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Hydridotris(3,5-dimethylpyrazolyl)borate Tungsten Alkyne Complexes for Nonlinear Optics

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Deprotonation of the propargyl site of racemic or enantiomerically pure Tp′(CO)IW($C_6H_5C{\equiv}CCH_3$) (Tp′= hydridotris(3,5-dimethylpyrazolyl)borate) yields an η^2-allenyl anion which has been reacted with a series of aldehydes and ketones possessing electron-donating substituents. Elimination under either acidic or basic conditions generates chiral trans conjugated enynes. Characterization has been accomplished by NMR, IR, UV−vis, and elemental analysis. Additionally, X-ray diffraction has been used to structurally characterize racemic Tp′(CO)IW($C_6H_5C{\equiv}CC\underline{H}{=}C(CH_3)C_5H_4FeC_5H_5$). The structural analysis reveals a centrosymmetric space group ($P\bar{1}$); cell dimensions of $a = 10.690(5)$ Å, $b = 13.360(7)$ Å, $c = 15.392(7)$ Å, $\alpha = 92.57(6)°$, $\beta = 101.70(5)°$, and $\gamma = 100.97(4)°$; Z = 2 molecules/unit cell; and $R_w = 4.7\%$ and $R = 3.9\%$. Second harmonic generation of the enynes has been measured by the Kurtz powder technique.

Introduction

Efforts to use organometallic complexes for nonlinear optics (NLO) have been expanding steadily since the first reports in the late 1980s.[1,2] Two reviews of organometallic complexes for NLO[3,4] indicate that responses in many cases have been disappointing due to the inability to produce noncentrosymmetric media.[5] An excellent full paper and a review of the calculational aspects of NLO[7] by Kanis et al. have addressed reasons for the lack of response for organometallics. In systems where an electron-rich metal fragment is strongly coupled to an electron acceptor, adequate asymmetry is frequently not achieved at the metal center. Limited asymmetry means that insufficient polarization will result upon interaction with the incident light, and therefore only moderate responses will be possible. In the less common role of the metal functioning as an electron acceptor, again, a highly asymmetric metal center is required for substantive NLO effects.

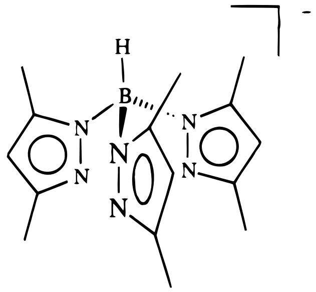

Figure 1. Tp′ structural representation.

Difficulties arise from the very characteristics which make organometallics attractive for NLO applications: intense, low-energy electronic transitions. An intense linear interaction with light may hint toward an intense nonlinear interaction with light. Since the NLO effect is a nonresonant phenomenon, a window in the visible spectrum is necessary in order to avoid absorption of either incident or propagating radiation.[8]

The goal of this research was to synthesize organometallic complexes for second-order NLO measurements. With the donor and acceptor linked by a conjugated organic bridge, significant distance for polarization can be accomplished. In this work, a chiral center is provided not by an organic substituent, but by the metal acceptor. Air and water stability make NLO studies more convenient.

Hydridotris(3,5-dimethylpyrazolyl)borate (Tp′, Figure 1) tungsten alkyne complexes, Tp′(CO)(I)W($RC{\equiv}CCH_2R'$) are formally 16-electron complexes.[9] However, if donation from the alkyne π parallel and also π perpendicular orbitals is included, the complexes are 18-electron species.[10,11] Regardless of the electron-counting formal-

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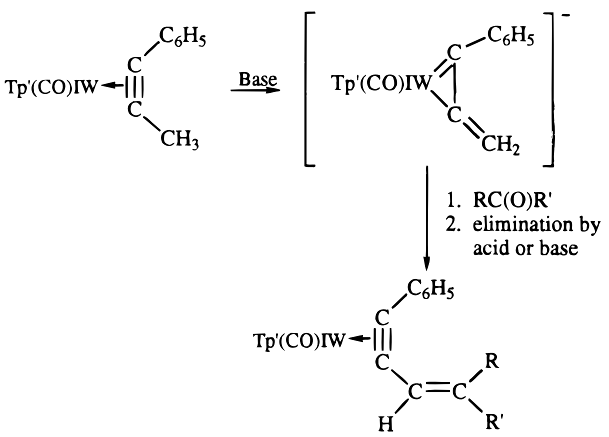
Scheme 1



ism employed, these monomers possess a relatively low-lying LUMO, which suggests that the metal could function as an electron acceptor. Furthermore, the Tp′(CO)(I)W($C_6H_5C{\equiv}CCH_3$) complex can be produced enantiomerically pure.[12]

In this report we describe the synthesis of Tp′ tungsten enyne complexes as racemic mixtures and as enantiomerically pure materials. The anionic η^2-allenyl intermediate formed by deprotonation of the neutral tungsten alkyne complex[11] was used to attack aldehydes and a ketone. Elimination of water from these complexes generates a series of enynes in which an electron donating group is in conjugation with the Tp′(CO)I W metal fragment (Scheme 1).

The Kurtz powder technique[13] was employed to measure the second order harmonic response of these enyne complexes in both racemic and single enantiomer solids.

Experimental Section

Materials and Methods. All reactions were performed under purified nitrogen using standard Schlenk techniques. Tetrahydrofuran (THF) and hexanes were distilled from potassium benzophenone ketyl; methylene chloride was distilled from phosphorus pentoxide. All other solvents were purged with nitrogen before use. Acetylferrocene[14] and formylferrocene[15] were prepared by literature methods. *p*-Anisaldehyde was stored over 4 Å sieves under nitrogen. 4-(Dimethylamino)benzaldehyde was crystallized from CH_2Cl_2 and hexanes and stored in the dark. Tp′W(CO)(I)($C_6H_5C{\equiv}CCH_3$)[9] and (−)-Tp′W(CO)(I)($C_6H_5C{\equiv}CCH_3$)[11] were prepared by literature methods. All other reagents were purchased and used without purification.

Infrared spectra were obtained with a Mattson Polaris FT IR as THF solutions in 0.10-mm calcium fluoride cells. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 400 (400 MHz) spectrometer. UV−vis spectra were recorded on a Perkin-Elmer Lambda-6 spectrometer. All analyses were performed by Atlantic Microlab of Norcross, GA.

Tp′W(CO)(I)($C_6H_5C{\equiv}CCH_2CH(OH)$(*p*-$C_6H_4OCH_3$)) (1). To a THF solution of Tp′W(CO)(I)($C_6H_5C{\equiv}CCH_3$) (1.00 g, 1.33 mmol) cooled in a dry ice/2-propanol bath to −78 °C, butyllithium (0.90 mL, 2.25 mmol) in hexane solution was added. The solution color quickly changed from green to red-brown. *p*-Anisaldehyde (*p*-HC(O)$C_6H_4OCH_3$, 0.30 mL, 2.63 mmol) was added via syringe, and immediately the solution color changed back to green. The reaction mixture was allowed to warm to room temperature, and then it was quenched with dilute aqueous HCl. All solvent was removed by rotary evaporation. The green solid which remained was dissolved in CH_2Cl_2 and then chromatographed on alumina. Starting material was first eluted with CH_2Cl_2; product was then eluted with THF. Solvent was removed and the solid was crystallized from CH_2Cl_2 and hexanes to yield bright green crystals (0.78 g, 66%). IR (THF) 1917 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 7.56−6.30 (9H, m, C_6H_5, *p*-$C_6H_4OCH_3$); 5.93, 5.90, 5.69 (1H each, s, Tp′C*H*); 5.21 (1H, m, $^3J_{HH}$ = 2.4 Hz, $^3J_{HH}$ = 4.4 Hz, $^3J_{HH}$ = 8.0 Hz, CH_2CH(OH)); 4.69 (1H, dd, $^3J_{HH}$ = 4.4 Hz, $^2J_{HH}$ = 12.4 Hz), 4.31 ($^3J_{HH}$ = 8.0 Hz, $^2J_{HH}$ = 12.4 Hz) (C*H*$_2$CH(OH)); 3.82 (3H, s, *p*-C_6H_4-OC*H*$_3$); 3.01 (1H, d, $^3J_{HH}$ = 2.4 Hz, CH_2CH (O*H*)); 2.94, 2.61, 2.52, 2.40, 1.73, 1.30 (3H each, s, Tp′CH_3). ^{13}C NMR (CH_2Cl_2) δ 232.5 (s, *C*O); 211.3, 206.1 (2 s, *C*≡*C*); 159.7, 155.7, 155.4, 150.1, 146.3, 145.8 (6 s, Tp′*C*CH_3); 144.6, 137.4, 136.5, 129.2, 128.9, 126.7, 127.6, 114.2 (*C*$_6$H$_5$, *C*$_6$H$_4$OCH$_3$); 108.9, 108.5, 107.4 (s, Tp′*C*H); 73.7 (s,CH_2*C*H(OH)); 47.6 (s, *C*H$_2$CH(OH)); 55.7 (s, *p*-C_6H_4O*C*H$_3$); 18.7, 18.3, 16.4, 13.0, 12.9 (Tp′*C*H$_3$). Anal. Calcd for $WC_{33}H_{38}N_6BO_3I$: C, 44.72; H, 4.09; N, 9.48. Found: C, 44.61; H, 4.40; N, 9.22.

Tp′W(CO)(I)($C_6H_5C{\equiv}CCH{=}CH$(*p*-$C_6H_4OCH_3$)) (2). To a THF solution of Tp′W(CO)(I)($C_6H_5C{\equiv}CCH_3$) (1.00 g, 1.33 mmol) at −78 °C in a dry ice/2-propanol bath, butyllithium (0.90 mL, 2.25 mmol) in hexane solution was added. The solution color quickly changed from green to red-brown. *p*-Anisaldehyde (*p*-HC(O)$C_6H_4OCH_3$, 0.30 mL, 2.63 mmol) was added via syringe. The solution was allowed to warm to room temperature, and then it was stirred overnight. Under positive N_2 pressure potassium-*tert*-butoxide (0.20 g, 1.78 mmol) was added. The solution color changed from green to brown. The solvent was removed by rotary evaporation. The residual brown tar was taken up in a minimum amount of CH_2Cl_2, and then it was chromatographed on alumina. The product was eluted with a 1/2 hexanes/CH_2Cl_2 mixture. Solvent was removed, and the product was crystallized from CH_2Cl_2 and hexanes to yield brown microcrystals (0.52 g, 45%). IR (THF) 1907 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 8.18 (1H, d, $^3J_{HH}$ = 16.0 Hz, CC*H* =CH(*p*-$C_6H_4OCH_3$)); 7.75 (1H, d, $^3J_{HH}$ = 16.0 Hz, CCH=C*H*(*p*-$C_6H_4OCH_3$)); 7.72−6.70 (9H, m, C_6H_5, *p*-C_6H_4-OCH$_3$); 5.92, 5.85, 5.74 (1H each, s, Tp′C*H*); 3.87 (3H, s, OC*H*$_3$); 2.94, 2.61, 2.56, 2.34, 1.70, 1.44 (3H each, s, Tp′C*H*$_3$). ^{13}C NMR (CD_2Cl_2) δ 234.7 ($^1J_{WC}$ = 144 Hz, *C*O); 212.2 ($^1J_{WC}$ = 56 Hz, C_6H_5*C*≡C); 198.5 ($^1J_{WC}$ = 14 Hz, $C_6H_5C{\equiv}$*C*); 161.4, 155.5, 155.2, 150.9, 146.1, 145.7 (s, Tp′*C*CH_3); 141.0 ($^1J_{HC}$ = 150 Hz), 122.8 ($^1J_{HC}$ = 159 Hz, *C*H=*C*H); 144.5, 138.7, 129.9, 129.0, 128.9, 128.7, 114.8 (*C*$_6$H$_5$, *p*-*C*$_6$H$_4$OCH$_3$); 108.7, 108.4, 107.4 (s, Tp′*C*H); 55.8 (s, O*C*H$_3$); 18.7, 18.3, 16.7, 13.1, 12.8 (Tp′*C*H$_3$). Anal. Calcd for $WC_{33}H_{36}N_6BO_2I$: C, 45.55; H, 4.17; N , 9.66. Found: C, 45.67; H, 4.15; N, 9.69. UV−vis (THF) λ = 491 nm, ϵ = 950 mL/(g cm); λ = 703 nm , ϵ = 170 mL/(g cm).

Conversion of Tp′W(CO)(I)($C_6H_5C{\equiv}CCH_2CH(OH)$(*p*-$C_6H_4OCH_3$) (1) to Tp′W(CO)(I)($C_6H_5C{\equiv}CCH{=}CH$(*p*-$C_6H_4OCH_3$)) (2). To a THF solution of Tp′W(CO)(I)(C_6H_5-$C{\equiv}CCH_2CH(OH)$(*p*-$C_6H_4OCH_3$)) (0.19 g, 0.21 mmol) at room temperature, potassium *tert*-butoxide (0.10 g, 0.89 mmol) was added under positive nitrogen pressure. The solution color changed quickly from green to brown. The solution was stirred for 30 min, and then the solvent was removed by rotary evaporation. The brown tar was dissolved in a minimum amount of CH_2Cl_2 and chromatographed on alumina. The product was eluted with CH_2Cl_2. The solvent was removed, and the solid was crystallized from CH_2Cl_2 and hexanes to yield brown microcrystals (0.14 g, 78%).

Tp′W(CO)(I)($C_6H_5C{\equiv}CCH_2CH(OH)$(*p*-$C_6H_4N(CH_3)_2$)) (3). To a THF solution of Tp′W(CO)(I)($C_6H_5C{\equiv}CCH_3$) (0.95 g, 1.26 mmol) at −78 °C in a dry ice/2-propanol bath, butyllithium (0.80 mL, 2.00 mmol) in hexane solution was added. A THF solution of 4-(dimethylamino)benzaldehyde (0.30 g, 2.20 mmol) was added via cannula. The solution rapidly turned green and the reaction solution was allowed to warm to room temperature. Aqueous dilute HCl was added to quench the reaction.

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Solvent was removed by rotary evaporation. The resulting green tar was dissolved in CH_2Cl_2, chromatographed on alumina, and eluted with CH_2Cl_2. Crystallization from CH_2Cl_2 and hexanes yielded dark green crystals (0.70 g, 61%). IR (THF) 1913 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 7.49−6.29 (9H, m, C_6H_5, p-$C_6H_4N(CH_3)_2$); 5.92, 5.89, 5.68 (1H each, s, Tp′C*H*); 5.16 (1H, dd, $^3J_{HH} = 4.4$ Hz, $^3J_{HH} = 8.0$ Hz, $CH_2CH(OH)$); 4.67 (1H , dd, $^3J_{HH} = 4.4$ Hz, $^2J_{HH} = 12.0$ Hz), 4.32 ($^3J_{HH} = 8.0$ Hz, $^2J_{HH} = 12.0$ Hz) ($CH_2CH(OH)$); 2.98 (1H, $CH_2CH(OH)$); 2.96 (6H, s, $N(CH_3)_2$); 2.93, 2.60, 2.51, 2.39, 1.72, 1.29 (3H each, s, Tp′CH_3). ^{13}C NMR (CD_2Cl_2) δ 232.6 ($^1J_{WC} = 142$ Hz, CO); 212.3, ($^1J_{WC} = 48$ Hz, $C_6H_5C\equiv C$); 206.3 ($^1J_{WC} = 16$ Hz, $C\equiv C$); 155.8, 155.4, 150.1, 146.2, 145.8, 144.5 (6 s, Tp′CCH_3); 137.5, 129.1, 129.0, 128.7, 127.3, 113.5 (C_6H_5, p-$C_6H_4N(CH_3)_2$); 108.9, 108.4, 107.4 (3 s, Tp′ CH); 73.3 ($^1J_{HC} = 142$ Hz, $CH_2CH(OH)$); 47.2 ($^1J_{HC} = 130$ Hz, $CH_2CH(OH)$); 41.3 (s, $N(CH_3)_2$); 18.7, 18.3, 16.4, 13.0, 12.8 (Tp′CH_3). Anal. Calcd for $WC_{34}H_{41}N_7BO_2I$: C, 45.31; H, 4.59; N, 10.87. Found: C, 45.31; H, 4.79; N, 10.60.

Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}CH(p$-$C_6H_4N(CH_3)_2$) (4). To a THF solution of Tp′W(CO)(I)($C_6H_5C\equiv CCH_3$) (1.50 g, 2.00 mmol) at −78 °C in a dry ice/2-propanol bath, butyllithium (1.20 mL, 3.00 mmol) in hexane solution was added. 4-(Dimethylamino)benzaldehyde (0.60 g, 4.40 mmol) in THF was added by cannula. The green solution was warmed to room temperature, and potassium *tert*-butoxide (0.90 g, 7.8 mmol) was added under positive nitrogen pressure. The solution color changed from green to brown, and it was allowed to stir overnight. After solvent was removed, the brown tar was taken up in a minimum amount of THF and chromatographed on alumina. The product was eluted with 2/1 hexanes/THF. Crystallization from toluene and hexanes yielded dark brown microcrystals (0.85 g, 57%). IR (THF) 1907 cm^{-1}. ^{1}H NMR (C_6D_6) δ 8.58 (1H, d, $^3J_{HH} = 15.6$ Hz, $CCH{=}CH(p$-$C_6H_4N(CH_3)_2)$; 8.12 (1H, d, $^3J_{HH} = 15.6$ Hz, $CCH{=}CH(p$-$C_6H_4N(CH_3)_2)$; 7.55−6.41 (9H, m, C_6H_5, p-$C_6H_4N(CH_3)_2$); 5.67, 5.41, 5.24 (1H each, s, Tp′C*H*); 3.30, 2.29, 2.15, 1.70, 1.49 (s, Tp′CH_3); 2.40 (6H, s, $N(CH_3)_2$). ^{13}C NMR (C_6D_6) δ 235.7 (s, CO); 211.2, 199.4 (2 s, $C\equiv C$); 155.6, 151.5, 150.9, 144.6, 144.2 (Tp′CCH_3); 143.2, 139.9, 130.1, 129.3, 128.5, 125.6, 124.3, 112.4 (C_6H_5, p-$C_6H_4N(CH_3)_2$); 142.4 ($^1J_{HC} = 150$ Hz), 120.7 ($^1J_{HC} = 158$ Hz) ($CH{=}CH$); 108.8, 108.5, 107.3 (3 s, Tp′CH_3); 39.8 (s, $N(CH_3)_2$); 19.0, 18.8, 16.7, 12.6, 12.5 (Tp′CH_3). Anal. Calcd for $WC_{34}H_{39}N_7BOI{\cdot}C_7H_8$: C, 50.48; H, 4.86; N, 10.05. Found: C, 50.22; H, 4.84; N, 10.22. UV−vis (THF): $\lambda = 429$ nm, $\epsilon = 32\,000$ mL/(g cm); $\lambda = 685$ nm , $\epsilon = 220$ mL/(g cm).

Conversion of Tp′W(CO)(I)($C_6H_5C\equiv CCH_2CH(OH)(p$-$C_6H_4N(CH_3)_2)$) (3) to Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}CH(p$-$C_6H_4N(CH_3)_2)$) (4). To a THF solution of Tp′W(CO)(I)($C_6H_5C\equiv CCH_2CH(OH)(p$-$C_6H_4N(CH_3)_2)$) (0.17 g, 0.19 mmol) at room temperature, potassium *tert*-butoxide (0.15 g, 1.30 mmol) was added under positive nitrogen pressure. The solution color quickly changed from green to brown. The solution was stirred for 3 h, and then it was chromatographed on alumina without prior solvent removal. The product was eluted with a 1/1 hexanes/THF mixture. The solvent was removed to yield a brown solid (0.11 g, 69%).

Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}CH(C_5H_4FeC_5H_5)$) (5). To a THF solution of Tp′W(CO)(I)($C_6H_5C\equiv CCH_3$) (1.00 g, 1.33 mmol) cooled to −78 °C in a dry ice/2-propanol bath, butyllithium (0.80 mL, 2.00 mmol) in hexane solution was added. The solution turned from green to red-brown. A THF solution of formylferrocene ($HC(O)C_5H_4FeC_5H_5$, 0.45 g, 2.10 mmol) at room temperature was added via cannula. The reaction mixture turned red over a period of 5 min, and the solution was allowed to warm slowly to room temperature. Dilute aqueous HCl was added and the solution was stirred overnight. Solvent was removed by rotary evaporation leaving a dark red oil. The product was dissolved in a minimum amount of CH_2Cl_2, chromatographed on alumina, and eluted with a 1/1 hexanes/CH_2Cl_2 mixture. Crystallization from THF and hexanes yielded dark red crystals (0.92 g, 73%). IR (THF) 1907 cm^{-1}. ^{1}H NMR (C_6H_6) δ 8.26 (1H, d, $^3J_{HH} = 16$ Hz, $CCH{=}CHC_5H_4FeC_5H_5$); 7.97 (1H, d, $^3J_{HH} = 16$ Hz, $CCH{=}CHC_5H_4FeC_5H_5$); 6.98−6.84 (5H, m, C_6H_5); 5.66, 5.40, 5.32 (1H each, s, Tp′C*H*); 4.44−4.15 (4H, m, $C_5H_4FeC_5H_5$); 4.05 (5H, s, $C_5H_4FeC_5H_5$); 3.25, 2.29, 2.18, 2.09, 1.96, 1.52 (3H each, s, Tp′CH_3). ^{13}C NMR (C_6H_6) δ 236.2 (s, CO); 210.4, 199.4 (s, $C\equiv C$); 155.6, 155.5, 150.6, 144.8, 144.4, 143.4 (6 s, Tp′CCH_3); 139.3, 128.7, 128.6, 128.5 (C_6H_5); 143.2, 122.5 (2 s, $CH{=}CH$); 108.8, 108.5, 107.3 (3 s, Tp′CH_3); 81.3, 71.1,71.0, 70.2, 69.1, 68.5 ($C_5H_4FeC_5H_5$); 23.0, 19.1, 19.0, 18.7, 16.8, 14.3 (Tp′CH_3). Anal. Calcd for $WC_{36}H_{38}N_6BOIFe$: C, 45.60; H, 4.04; N, 8.86. Found: C, 45.35; H, 4.06; N, 8.77. UV−vis (THF) $\lambda = 495$ nm, $\epsilon = 2300$ mL/(g cm); $\lambda = 691$ nm , $\epsilon = 170$ mL/(g cm).

Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}C(CH_3)(C_5H_4FeC_5H_5)$) (6). To a THF solution of acetylferrocene (0.50 g, 2.19 mmol) at 0 °C BF_3 etherate (0.40 mL, 3.25 mmol) was added, and the solution was stirred for 30 min. Butyllithium (0.80 mL, 2.00 mmol) in hexane solution was added to a THF solution of Tp′W(CO)(I)($C_6H_5C\equiv CCH_3$) (1.00 g, 1.33 mmol) at −78 °C, in a dry ice/2-propanol bath. The acetylferrocene·BF_3 etherate solution was added to the tungsten complex via cannula. After this was warmed to room temperature, dilute aqueous HCl was added, and the solution was stirred overnight. Solvent was removed, and the brown tar was taken up in a minimum amount of CH_2Cl_2 before it was chromatographed on alumina. The product was eluted with 1/1 hexanes/CH_2Cl_2, and solvent was removed. Crystallization from THF and hexanes yielded dark brown crystals (1.03 g, 81%). IR (THF) 1907 cm^{-1}. ^{1}H NMR (CD_2Cl_2) δ 7.58 (1H, s, $CCH{=}C(CH_3)(C_5H_4FeC_5H_5)$; 7.16−6.53 (5H, m, C_6H_5); 5.80, 5.76, 5.67 (1H each, s, Tp′C*H*); 4.71−4.34 (4H, m, $C_5H_4FeC_5H_5$); 4.12 (5H, s, $C_5H_4FeC_5H_5$); 2.82, 2.52, 2.47, 2.30, 1.59, 1.46 (3H each, s, Tp′CH_3); 2.04 (3H, s, $CH{=}C(CH_3)(C_5H_4FeC_5H_5$). ^{13}C NMR ($CD_2Cl_2$): δ 234.1(CO); 210.5, 198.9 (2 s, $C\equiv C$); 155.4, 155.3, 151.0, 146.7, 146.3, 145.5 (Tp′CCH_3); 138.8, 129.4, 128.9, 128.3 (C_6H_5); 144.4, 121.8 ($CH{=}CCH_3$); 108.7, 108.2, 107.2 (3 s, Tp′CH); 85.9, 70.6, 70.6, 70.2, 67.4, 67.3 ($C_5H_4FeC_5H_5$); 20.0 (s, $CH{=}C(CH_3)(C_5H_4FeC_5H_5)$; 18.6, 18.5, 16.5, 13.1, 12.9 (Tp′CH_3). Anal. Calcd for $WC_{37}H_{40}N_6BOIFe$: C, 46.19; H, 4.19; N, 8.73. Found: C, 45.92; H, 4.22; N, 8.66. UV−vis (THF) $\lambda = 328$ nm , $\epsilon = 16\,400$ mL/(g cm); $\lambda = 472$ nm, $\epsilon = 1300$ mL/(g cm); $\lambda = 694$ nm, $\epsilon = 190$ mL/(g cm).

Synthesis of (−)-Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}CH(p$-$C_6H_4OCH_3)$), (−)-Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}CH(p$-$C_6H_4N(CH_3)_2)$), and (−)-Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}C(CH_3)(C_5H_4FeC_5H_5)$). The procedures above were repeated utilizing (−)-Tp′W(CO)(I)($C_6H_5C\equiv CCH_3$) as starting material instead of racemic Tp′W(CO)(I)($C_6H_5C\equiv CCH_3$).

X-ray Structure of Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}CCH_3(C_5H_4FeC_5H_5){\cdot}C_6H_{14}$) (6). Crystals of Tp′W(CO)(I)($C_6H_5C\equiv CCH{=}C(CH_3)(C_5H_4FeC_5H_5)$) were grown from hot THF/hexanes. The crystal was triclinic ($P\bar{1}$ space group). The cell dimensions were $a = 10.690(5)$ Å, $b = 13.360(7)$ Å, and $c = 15.392(7)$ Å with $\alpha = 92.57(6)°$, $\beta = 101.70(5)°$, $\gamma = 100.97(4)°$. The cell volume was 2105.2(18) Å^3 , $Z = 2$ molecules/unit cell, $D_{calc} = 1.654$ g/cm^3 , λ(Mo Kα) = 0.709 30 Å, $\mu = 3.90$ mm^{-1}, and $F(000) = 1037.28$. The X-ray data were collected on an Enraf-Nonius CAD-4 automated diffractometer using the $\theta/2\theta$ scan mode. Experimental details are given in Table 1. Of the 5537 unique reflections, 4309 reflections possessed $I > 2.5\sigma(I)$, and these were used in structure determination. Final agreement indexes for all reflections were $R = 3.9\%$ and $R_w = 4.7\%$, and hydrogens were placed in computed positions 0.96 Å from the bonded atom and included in the refinement using a riding model. All other atoms were refined anisotropically. An ORTEP drawing is shown in Figure 2.

Results and Discussion

Synthesis. The coordinated η^2-allenyl anion formed by deprotonation of Tp′(CO)IW($C_6H_5C\equiv CCH_3$) can be used to attack electron-rich aldehydes such as p-anisaldehyde, (p-$HC(O)C_6H_4OCH_3$). Protonation of the alkoxy intermediate and chromotagraphy yields one diastereomer of the air-stable chiral alcohol, Tp′(CO)IW($C_6H_5C\equiv CCH_2CH(OH)(C_6H_4OCH_3)$) (**1**, Scheme 2). The aliphatic chain linking the substituted arene to the metal center provides for distinctive resonances in the ^{1}H NMR spectrum. The diastereotopic methylene pro-

Table 1. Crystallographic Data Collection Parameters for $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CCH_3(C_5H_4FeC_5H_5))\cdot{}^1/_2C_6H_{14}$

molecular formula	$C_{43}H_{54}FeN_6OIW$
formula weight, g/mol	1048.34
crystal dimensions, mm	0.40 × 0.16 × 0.08
space group	$P\bar{1}$
cell parameters	
a, Å	10.690(5)
b, Å	13.360(7)
c, Å	15.392(7)
α, deg	92.57(6)
β, deg	101.70(5)
γ, deg	100.97(4)
volume, Å^3	2105.2(18)
Z	2
density calculated, g cm^{-3}	1.654
Collection and Refinement Parameters	
radiation (wavelength Å)	Mo Kα (0.709 30)
monochromator	graphite
linear abs coeff, cm^{-1}	39
scan type	ω scan mode
background	0.1 of scan time
θ limits, deg	5 to 45
h; k; l ranges	−11, 11; 0, 14; −16, 16
total no. of reflections	7703
data with $I \geq 2.5\sigma(I)$	4309
R significant, [all others], %	3.9 [6.2]
Rw significant, [all others], %	4.7 [5.0]
GOF	1.51
no. of parameters	487
largest parameter shift	0.076

tons found at 4.69 and 4.31 ppm are coupled to each other ($^2J_{HH}$ =12.4 Hz) , and to the CH proton ($^3J_{HH}$ = 4.4 Hz and 8.0 Hz). The CH proton at 5.21 ppm is also coupled to the hydroxy proton which appears as a doublet at 3.0 ppm with $^3J_{HH}$ = 2.4 Hz. The nonequivalent Tp′ methyl signals appear as six singlets between 2.94 and 1.30 ppm. The pyrazole protons are found between 5.93 and 5.69 ppm as three singlets. Nonequivalent resonances are observed in the ^{13}C NMR for the carbons of the Tp′ ligand indicative of a chiral metal center. The alkyne carbons resonate at 211 and 206 ppm, well within the range for a four-electron donor alkyne.[10] Solution IR of the complex shows that the lone carbonyl stretching frequency (1917 cm^{-1}) has shifted very little relative to the starting material (1907 cm^{-1}).

Deprotonation of the alcohol at room temperature with potassium *tert*-butoxide provides one method of synthesizing the elimination product, $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CH(C_6H_4OCH_3))$ (**2**, (Scheme 2). It was not necessary to further derivatize the alcohol complex with a better leaving group prior to elimination as was required in the benzaldehyde case,[11] since here elimination occurred easily with the addition of strong base. A more efficient method of synthesis is the direct addition of base to the reaction mixture instead of adding dilute aqueous acid. This produces the enyne product in a 45% yield. This enyne was not observed from the addition of acid to the alcohol, presumably due to insufficient electron density to stabilize the carbocation required for acid-catalyzed elimination.

Identification of the enyne as the trans product was made on the basis of proton NMR data. In CD_2Cl_2, doublets at 8.18 and 7.75 ppm with a coupling of 16.0 Hz are observed. The magnitude of the coupling constant is clearly indicative of a trans disposition of the olefinic protons . The resonances for the Tp′ ligand are similar to those observed in the alcohol precursor. The olefinic carbons are seen in the ^{13}C NMR at 141.0 and 122.8 ppm with $^1J_{CH}$ = 150 and 159 Hz, respectively. The alkyne carbons at 212.2 and 198.5 ppm with tungsten coupling of 56 and 14 Hz are again well within the expected chemical shift range for a four electron donor alkyne. The solution IR reveals the CO absorption at 1907 cm^{-1}, identical with that of the parent propynyl tungsten complex.

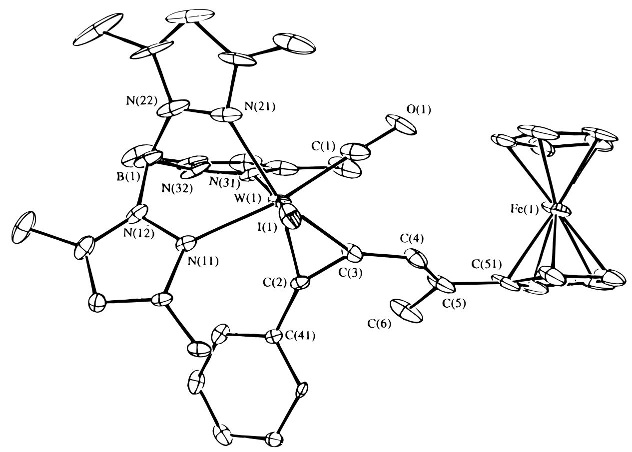
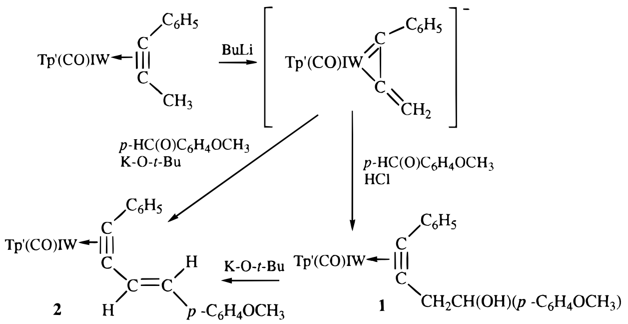
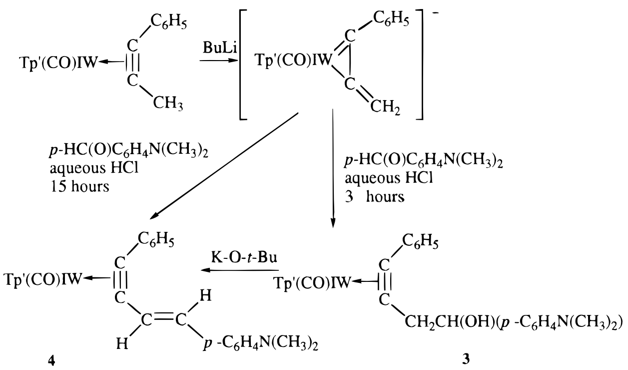


Figure 2. ORTEP of $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}C(CH_3)C_5H_4FeC_5H_5)$.

Scheme 2

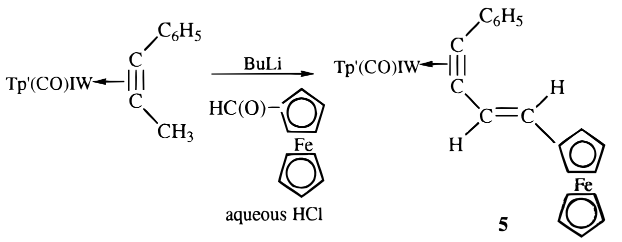


Scheme 3

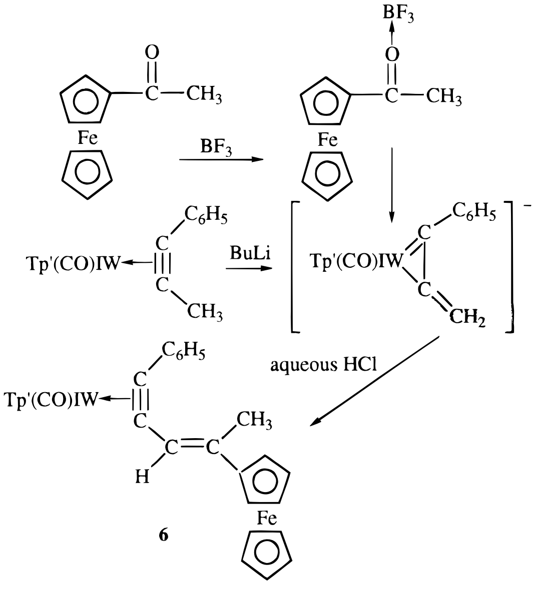


In a similar fashion the η^2-allenyl anion can be used to add 4-(dimethylamino)benzaldehyde (Scheme 3). Addition of acid again yields the alcohol, although if treated with acid for an extended period of time, the *trans*-enyne results from elimination. ^1H NMR (CD_2Cl_2) data are indicative of the chiral diastereomeric alcohol product $Tp'(CO)IW(C_6H_5C{\equiv}CCH_2CH(OH)C_6H_4N(CH_3)_2)$ (**3**). The diastereotopic methylene protons were observed at 4.67 and 4.32 ppm with geminal coupling of 12.0 Hz. The CH proton is coupled to the methylene protons, $^3J_{HH}$ = 4.4 and 8.0 Hz, but in this case no coupling to the hydroxy proton is observed. The alcohol proton is a broad peak observed in the base of a Tp′ methyl signal at 2.98 ppm. The CO stretching frequency for the

Scheme 4



Scheme 5



dimethylamino alcohol product (1913 cm^{-1}) is slightly lower than for the analogous methoxy derivative (1917 cm^{-1}).

The dimethylamino enyne derivative can be synthesized by the addition of either acid or base to the anion and aldehyde reaction mixture (Scheme 3). The ability of the complex to eliminate with dilute aqueous acid can be explained by the increase in electron density donated by the amino group compared to the methoxy group. This allows better stabilization of the positively charged carbon in the transition state. Again, addition of a strong base provides a more direct method for the synthesis of the enyne Tp′(CO)IW($C_6H_5C\equiv CCH=CHC_6H_4N(CH_3)_2$) (**4**). Olefinic protons observed in the ^1H NMR spectrum in C_6D_6 at 8.58 and 8.12 ppm with a $^2J_{HH}$ coupling of 15.6 Hz are diagnostic of the *trans*-enyne. The olefinic carbons are observed at 142.4 ppm ($^1J_{CH}$ = 150 Hz) and 120.7 ppm ($^1J_{CH}$ = 158 Hz); the alkyne carbons are found at 211.2 and 199.4 ppm. Solution IR reveals a carbonyl stretching frequency of 1907 cm^{-1} in THF.

In an effort to employ an organometallic donor and acceptor within the same complex, electron rich formyl ferrocene, $HC(O)C_5H_4FeC_5H_5$, was used as the aldehyde in the reaction with the tungsten anion (Scheme 4). Protonation with dilute acid did not lead to isolation of the alcohol, but rather elimination occurred to yield the enyne Tp′(CO)IW($C_6H_5C\equiv CCH=CHC_5H_4FeC_5H_5$) (**5**). The ability of ferrocene to stabilize carbocations has been well documented,[16] and this would account for the spontaneous elimination reaction we observe. ^1H NMR (C_6D_6) reveals a trans complex with olefinic resonances at 8.26 and 7.97 ppm with vicinal coupling of 16 Hz. The ferrocene resonances are observed between 4 and 4.5 ppm. Carbon NMR data reveal the olefin carbons at 143.2 ppm and 122.5 ppm with the alkyne carbons at 210.4 and199.4 ppm. The carbonyl stretching frequency was observed at 1907 cm $^{-1}$ as was found for the other enyne complexes.

Addition of the η^2-allenyl anion to acetyl ferrocene in a similar manner yielded only starting material. Activation of acetyl ferrocene with BF_3 etherate before addition of deprotonated Tp′(CO)IW($C_6H_5C\equiv CCH_3$) promotes the addition reaction (Scheme 5).[17] Addition of dilute acid yields the enyne product, **6**, directly for the reasons mentioned previously (Scheme 5). The olefin linkage is seen in the proton NMR (CD_2Cl_2) by a one-proton singlet at 7.58 ppm and a methyl signal at 2.04 ppm. No coupling information is available to distinguish whether the *E* or *Z* isomer was synthesized, but in accord with the pattern of *E* isomers seen for the other enyne complexes an X-ray study revealed a trans disposition of the bulky metal groups (vide supra). The carbon NMR data revealed the olefinic carbons at 144.4 and 121.8 ppm with the alkyne carbons at 210.5 and 198.9 ppm. Once again the CO stretching frequency is the same as that of the starting material, 1907 cm^{-1}.

Electronic Structure. Since linear electronic absorption data is germane to NLO response behavior UV−vis spectra were obtained for all of the enyne complexes. The starting material Tp′(CO)IW($C_6H_5C\equiv CCH_3$) has an absorbance at 677 nm in THF with an ϵ of 300 L/(mol cm). This is assigned to the HOMO to LUMO transition localized in the dπ manifold of the tungsten d^4 metal center. A similar absorption near 700 nm is present in all of the enyne derivatives. All of the enynes also possess very intense absorptions near 220 nm with $\epsilon > 50\,000$ L/(mol cm), and an additional absorption occurs between 300 and 400 nm.

In the methoxyenyne derivative, Tp′(CO)IW($C_6H_5C\equiv CCH=CHC_6H_4OCH_3$) (**2**), a band at 491 nm (ϵ = 830 L/(mol cm)) is observed that is not present in Tp′(CO)IW($C_6H_5C\equiv CCH_3$). The dimethylamino derivative Tp′(CO)IW($C_6H_5C\equiv CCH=CHC_6H_4N(CH_3)_2$) (**4**) possesses a band at 429 (ϵ = 28 000 L/(mol cm)). The origin of this band has not been assigned, but it is believed to result from conjugation with the arene. The ferrocenyl derivatives possess nearly identical spectra. Tp′(CO)IW($C_6H_5C\equiv CCH=CHC_5H_4FeC_5H_5$) (**5**) has an absorption at 495 nm (ϵ = 2200 L/(mol cm)) and Tp′(CO)IW($C_6H_5C\equiv CCH=C(CH_3)C_5H_4FeC_5H_5$) (**6**) has an absorption at 472 nm (ϵ = 1300 L/(mol cm)). Table 2 lists λ_{max} and the extinction coefficient from the UV−vis data along with the magnitude of the absorbance at 532 nm. This is the wavelength at which second harmonic generation (SHG) was measured from the 1064 nm line of a Nd:YAG laser.

X-ray Structure. X-ray crystallography was used to establish the structure for racemic Tp′(CO)IW($C_6H_5C\equiv CCH=CCH_3(C_5H_4FeC_5H_5)$) (**6**, Figure 2). The enyne cocrystallizes with hexanes in the crystal lattice, a rare phenomenon for complexes of this type. Within the ferrocenyl moiety there is marked disorder . The structure confirms the *E* isomer of the enyne, which places the bulky metal centers as far apart as possible.

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(17) Terry, M. R.; Kelley, C.; Lugan, N.; Geoffroy, G. L.; Haggerty, B. S.; Rheingold, A. L. *Organometallics* **1993**, *12*, 3607.

Table 2. Electronic Absorption Data for the Alkyne and Enyne Complexes

complex	λ (nm), [ϵ (L/(mol cm)]	532 nm, ϵ (L/(mol cm))
$Tp'(CO)IW(C_6H_5C{\equiv}CCH_3)$	677 [300]	
$Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CH\text{-}p\text{-}C_6H_4OCH_3)$	491 [830] 703 [150]	640
$Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CH\text{-}p\text{-}C_6H_4N(CH_3)_2)$	429 [28,000] 685 [200]	500
$Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CHC_5H_4FeC_5H_5)$	495 [2200] 691 [160]	2500
$Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CCH_3C_5H_4FeC_5H_5)$	472 [1300] 694 [180]	1500

Table 3. Selected Bond Distances (Å) for $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}C(CH_3)(C_5H_4FeC_5H_5))\cdot{}^1/_2C_6H_{14}$

W(1)−I(1)	2.78(16)	C(1)−O(1)	1.15(14)
W(1)−C(1)	1.97(12)	C(2)−C(3)	1.32(12)
W(1)−C(2)	2.02(7)	C(3)−C(4)	1.43(13)
W(1)−C(3)	2.08(9)	C(4)−C(5)	1.35(13)
W(1)−N(11)	2.23(7)	C(5)−C(6)	1.51(15)
W(1)−N(21)	2.27(8)	C(5)−C(51)	1.48(16)
W(1)−N(31)	2.16(9)	Fe(1)−C(51)	2.06(9)
		C(2)−C(41)	1.46(11)

Table 4. Selected Bond Angles (deg) for $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CCH_3(C_5H_4FeC_5H_5))\cdot{}^1/_2C_6H_{14}$

I(1)−W(1)−C(1)	89(3)	C(3)−W(1)−N(31)	98(3)
I(1)−W(1)−C(2)	105.0(23)	N(11)−W(1)−N(21)	82(3)
I(1)−W(1)−C(3)	99(3)	N(11)−W(1)−N(31)	88(3)
I(1)−W(1)−N(11)	84.9(17)	N(21)−W(1)−N(31)	77(3)
I(1)−W(1)−N(21)	87.5(23)	W(1)−C(1)−O(1)	177(9)
I(1)−W(1)−N(31)	163.3(20)	W(1)−C(2)−C(3)	73(5)
C(1)−W(1)−C(2)	108(4)	W(1)−C(2)−C(41)	143(6)
C(1)−W(1)−C(3)	70(4)	C(3)−C(2)−C(41)	143(8)
C(1)−W(1)−N(11)	168(3)	W(1)−C(3)−C(2)	68(5)
C(1)−W(1)−N(21)	87(4)	W(1)−C(3)−C(4)	148(6)
C(1)−W(1)−N(31)	95(4)	C(2)−C(3)−C(4)	143(8)
C(2)−W(1)−C(3)	37(3)	C(3)−C(4)−C(5)	128(9)
C(2)−W(1)−N(11)	83(3)	C(4)−C(5)−C(6)	122(10)
C(2)−W(1)−N(21)	159(4)	C(4)−C(5)−C(51)	122(9)
C(2)−W(1)−N(31)	89(3)	C(6)−C(5)−C(51)	116(9)
C(3)−W(1)−N(11)	120(9)	Fe(1)−C(51)−C(5)	127(7)
C(3)−W(1)−N(21)	157(3)		

Relevant bond lengths and angles are given in Tables 3 and 4, respectively. The geometry about tungsten is similar to other d^4 metal carbonyl alkyne complexes which have been previously characterized. The carbonyl and the alkyne are parallel in order to optimize the alkyne's donor and acceptor properties. The alkyne may be slightly less tightly bound (2.02 and 2.08 Å) than in $Tp'(CO)IW(C_6H_5C{\equiv}CCH_3)$ (1.98 and 2.01 Å), but the standard deviations are too large to draw firm conclusions. The double bond of the enyne is 1.35 Å. The metal centers are separated by 8.40 Å through the conjugated organic bridge.

Central to a finite second order NLO response is the absence of an inversion center. $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CCH_3(C_5H_4FeC_5H_5))$ crystallizes in the $P\bar{1}$ space group with the 2 molecules/unit cell related to one another by the inversion center. To eliminate the possibility of an inversion center in the solid state, three of the enynes were synthesized in enantiomerically pure form from (−)-$Tp'(CO)IW(C_6H_5C{\equiv}CCH_3)$. The Kurtz powder technique was employed to measure the SHG of all four racemic enynes and the three enantiomerically pure anisaldehyde, (dimethylamino)benzaldehyde, and acetylferrocene enynes.

NLO Results. Only one of the enynes ($Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CHC_6H_4OCH_3)$) (**2**) was NLO active in its racemic form (Table 5). It possessed an efficiency of 0.1 of that of urea. However, the enantomerically pure enyne solid of this same methoxy derivative scattered light so severely that accurate SHG measurements were not accomplished. $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CHC_6H_4N(CH_3)_2)$ (**4**) was not active in its racemic form but did possess a response of 0.1 of that of urea as a single enantiomer. $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CH(C_5H_4FeC_5H_5))$ (**5**) was measured only as a racemic mixture and exhibited no NLO activity. $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CCH_3(C_5H_4FeC_5H_5))$ (**6**) was tested as a racemate, and no response was observed. This is consistent with the presence of a center of symmetry as was determined be X-ray analysis. As a single enantiomer $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CCH_3(C_5H_4FeC_5H_5))$ exhibited a response of 0.2 of that of urea.

A noncentrosymmetric space group is guaranteed for enantiomerically pure complexes. This does not eliminate the possibility that the hyperpolarizability of one molecule within the unit cell will be spatially oriented to effectively cancel out the response of another molecule.

The dimethylamino, methoxy, and ferrocenyl groups have been well documented to function as electron donors in NLO materials. The 14 electron chiral $Tp'(CO)IW$ fragment provides a metal center which efficiently utilizes both the donor and acceptor capabilities of the alkyne. The ability of the alkyne to function as a four electron donor creates a relatively low lying LUMO, and the resonance structure possible with **4** is shown below (Scheme 6).

In this highly polarized resonance structure the acceptor fragment is surrounded by a very asymmetric electronic environment. However, the lack of any change in the CO stretching frequency between the enyne complexes and the starting alkyne complex seems to indicate little contribution from this resonance form.

Table 2 lists the asorbance of each of the complexes at 532 nm. The molar absorptivities range from 500 to 2500. Both $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CCH_3(C_5H_4FeC_5H_5))$ (**6**) and $Tp'(CO)IW(C_6H_5C{\equiv}CCH{=}CHC_6H_4N(CH_3)_2)$ (**4**) exhibit a NLO response in their enantiomerically pure form but with an efficiency of only 0.2 and 0.1, respectively, compared to urea. The absorption at 532 nm in both cases is sufficiently strong to effectively eliminate the propagating light at the second harmonic frequency by the reabsorption of this radiation by the enynes. Any application of these organometallics will be severely limited by the necessity of using only a limited spectral window in which electronic absorptions do not occur.

Summary

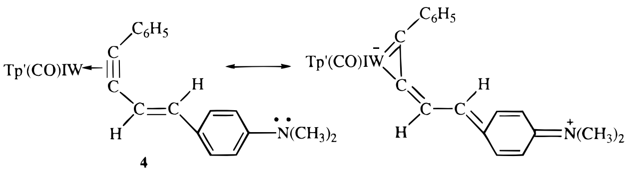
Deprotonation at the propargyl site of coordinated alkynes yields an η^2- allenyl anion which reacts with aldehydes to yield chiral enynes. These trans enynes possess electron donating and accepting groups sepa-

Table 5. Kurtz Powder Technique Data for Racemic and Enantiomerically Pure Enynes

complex	SHG efficiency vs urea standard[a]
Tp′(CO)IW($C_6H_5C{\equiv}CCH{=}CH(p\text{-}C_6H_4OCH_3)$)	
racemic	0.1
enantiomerically pure	b
Tp′(CO)IW($C_6H_5C{\equiv}CCH{=}CH(p\text{-}C_6H_4N(CH_3)_2)$)	
racemic	0.0
enantiomerically pure	0.1
Tp′(CO)IW($C_6H_5C{\equiv}CCH{=}CH(C_5H_4FeC_5H_5)$)	
racemic	0.0
enantiomerically pure	not synthesized
Tp′(CO)IW($C_6H_5C{\equiv}CCH{=}C(CH_3)(C_5H_4FeC_5H_5)$)	
racemic	0.0
enantiomerically pure	0.2

[a] Measurements made using the Kurtz powder technique. Radiation provided by 1064 nm line of Nd:YAG laser. SHG measured at 532 nm. [b] Measurements could not accurately be made due to severe light scattering.

Scheme 6



rated by a conjugated organic bridge. An X-ray structure of Tp′(CO)IW($C_6H_5C{\equiv}CCH{=}CCH_3C_5H_4FeC_5H_5$) revealed a $P\bar{1}$ space group with a center of symmetry. Three of the enyne complexes were synthesized in enantiomerically pure form to ensure a noncentrosymmetric space group for the isolated solid. Noncentrosymmetric space groups are necessary but not sufficient for nonzero NLO responses. SHG measurements showed either no response or a response less than that of a urea standard. Absorptions at 532 nm, insufficient asymmetry at metal center, and cancellations due to molecular orientations within the crystal lattice are all possible explanations for the low NLO response.

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Supporting Information Available: Tables of atomic positions, thermal parameters, complete bond distances and angles (8 pages); tables of crystal structure factors (18 pages). Ordering information is given on any current masthead page.

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