc as eluent. The dark green powdery **26** was isolated in 83% yield (350 mg). MS (FAB): *m/e* 874 (M^+, ^{102}Ru). IR (KBr, cm^{-1}): 2214 (m), ν(C≡N), 2017 (s), ν(C≡C). ^{13}C NMR (CD_2Cl_2): δ 161.7 (t, J_{C-P} = 23.8, Ru−*C*≡C), 148.5 (s, ═*C*H), 144.4 (s, ═*C*S), 141.9 (s, ═*C*H), 137.9 (t, J_{C-P} = 21.6, C_{ipso} of PPh$_3$), 133.6 (t, J_{C-P} = 4.7, C_{ortho} of PPh$_3$), 129.5 (s, ═*C*S), 129.0 (s, C_{para} of PPh$_3$), 127.6 (t, J_{C-P} = 4.1, C_{meta} of PPh$_3$), 127.2 (s, ═*C*H), 116.3 (s, *C*N), 115.4 (s, *C*N), 114.5 (s, RuC≡*C*), 86.4 (s, C_5H_5), 68.4 (s, *C*(CN)$_2$). Anal. Calcd for $C_{51}H_{38}N_2P_2SRu$: C, 70.09; H, 4.38; N, 3.21. Found: C, 69.67; H, 4.41; N, 3.15.

Ru(C≡C-th-(*E*)-CH═CH-th-(*E*)-CH═(CN)$_2$)(PPh$_3$)$_2$(η^5-C$_5$H$_5$) (27). Complex **27** was synthesized by the same procedures as employed for **26**, except that **4** was utilized instead of **2** and the reaction time was 5 h. Dark black powdery **27** was isolated in 57% yield. MS (FAB): *m/e* 984 (M^+, ^{104}Ru). IR (KBr, cm^{-1}): 2219 (m), ν(C≡N); 2038 (s), ν(C≡C). ^{13}C NMR (CD_2Cl_2): δ 156.2 (s, ═*C*S), 149.7 (s, ═*C*H), 140.7 (s, ═*C*H), 139.5 (t, J_{C-P} = 23.9, Ru−*C*≡C), 138.5 (t, J_{C-P} = 21.6, C_{ipso} of PPh$_3$), 135.1 (s, ═*C*S), 134.5 (s, ═*C*S), 133.7 (t, J_{C-P} = 4.7, C_{ortho} of PPh$_3$), 132.5 (s, ═*C*S), 131.2 (s, ═*C*H), 128.7 (s, C_{para} of PPh$_3$), 128.6 (s, ═*C*H), 127.4 (t, J_{C-P} = 4.1, C_{meta} of PPh$_3$), 126.6 (s, ═*C*H), 125.7 (s, ═*C*H), 115.8 (s, ═*C*H), 115.0 (s, *C*N), 114.2 (s, *C*N), 109.5 (s, RuC≡*C*), 85.7 (s, C_5H_5), 73.7 (s, *C*(CN)$_2$). Anal. Calcd for $C_{57}H_{42}N_2P_2S_2Ru$: C, 69.71; H, 4.31; N, 2.85. Found: C, 69.61; H, 4.32; N, 2.76.

Table 1. Crystal Data for Compounds 7 and 26

	7	**26**
chem formula	$C_{55}H_{43}NO_2P_2SRu$	$C_{51}H_{38}N_2P_2SRu$
fw	945.03	873.95
cryst size, mm	0.38 × 0.25 × 0.25	0.11 × 0.13 × 0.38
cryst system	monoclinic	orthorhombic
space group	$P2_1/n$	$Pna2_1$
a, Å	11.111(1)	25.102(4)
b, Å	19.121(2)	16.726(2)
c, Å	21.230(3)	9.917(2)
β, deg	100.25(1)	
V, Å^3	4438.4(9)	4164(1)
Z	4	4
T, °C	+20	+20
F(000)	1944	1792
λ(Mo Kα), Å	0.7107	0.7107
ρ_{calc}, g cm^{-3}	1.414	1.394
μ, cm^{-1}	5.042	5.290
transm coeff	1.00−0.97	1.00−0.95
$2\theta_{max}$, deg	50	50
h, *k*, *l* range	−13 to 12, 0 to 22, 0 to 25	0 to 29, 0 to 19, 0 to 11
tot. reflns	8222	3881
unique reflns	7791	3881
obsd reflns ($I > n\sigma(I)$)	5103 (n = 2.5)	2737 (n = 2.0)
refined params	559	515
R^a	0.040	0.034
$R_w{}^b$	0.046	0.035
GOF(F^2)^c	1.04	1.05

^{a} $R = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$; $w = 1/[\sigma^2(F_o) + kF_o^2]$ where, k = 0.0001 for **7** and 0.0003 for **26**. ^{c} GOF $= [\sum w(|F_o| - |F_c|)^2/(n - p)]^{1/2}$, where n = no. of observed reflections and p = number of variables.

Crystallographic Studies. Crystals of **7** and **26** were grown by slow diffusion of hexane into a concentrated solution of complex **7** in CH_2Cl_2. Crystals were mounted on a glass fiber covered with epoxy. Diffraction measurements were made on an Enraf-Nonious CAD4 diffractometer by using graphite-monochromated Mo Kα radiation (λ = 0.7107 Å) with the $\theta-2\theta$ scan mode. Unit cells were determined by centering 25 reflections in the suitable 2θ range. Other relevant experimental details are listed in Table 1. The structure was solved by direct methods using NRCVAX[18] and refined using full-matrix least-squares techniques. All non-hydrogen atoms were refined with anisotropic displacement parameters, and

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Table 2. Selected Bond Distances (Å) and Angles (deg) for Complexes 7 and 26

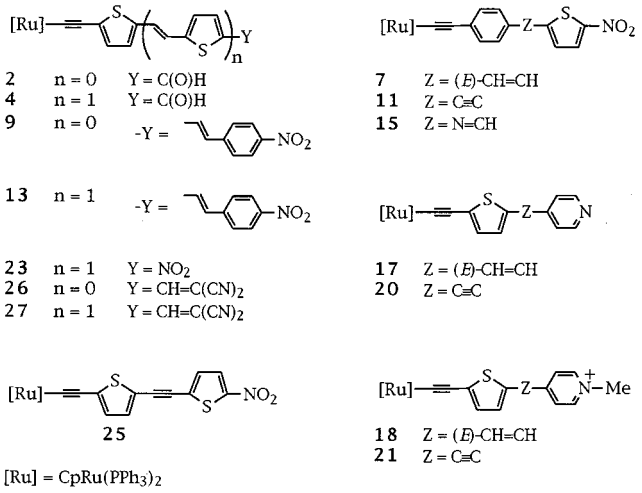
	7	26
	Distances	
Ru−C1	2.215(5)	2.213(8)
Ru−C2	2.229(5)	2.246(7)
Ru−C3	2.231(5)	2.263(7)
Ru−C4	2.234(5)	2.235(7)
Ru−C5	2.228(5)	2.216(9)
Ru−C6	2.013(5)	1.974(7)
Ru−P1	2.292(1)	2.293(2)
Ru−P2	2.282(1)	2.299(2)
C6−C7	1.190(7)	1.23(1)
C7−C8	1.438(7)	1.42(1)
C8−C9	1.394(8)	1.37(1)
C9−C10	1.376(8)	1.39(1)
C10−C11	1.402(8)	1.40(1)
C11−C12	1.379(8)	1.39(1)
C12−C13	1.369(8)	1.37(2)
C13−C8	1.391(8)	
C13−C14		1.42(2)
C13−C15		1.43(1)
C11−C14	1.476(8)	
C14−C15	1.298(9)	
C15−C16	1.471(9)	
C14−N14		1.14(2)
C15−N15		1.12(1)
C16−C17	1.343(9)	
C17−C18	1.29(1)	
C18−C19	1.30(1)	
S−C8		1.745(8)
S−C11		1.730(8)
S−C19	1.716(7)	
S−C16	1.697(6)	
N−C19	1.421(9)	
N−O1	1.22(1)	
N−O2	1.26(1)	
	Angles	
P1−Ru−P2	99.35(5)	100.84(8)
P1−Ru−C6	91.4(1)	90.4(2)
P2−Ru−C6	90.1(1)	90.6(2)
Ru−C6−C7	174.5(4)	173.7(6)
C6−C7−C8	177.4(5)	172.2(8)
C11−C12−C13		129.0(9)
C11−C14−C15	126.0(6)	
C12−C13−C14		125.4(7)
C12−C13−C15		119.3(9)
C13−C14−N14		178(1)
C13−C15−N15		180(1)
C14−C15−C16	128.6(6)	
C16−S−C19	89.5(3)	
O1−N−O2	125.7(7)	

all hydrogen atoms were placed in idealized positions. The selected interatomic distances and bond angles are given in Table 2. All other crystal data for **7** and **26** are given in the Supporting Information.

HRS Experiment. An optical parametric oscillating (OPO) laser (Continuum Mirage 500) generating 8 ns tunable laser pulses from 400 to 2000 nm with a 10 Hz repetition rate was used as the light source in the Hyper-Rayleigh scattering (HRS) experiment. Recently, HRS from some molecules excited by the 1064 nm fundamental radiation have been found to be accompanied by the two-photon absorption (TPA) induced fluorescence.[19] Consequently, the β value determined by short wavelength HRS experiment such as 1064 nm could be too large.[19c] The fundamental wavelength of excitation laser in this HRS experiment was shifted to a longer wavelength at 1560 nm to block the TPA process and obtain the correct β value. The experimental setup of long wavelength HRS experiment was the same as that of 1064 nm HRS experiment[19a,19b] except that a 1064 nm half-wave plate and a 532 nm interference filter were replaced by an achromatic half-wave plate and a 780 nm interference filter, respectively. To ensure no multiple photon absorption-induced fluorescence (MPAIF) occurs in the vicinity of second harmonic wavelength, a 820 nm interference filter was put in front on photomultiplier to check the MPAIF signal. Except for **15**, the MPAIF was found to be negligible. The errors in the measured β values were estimated to be ±15% on the basis of the largest deviation from the least-squares fitting plot of $I_{2\omega}/I_{\omega}^2$ vs the number densities of chromophores in the solution.[19a]

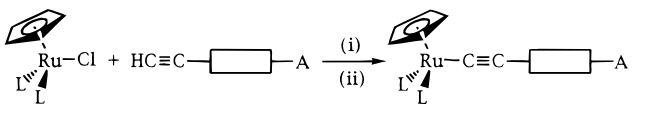
In this experiment, a solution of Disperse Red 1 (DR1) in CH_2Cl_2 was used as external reference. Using the undamped two-state model and the dispersion free β value (β_o) of DR1 in $CHCl_3$ ($\beta_o = 38 \times 10^{-30}$ esu),[20] the β value of DR1 in $CHCl_3$ was found to be 69.2×10^{-30} esu. Considering the dependence of the β value of a chromophore on the solvent with the dielectric constant ϵ (i.e., $\beta \propto (\epsilon - 1)/(2\epsilon + 1)$),[21] the β value of DR1 in CH_2Cl_2 at 1560 nm was determined to be 78.8×10^{-30} esu.[22]

Chart 1



Results and Discussion

Syntheses and Characterization of Ruthenium Complexes. Ruthenium σ-acetylides synthesized in this study are depicted in Chart 1. Most complexes were prepared from $RuCl(PPh_3)_2(\eta^5\text{-}C_5H_5)$ and the corresponding terminal alkynes according to a well-known procedure[23] (eq 1). Deterioration of dicyanovinyl moiety



(1)

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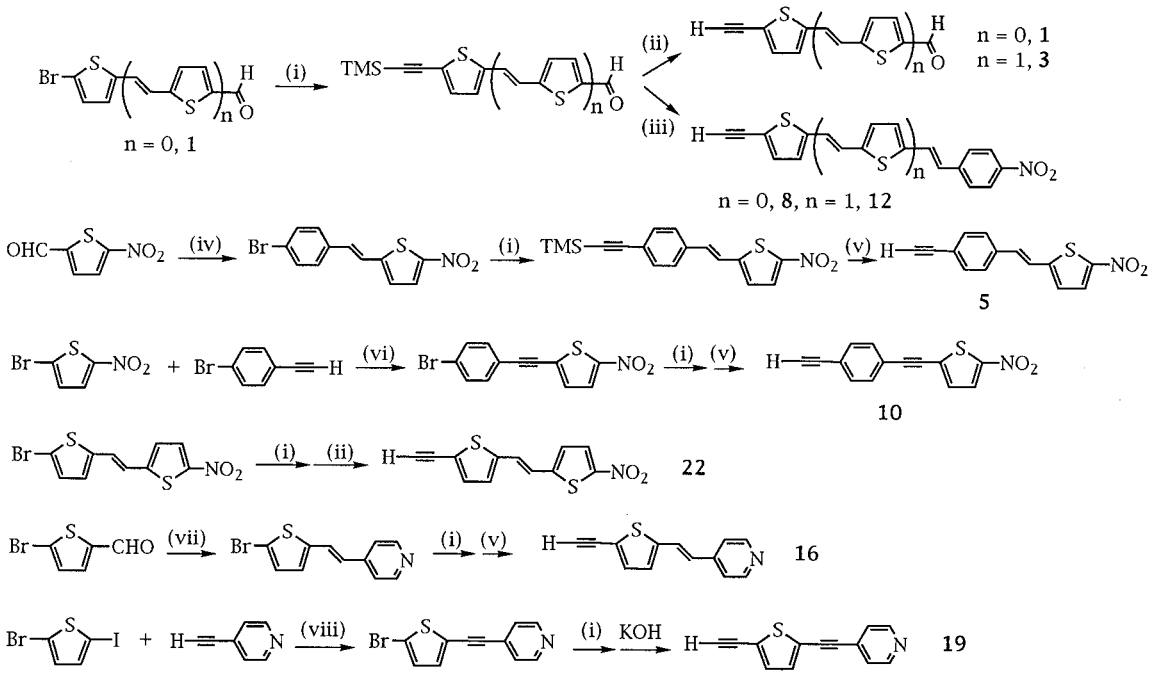
Scheme 1[a]



[a] (i) (Trimethylsilyl)acetylene, $PdCl_2(PPh_3)_2$ (2%), CuI (1%), Et_2NH; (ii) KOH/MeOH; (iii) $Ph_3PCH_2(C_6H_4)NO_2$-4, MeONa (2.2 equiv); (iv) $Ph_3PCH_2(C_6H_4)Br$-4; NaH; (v) n-$Bu_4N^+F^-$; (vi) $PdCl_2(PPh_3)_2$ (2%), CuI (1%), Et_3N, 25 °C, 10 h; (vii) γ-picoline, Ac_2O; (viii) $PdCl_2(PPh_3)_2$ (2%), CuI (1%), Et_2NH.

occurred during base treatment of vinylidenes to form σ-acetylides, therefore, complexes **26** and **27** have to be synthesized indirectly from **2** and **4**, respectively. Terminal alkynes were synthesized as described in Scheme 1. Sonogashira coupling[24] and Wittig reaction[25] were used to construct alkyne and alkene entities, respectively. Although the traditional Wittig reaction of triphenyl phosphorane frequently resulted in formation of both *E* and *Z* isomers, no attempt was made to separate the two until terminal alkynes were introduced. At the end we were able to isolate only the *E* isomers which possessed characteristic coupling constants (ca. 16 Hz) between the two trans olefinic protons. The *E* conformation of alkene moiety was preserved in the corresponding ruthenium σ-acetylides on the basis of coupling constants for olefinic protons (Table 3) and a single-crystal X-ray structural determination on **7** (vide infra). The first step in eq 1 likely provides a vinylidene intermediate,[23] although no attempt was made to isolate these intermediates in all of reactions except for **6**. The β-H atoms of complex **6** has characteristic chemical shifts at ca. 5.37 ppm and a small coupling (ca. 2.4 Hz) to two equivalent phosphorus atoms. The chemical shifts of phosphine ligands also have a more significant upfield shift (ca. 7 ppm) than those of the corresponding σ-acetylide complexes in the $^{31}P\{H\}$ NMR spectra. The chemical shifts of the C_β carbons (108.1−116.3 ppm) of the σ-acetylide complexes ($Ru-C_\alpha\equiv C_\beta$) in the $^{13}C\{H\}$ NMR spectra are insensitive to changes in acetylide ligands, whereas those of C_α (with a coupling to two equivalent phosphorus atoms) appear to be more informative. In general, a stronger electron acceptor results in downfield shift of $\delta(C_\alpha)$, and such an effect is more prominent for complexes with a shorter conjugation chain. For instance, complexes $Ru-C_\alpha\equiv C_\beta$-th=th-X exhibit $\delta(C_\alpha)$ at 130.9, 135.6, 138.2, and 139.5 ppm for X = H, CHO, NO_2, and $CH=C(CN)_2$, respectively, while complexes $Ru-C_\alpha\equiv C_\beta$-th-X have $\delta(C_\alpha)$ at 145.8, 154.5, and 161.7 ppm for X = CHO, NO_2, and $CH=C(CN)_2$, respectively. The larger upfield shift of C_α in complexes with shorter conjugation chain implies that there is more contribution of a vinylidene form in the former. Another characteristic feature of σ-acetylide complexes is the existence of a $\nu(C\equiv C)$ stretching (2061−2017 cm^{-1}) in the infrared spectra.

Optical Absorption Spectra. Table 4 illustrates the optical absorption spectra of the σ-acetylide complexes in CH_2Cl_2. A very prominent feature in these complexes is the existence of a fairly intense low-lying charge-transfer band, indicating the indispensable roles of both ruthenium moiety and the electron acceptor. For instance, upon replacement of $CpRu(PPh_3)_2$ of **23**, **25**, and **27** with H, the resulting terminal alkyne exhibits only a $\pi-\pi^*$ transition at much shorter wavelength (λ_{max} = 386, 403, and 474 nm, respectively) (Figure 1). The thiophene moiety can provide effective conjugation compared with benzenoid moieties,[26] and the important role of thiophene moiety in lowering the energy of the charge-transfer transition is also evident, i.e., λ_{max} (524 nm) of **A**[7] > λ_{max} (460 nm) of **D**,[8a] λ_{max} (526 nm) of **7** > λ_{max} (476 nm) of **B**,[8b] λ_{max} (516 nm) of **9** > λ_{max} (476 nm) of **B**, and λ_{max} (548 nm) of **15** > λ_{max} (496 nm) of **C**.[8b] The variation of λ_{max} for **7** (526 nm), **9** (516 nm), and **13** (532 nm) appears to be in agreement with a recent report[27] that placement of thiophene at the acceptor end of the molecule led to a more effective charge transfer.

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Table 3. ^{1}H and ^{31}P{H} NMR Spectral Data for the Compounds

compd	δ (ppm)[a,b] (J(Hz))	δ (ppm)[a,c] (J(Hz))
2	9.63 (s, 1 H, C*H*O), 7.52 (d, 1 H, J = 3.9, SCC*H*), .41−7.08 (m, 30 H, C_6H_5), 6.59 (d, 1 H, SCC*H*), 4.36 (s, 5 H, C_5H_5)	50.6 (s)
4	9.79 (s, 1 H, C*H*O), 7.59 (d, 1 H, J = 3.8, SCC*H*), 7.45−7.07 (m, 31 H, Ph and C*H*═), 7.02 (d, 1 H, J = 3.8, SCC*H*), 6.89 (d, 1 H, J = 3.8, SCC*H*), 6.75 (d, 1H, C*H*═), 6.48 (d, 1 H, J = 3.8, SCC*H*), 4.33 (s, 5 H, C_5H_5)	50.6 (s)
7	7.94 (d, 1 H, J = 4.5, SCC*H*), 7.50−7.10 (m, 37 H, Ph and SCC*H* 7 C*H*═), 7.21 (d, 1 H, SCC*H*), 4.36 (s, 5 H, C_5H_5)	48.6 (s)
9	8.15 (d, 2 H, J = 8.9, C_6H_4), 7.50 (d, 2 H, C_6H_4), 7.46−7.08 (m, 30 H, Ph), 7.24 (d, 1 H, J = 15.9, C*H*═), 6.93 (d, 1 H, J = 3.8, SCC*H*), 6.67 (d, 1 H, C*H*═), 6.50 (d, 1 H, SCC*H*), 4.34 (s, 5 H, C_5H_5)	50.6 (s)
11	7.99 (d, 2 H, J = 4.2, SCC*H*), 7.56−7.11 (m, 34 H, Ph), 7.32 (d, 2 H, SCC*H*), 4.42 (s, 5 H, C_5H_5)	48.5 (s)
13	8.18 (d, 2 H, J = 8.8, C_6H_4), 7.53 (d, 2 H, C_6H_4), 7.47−7.08 (m, 30 H, Ph), 7.30 (d, 1 H, J = 15.9, C*H*═), 7.00 (d, 1 H, J = 3.8, SCC*H*), 6.97 (d, 1 H, J = 15.7, C*H*═), 6.87 (d, 1 H, J = 3.8, SCC*H*), 6.83 (d, 1 H, J = 15.9, C*H*═), 6.82 (d, 1 H, J = 3.7, SCC*H*), 6.76 (d, 1 H, J = 15.7, C*H*═), 6.49 (d, 1 H, J = 3.7, SCC*H*), 4.33 (s, 5 H, C_5H_5)	50.6 (s)
15	8.87 (s, 1 H, N═C*H*), 8.06 (d, 1 H, J = 4.3, SCC*H*), 7.62 (d, 1 H, SCC*H*), 7.55−7.13 (m, 34 H, C_6H_4 and Ph), 4.36 (s, 5 H, C_5H_5)	55.7 (s)
17	8.45 (d, 2 H, J = 6.0, NC*H*), 7.53 (d, 1 H, J = 15.9, C*H*═), 7.50−7.15 (m, 30 H, Ph), 7.41 (d, 2 H, NCHC*H*), 6.99 (d, 1 H, J = 3.9, SCC*H*), 6.50 (d, 1 H, SCC*H*), 4.36 (s, 5 H, C_5H_5)	48.3 (s)
18	8.69 (d, 2 H, J = 6.6, NC*H*), 8.07 (d, 2 H, NCHC*H*), 8.03 (d, 1 H, J = 15.6, C*H*═), 7.44−7.16 (m, 31 H, Ph and SCC*H*), 6.83 (d, 1 H, C*H*═), 6.60 (d, 1 H, J = 3.6, SCC*H*), 4.42 (s, 5 H, C_5H_5), 4.40 (s, 3 H, C*H*$_3$)	48.1 (s, 2 P, Ru*P*), −145 (heptet, 1 P, J_{P-F} = 702, *P*F$_6$)
20	8.56 (d, 2 H, J = 6.3, NC*H*), 7.48−7.10 (m, 31 H, Ph and SCC*H*), 7.38 (d, 2 H, NCHC*H*), 6.51 (d, 1 H, J = 3.9, SCC*H*), 4.38 (s, 5 H, C_5H_5)	48.2 (s)
21	8.93 (d, 2 H, J = 6.9, NC*H*), 7.69 (d, 2 H, NCHC*H*), 7.39−7.08 (m, 31 H, Ph and SCC*H*), 6.52 (d, 1 H, J = 4.2, SCC*H*), 4.51 (s, 3 H, C*H*$_3$), 4.36 (s, 5 H, C_5H_5)	48.1 (s, 2 P, Ru*P*), −145 (heptet, 1 P, J_{P-F} = 702, *P*F$_6$)
23	7.92 (d, 1 H, J = 4.3, SCC*H*), 7.49−7.12 (m, 32 H, Ph, C*H*═, and SCC*H*), 7.10 (d, 1 H, J = 3.8, SCC*H*), 6.88 (d, 1 H, J = 15.4, C*H*═), 6.53 (d, 1 H, J = 3.8, SCC*H*), 4.38 (s, 5 H, C_5H_5)	48.2 (s)
25	7.99 (d, 1 H, J = 4.4, SCC*H*), 7.50−7.16 (m, 32 H, Ph and SCC*H*), 6.54 (d, 1 H, J = 3.9, SCC*H*), 4.39 (s, 5 H, C_5H_5)	48.2 (s)
26	7.99 (s, 1 H, C*H*═C(CN)$_2$), 7.72 (d, 1 H, J = 4.1, SCC*H*), 7.43−7.19 (m, 20 H, Ph), 6.69 (d, 1 H, SCC*H*), 4.49 (s, 5 H, C_5H_5)	48.0 (s)
27	8.26 (s, 1 H, C*H*═C(CN)$_2$), 7.82 (d, 1 H, J = 4.1, SCC*H*), 7.49−7.16 (m, 32 H, C*H*═, SCC*H*, and Ph), 7.34 (d, SCC*H*), 6.99 (d, 1 H, J = 15.8, SCC*H*), 6.54 (d, 1 H, SCC*H*), 4.39 (s, 5 H, C_5H_5)	

[a] Compounds **2**−**13** and **21** were measured in $CDCl_3$ solution; others were measured in acetone-d_6. [b] Reported in ppm relative to δ(Me_4Si) 0 ppm. [c] Reported in ppm relative to δ(85% H_3PO_4) 0 ppm. Abbreviations: s = singlet, d = doublet, t = triplet, m = multiplet.

Table 4. Electronic Absorption Spectral Data for the Compounds [λ_{max} nm ($10^{-4}\epsilon$)][a]

compd	CH_2Cl_2	THF
2	438 (2.86)	426 (2.61)
4	517 (4.11)	510 (3.88)
7	533 (2.42)	526 (2.41)
9	522 (3.37)	516 (3.20)
11	505 (1.98)	495 (2.01)
13	536 (4.47)	532 (4.18)
15	562 (1.27)	548 (0.74)
17	455 (3.56)	451 (3.79)
18	659 (5.09)	578 (>2.45)
20	435 (2.88)	431 (2.43)
21	622 (2.63)	550 (3.20)
23	588 (2.79)	577 (3.10)
25	552 (3.10)	542 (1.78)
26	562 (4.76)	551 (5.98)
27	638 (4.91)	622 (6.02)
A	531 (3.39)	524 (2.48)
B	478 (2.91)	476 (3.0)
C		496 (1.4)
D		460 (4.0)

[a] **A** = Ru(C≡C-th-NO_2)(PPh_3)$_2$(η^5-C_5H_5), **B** = Ru(C≡CC_6H_4CH═CHC$_6H_4$$NO_2$-4)($PPh_3$)$_2$($\eta^5$-$C_5H_5$), **C** = Ru(C≡C$C_6H_4$N═C$HC_6H_4$$NO_2$-4)($PPh_3$)$_2$($\eta^5$-$C_5H_5$), and **D** = Ru(C≡C$C_6H_4$$NO_2$−4)($PPh_3$)$_2$($\eta^5$-$C_5H_5$).

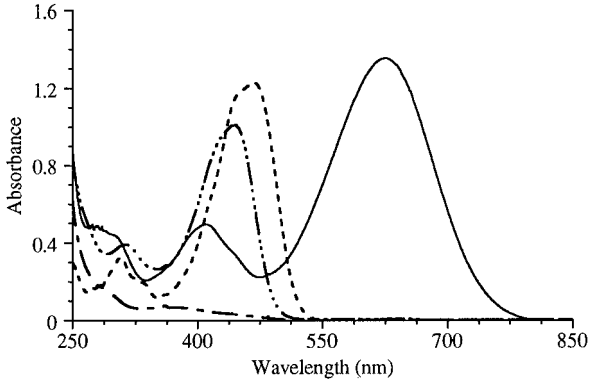

Figure 1. Electronic spectra (2.5×10^{-5} M in CH_2Cl_2) of compounds Ru(C≡C-th-(*E*)-CH═CH-th-(*E*)-CH═(CN)$_2$)(PPh_3)$_2$(η^5-C_5H_5) (**27**) (—), HC≡C-th-(*E*)-CH═CH-th-(*E*)-CH═(CN)$_2$ (- - -), Ru(C≡C-th-(*E*)-CH═CH-th)(PPh_3)$_2$(η^5-C_5H_5): (— - - -), and RuCl(PPh_3)$_2$(η^5-C_5H_5) (— -).

Other trends appear to be normal: (a) The λ_{max} of the charge-transfer band is found to increase in accordance with the order of electron accepting ability, aldehyde < nitro < dicyanovinyl < *N*-methylpyridinium.[4a,28] (b) In homologues which have thiophenes as the only aromatic ring in the conjugation chain, elongation of the conjugation length results in a decrease in the energy of the charge-transfer band.[29] (c) Replacement of an alkene moiety by an alkyne moiety diminishes the charge-transfer absorption wavelength due to the mismatch of a phenyl (or thienyl) p orbital and an alkynyl p orbital in energy.[30] Similar to literature reports,[8b,31] replace-

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Table 5. Redox Potentials for Complexes in CH_2Cl_2 at 298 K[a]

complex	E_{ox} (ΔE_p)/Ru(+2/+3)	E_{red} (ΔE_p)[b]
2	+0.11 (92)	>−2.0
4	−0.08 (91), +0.54 (92)	−1.96 (i)
7[b]	+0.02 (80)	−1.39 (103)
9	−0.06 (94)	−1.58 (85)
11	+0.07 (86)	−1.35 (99)
13	−0.13 (92), +0.34 (78)	−1.53 (114)
15	+0.002 (85)	−1.29 (115)
17	−0.018 (i)	>−2.0
18	+0.018 (94)	−1.41 (137))
20	−0.05 (74)	>−2.0
21	+0.15 (103)	−1.44 (i)
23	−0.06 (95), +0.51 (91)	−1.40 (91)
25	+0.03 (93), +0.64 (76)	−1.34 (104)
26	+0.18 (88)	−1.79 (i)
27	−0.06 (91), +0.52 (97)	−1.67 (i)
A	+0.22 (96)	−1.62 (98)
B	+0.01 (88)	−1.56 (100)

[a] Analyses were performed in 10^{-3} M deoxygenated CH_2Cl_2 solutions containing 0.1 M TBAP; scan rate is 60 mV. All potentials in V vs ferrocene (0.00 V with peak separation of 105 mV in CH_2Cl_2); scan range +0.4 to −2.0 V; i = irreversible process. [b] $\Delta E_p = E_{pa} - E_{pc}$, mV.

ment of an alkene entity in the conjugation chain of ruthenium complexes by an imine entity resulted in a decrease in the charge-transfer energy, i.e., **7** (533 nm) vs **15** (562 nm). However, the significantly lower oscillator strength of the charge-transfer transition in **15** ($f = 0.34$ vs $f = 0.60$ for **7**) may be detrimental to the quadratic optical nonlinearity.

Electrochemistry. On the basis of theoretical calculations,[32] the HOMO of Ru(C≡CR)$(PH_3)_2(\eta^5$-$C_5H_5)$ (R = H, C_6H_5, C_6H_4-4-NO_2) is a metal-centered orbital mixed with the π and π^* of the alkyne moiety. Therefore, the oxidation potentials of ruthenium metals in these complexes and analogues should change as the σ-acetylide substituent varies. The oxidation potentials of Ru(II)/Ru(III) (Table 5) for the complexes in this study were found to be reversible except for **17**. The oxidation potential, Ru(II)/Ru(III), decreases as the conjugation length increases, i.e., **2** (+0.11 V) vs **4** (−0.08 V), **9** (−0.06 V) vs **13** (−0.13 V), and **26** (+0.18 V) vs **27** (−0.06 V). This observation is analogous to what has been reported for $Cp_2Fe[C{\equiv}CC_6H_4]_nSO_2Me$,[33] bimetallic sesquifuvalene complexes,[34] ruthenium σ-acetylide complexes,[7] and nickel σ-acetylide complexes.[35] In the same report[32] the ionization potential of Ru(C≡CC_6H_4-4-NO_2)-$(PH_3)_2(\eta^5$-$C_5H_5)$ was also calculated to be higher than that of Ru(C≡CC_6H_5)$(PH_3)_2(\eta^5$-$C_5H_5)$. Previously Humphrey[8a] and we[7] found that a better electron acceptor raised the oxidation potential of the ruthenium atom in ruthenium σ-acetylides. Complexes in this study

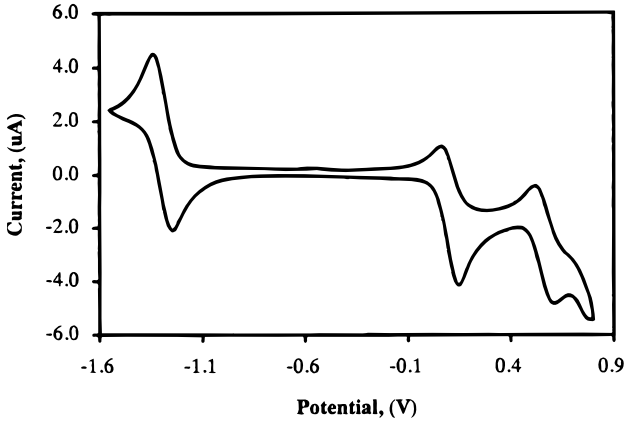

Figure 2. Cyclic voltammogram of compound **13** in CH_2Cl_2 containing 0.1 M TBAP at 25 °C. Potentials are in V versus Ag/$AgNO_3$ (0.01 M in MeCN; scan rate 60 mV s^{-1}).

were found to have a similar trend; however, the effect is more prominent for complexes with a shorter conjugation chain. For instance, **2** (+0.11 V) vs **26** (+0.18 V) and Ru(C≡C-th-NO_2)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (**A**) (+0.22 V),[7] **20** (−0.05 V) vs **21** (+0.15 V), and Ru(C≡C-th-(*E*)-CH=CH-th-Br)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (−0.13 V)[33] vs **4** (−0.08 V), **23** (−0.06 V), and **27** (−0.06 V). All complexes with a nitro substituent have fully reversible reductive waves within the −1.29 to −1.60 V range, which can be assigned to reduction of the nitro substituent.[8a] The corresponding terminal alkynes have such reversible reduction waves appearing at somewhat lower reduction potentials (−1.36 V of **22** vs −1.40 V of **23**; −1.30 V of **24** vs −1.34 V of **25**), whereas no such reduction waves were observed in complexes without a nitro substituent, such as Ru(C≡C-th-(*E*)-CH=CH-th-Y)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (Y = H, Br).[36] The cyclic voltammogram of **13** is shown in Figure 2. It is interesting to note that complexes with two thienyl rings have a second reversible oxidation wave, which is tentatively assigned as the oxidation potential of Ru(III)/Ru(IV). This oxidation wave is not observed in the corresponding terminal alkynes or (*E*)-1-(5-ferrocenylethynyl-2-thienyl)-2-(5-nitro-2-thienyl)-ethylene. We suspect that sulfur atoms in the thiophene rings help to stabilize the ruthenium metal center after removal of two electrons.

NLO Measurements. Hyper-Rayleigh scattering (HRS) experiments were performed on complexes **7**, **9**, **11**, **13**, **15**, **A**, and **H** using an optical parametric oscillating (OPO) laser source of wavelength 1560 nm (see Experimental Section). The first hyperpolarizabilities (β, 10^{-30} esu, ±15%) obtained for **7**, **9**, **11**, **13**, **15**, **A**, and **H** are 294, 333, 210, 419, 308, 89, and 186, respectively. The calculated static hyperpolarizabilities (β_0, 10^{-30} esu)[37] are 138 (**7**), 163 (**9**), 109 (**11**), 195 (**13**), and 129 (**15**), 42 (**A**), and 105 (**H**). The β_0 value for Ru((*E*)-4,4′−C≡CC_6H_4CH=CH$C_6H_4NO_2$)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (**H**)[8b] in this study was lower than that measured at 1064 nm, possibly due to the use of different solvents and inadequacy of the undamped two-state model. Thiophene rings were superior to benzene rings in enhancing the molecular nonlinearity of organic chromophores.[38] In this study, we found that incorporation

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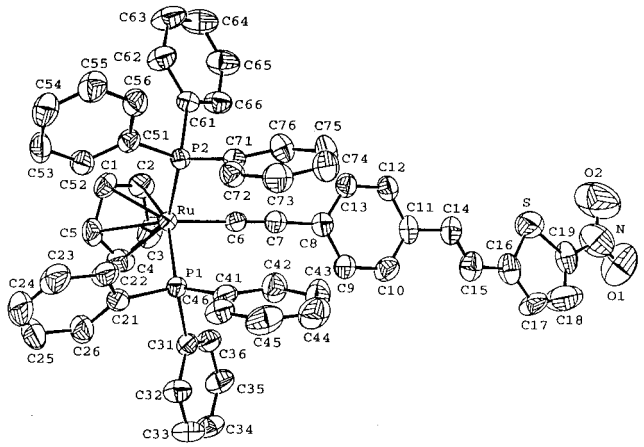

Figure 3. ORTEP drawing of complex **7**. Thermal ellipsoids are drawn with 50% probability boundaries.

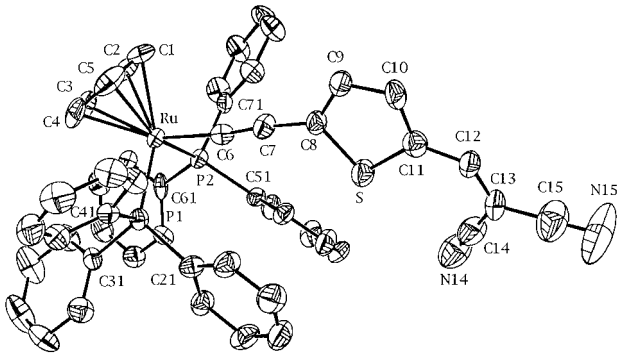

Figure 4. ORTEP drawing of complex **26**. Thermal ellipsoids are drawn with 50% probability boundaries.

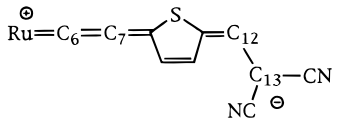

Figure 5. Charge-separated canonical resonance form of complex **26**.

of thiophene rings in the conjugating bridges was also beneficial for second-order optical nonlinearity of ruthenium σ-acetylides. For instance, replacement of either of the benzene ring in **H** by thiophene ring results in formation of **7** or **9**, which has higher first hyperpolarizability. It was reported that thiophene leads to a larger β values more effectively at the acceptor end;[27] we did not find similar trend in this study. It is worth noting that complex **11** has a β_0 value comparable to that of **H** despite the presence of a thienyl moiety in the former. Apparently, mismatch of a phenyl p orbital and an alkynyl p orbital in energy results in diminishing the effect of thiophene ring for efficient charge transfer.[29b,30] Elongation of the conjugation chain is an efficient route for enhancement of first hyperpolarizability as long as saturation does not occur.[38] Our results in this study fulfill this trend, e.g., **A** < **H** or **7** and **9** < **13**. Despite the contribution of multiple photon absorption-induced fluorescence to the first hyperpolarizability of **15**, which was not deducted, the β_0 value of **15** is still lower than that of **7**. This observation may be attributed to the significantly smaller oscillator strength of the charge-transfer transition in **15**. This is in agreement with Humphrey's report on **H** and Ru((*E*)-4,4′-C≡CC_6H_4N═$CHC_6H_4NO_2$)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (β_0 = 86 × 10^{-30} esu).[8b] In view of the highly intense charge-transfer absorption with low transition energy for some complexes such as **18**, **21**, and **27**, one can be optimistic that excellent optical nonlinearity is achievable for ruthenium σ-acetylides containing the thienyl moiety. Certainly, use of OPO laser source with even longer wavelength than 1560 nm is necessary to probe off-resonance nonlinearity of such complexes. A more comprehensive investigation on optical nonlinearity of complexes in this study and congener should be useful in molecular engineering and will be the subject of future publication. Syntheses of other organometallic thienyl chromophores aiming at greater transparency in the visible spectrum are also in progress.

Molecular Structures of Ru(C≡CC_6H_5-(*E*)-CH═CH-th-NO_2)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (7) and Ru(C≡C-th-CH═C$(CN)_2$)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (26). ORTEP drawings of **7** and **26** are shown in Figures 3 and 4, respectively. Ru−C6 (**7**, 2.013(5) Å; **26**, 1.974(7) Å), C6≡C7 (**7**, 1.190(7) Å; **26**, 1.23(1) Å), and C7−C8 (**7**, 1.438(7) Å; **26**, 1.42(1) Å) distances all fall within the range observed for related ruthenium(II) σ-acetylide complexes.[39] The extent to which the acetylide participates in metal-to-ligand back-bonding is in general difficult to be addressed from the structural data because of the relative insensitivity of both metal−C and C≡C bond lengths to small changes in populations of the π or π* orbitals.[39] Nevertheless, complex **26** was found to have a shorter Ru−C6 distance and a longer C6≡C7 distance than that observed for Ru(C≡CPh)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (Ru−C, 2.017(5) Å; C≡C, 1.1214(7) Å),[8a] Ru(C≡$CC_6H_4NO_2$-4)$(PPh_3)_2(\eta^5$-$C_5H_5)$ (Ru−C, 1.994(5) Å; C≡C, 1.202(8) Å),[8a] and **H** (Ru−C, 2.008(6) Å; C≡C, 1.199(7) Å).[8b] It is noteworthy that the latter three complexes possess shorter Ru−C and longer C≡C distances than other available ruthenium σ-acetylides.[8a] We believe that there is an important contribution of the charge-separated vinylidene form (Figure 5) to the ground state of **26**, on the basis of these observations together with the following structural data: (1) C7−C8 (1.42(1) Å) and C11−C12 (1.39(1) Å) distances are somewhat short compared to C_{sp}−C_{sp^2} (1.43 Å) and C_{sp^2}−C_{sp^2} (1.48 Å),[40] respectively. (2) The olefinic C12−C13 (1.37(2) Å) distance is significantly longer than that of a normal C_{sp^2}═C_{sp^2} (1.32 Å).[40] Other supporting evidence for charge-separated character of **26** include: (1) low C≡C stretching frequency ($\nu_{C\equiv C}$ = 2017 cm^{-1}) among ruthenium σ-acetylides;[39] (2) very downfield shift of C_α (δ = 161.7 ppm) in ^{13}C NMR spectra; (3) upfield shift of dicyanomethine carbon ($C(CN)_2$) (δ = 68.4 ppm) compared to that in thiophene-2-ylmethylene malononitrile (δ = 75.9 ppm).[41]

There is interesting dissimilarity in structure between **7** and **26**, i.e., the relative orientation of the arylacetylide (or thienylacetylide) plane to the plane σ_v, defined as the plane perpendicular to the plane P−Ru−P and bisecting angle P−Ru−P. The phenylacetylide plane of

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7 is nearly perpendicular to σ_v, whereas the thienylacetylide plane of **26** is almost parallel to σ_v. The relative orientation of arylacetylide to the metal coordination sphere in **26** is the same as that observed for $Ru(C{\equiv}CC_6H_4NO_2\text{-}4)(L)_2(\eta^5\text{-}C_5H_5)$ (L = PMe_3, PPh_3).[8a] Although such a conformation is slightly beneficial for first hyperpolarizability as pointed out by a theoretical calculation on $Ru(C{\equiv}CC_6H_4NO_2\text{-}4)(L)_2(\eta^5\text{-}C_5H_5)$,[8a] it is uncertain whether the conformation retains in solution.

Other important structural features for **7** and **26** include the linearity of Ru−C6−C7−C8 (**7**, Ru−C6−C7 angle, 174.5(4)°, and C6−C7−C8 angle, 177.4(5)°; **26**, Ru−C6−C7 angle, 173.7(6)°, and C6−C7−C8 angle, 172.2(8)°) and the *E* conformation of the olefin (C14)H═(C15)H (C11−C14−C15 angle, 126.0(6)°; C14−C15−C16 angle, 128.6(6)°) in **7**. The slight deviation of the benzene ring and the thiophene ring in **7**, or the thiophene ring and the dicyanovinyl plane in **26**, from coplanarity (dihedral angle: **7**, 10.8(3)°; **26**, 15.5(3)°) is possibly due to the crystal packing forces.

Conclusion

We synthesized the first series of organometallic second-order nonlinear optical chromophores which incorporate a thiophene moiety in the conjugation chain. These complexes were found to possess promising quadratic hyperpolarizabilities determined from hyper-Rayleigh scattering (HRS) experiments using an OPO laser source.

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Supporting Information Available: Tables of atomic coordinates (including hydrogen atoms), thermal parameters, and bond distances and angles and stereoviews for complexes **7** and **26** (23 pages). Ordering information is given on any current masthead page.

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