= 120 s^{-1}, and (c) the combination of (a) and (b). Clearly in (a) only groups 2 and 4 are affected; peaks in groups 1 and 3 are not affected by the jump process because of our neglect of the shift anisotropy of the aliphatic carbons. In (b) all the peaks are affected because the Cope rearrangement intermixes all carbon atoms in the molecule. However, when both the threefold jumps and the Cope rearrangement take place simultaneously marked nonmonotonous behavior can occur as demonstrated in part c.

The rate constants k_J and k_C used to calculate the plots in Figure 7c were chosen so as to mimic the behavior of the experimental results, which are also included in this part of the figure with the same set of symbols as for Figure 6. Note that the major features of the four curves occur in the first 30 ms of the plots and that only when both the effect of the threefold jump and the Cope rearrangement are included does the theory resemble the experimental data in this region. In fact the rate constants used for the calculations also fall close to those estimated from the one-dimensional spectra in Figure 4. The fit could no doubt be improved by varying k_J and k_C and by including corrections to account for possible small differences in the cross-polarization efficiency of the different carbon atoms, longitudinal relaxation during the mixing time, and even slow spin diffusion. In view of the uncertainty associated with the peak volume integration we have not pursued a more extensive analysis. We feel, however, that the quality of the fit obtained with the approximate rate constants and without further refinement is quite satisfactory.

Since the activation energy of the threefold jumps is higher than for the Cope rearrangement (Figure 4), the ratio k_J/k_C decreases with decreasing temperature and the competing effect of the two processes becomes less pronounced. This was clearly observed in results obtained at −20 °C, where the maximum in the total intensity of the group 4 peaks with respect to the mixing time became flatter. On the other hand, above −10 °C, exchange broadening sets in, rendering the recording of such two-dimensional spectra impossible.

Summary and Conclusions

The results reported here on the dynamic processes in solid bullvalene are in good agreement with the earlier deuterium NMR study of a single crystal.[12] In particular, both the deuterium and carbon-13 studies indicate the occurrence of two independent dynamic processes: the symmetric threefold jumps and a concerted Cope rearrangement/reorientation process. Both deuterium and carbon-13 NMR studies have been used extensively to investigate dynamic processes in solids. The former approach has the disadvantage that it requires specific chemical labeling of the compound of interest because of the low natural abundance of deuterium. The sensitivity of natural abundance carbon-13 NMR spectroscopy is normally acceptable but static samples give complicated spectra due to the overlap of signals from different carbon atoms. The low spinning rate carbon-13 MAS experiment employed here for the case of bullvalene provides increased spectral resolution, while the surviving sidebands contain information about the chemical shift anisotropy and thus about reorientation processes. Specific chemical labeling is unnecessary. When applicable this approach should be the method of choice for studying dynamic processes in solids.

Acknowledgment. We thank Prof. G. Schröder for a generous gift of the bullvalene sample used in our experiments. J.J.T. thanks the Science and Engineering Research Council of Great Britain for a NATO postdoctoral fellowship. Z.L. thanks the Minerva Foundation for a visiting scientist fellowship.

Registry No. Bullvalene, 1005-51-2.

Diastereoselective Reactions of Tungsten η^2-Propargyl Complexes with Alkyl Halides and Aldehydes

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Abstract: Deprotonation of the alkyne methyl group in $\mathrm{Tp'(CO)(I)W(PhC{\equiv}CCH_3)}$ [Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate] produces a nucleophilic propargyl synthon. Reaction of the complex anion with MeI or $\mathrm{PhCH_2Br}$ yields an elaborated alkyne and avoids the propargyl/allenyl regiochemical control problem. Deprotonation of $\mathrm{Tp'(CO)(I)W(PhC{\equiv}CCH_2Me)}$ followed by benzylation produces a single diastereomer as determined by ^{1}H NMR, while methylation of the anion formed from $\mathrm{Tp'(CO)(I)W(PhC{\equiv}CCH_2Bz)}$ yields the opposite diastereomer. Pivaldehyde or benzaldehyde adds to the coordinated η^2-propargyl carbanion, $\mathrm{Li[Tp'(CO)(I)W(\eta^2\text{-}PhC{=}C{=}CHMe)]}$, to form alcohol products. Conversion to a coordinated enyne was achieved for the benzaldehyde adduct by first forming the mesyl derivative and then eliminating $\mathrm{HOSO_2Me}$ to yield $\mathrm{Tp'(CO)(I)W(PhC{\equiv}CCMe{=}CHPh)}$.

Introduction

Alkynes are versatile organic building blocks.[1] Although alkynes are of demonstrated value in organic synthesis, regiocontrol of electrophilic addition to propargyl carbanion equivalents has been difficult to achieve with classical metalated propargyl reagents (eq 1).[2]

$$\mathrm{RC{\equiv}CCH_3} \xrightarrow{\text{base}} \mathrm{RC{\equiv}C\text{-}\bar{C}H_2} \leftrightarrow \mathrm{R\bar{C}{=}C{=}CH_2} \tag{1}$$

In 1968, Corey and Kirst reported a method for propargylating an alkyl halide by reacting the halide with lithio-1-trimethylsilylpropyne.[3] Alkylation occurred almost exclusively at the propargyl site to yield alkyne products as the trimethylsilyl group limited alkylation at the alkyne carbon. Thus allene products were avoided; the trimethylsilyl protecting group was easily removed.

Nicolas has achieved regiocontrol of nucleophilic addition to a cationic propargyl synthon through coordination of an alkyne

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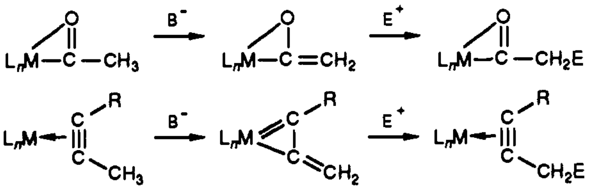
ligand to a cobalt dimer.[4] We now report complementary results using d^4 tungsten monomers which bind the alkyne triple bond, increase the acidity of the propargyl protons, and provide both regiocontrol and stereocontrol for reactions of coordinated propargyl anions formed by alkyne deprotonation.

Evidence that alkyne ligands in complexes where donation from $\pi_\perp$ is important are susceptible to deprotonation to form allenyl (or propargyl) intermediates was provided by Watson and Bergman in 1980.[5] Deuteration of the butyne methyl groups in [Cp(CO)Mo(CH$_3$C$\equiv$CCH$_3$)$_2$]$^+$ was effected with NEt$_3$ in deuterioacetone solution. More recently Feher, Green, and Rodrigues have isolated an η^2-allenyl complex formed by deprotonation of Cp[P(OMe)$_3$]$_2$Mo(PhC$\equiv$CCH$_2$Ph)]$^+$.[6] Protonation and methylation reactions of the η^2-allenyl complex accessible from [(Ph$_2$PCH$_2$CH$_2$PPh$_2$)(R$_2$NCS$_2$)(CO)W(MeOC$\equiv$CCH$_2$Ph)]$^+$ have been studied.[7]

In an effort to combine the stereochemical control offered by the Tp′(CO)LM fragment [M = Mo,[8] W;[9] Tp′ = hydridotris(3,5-dimethylpyrazolyl)borate] and exploit the analogy between reactions of anionic metal enolate and metal η^2-allenyl complexes (eqs 2 and 3), we have explored alkylation and aldehyde addition reactions of anionic complexes formed by deprotonation of Tp′(CO)(I)W(PhC$\equiv$CCH$_2$R) reagents.



(2)

(3)

Experimental Section

Materials and Methods. Reactions were performed under a dry nitrogen atmosphere with standard Schlenk techniques. Tetrahydrofuran (THF) was distilled from potassium benzophenone ketyl. All other solvents were purged with nitrogen and used without further purification. Iodomethane (MeI), benzyl bromide (BzBr), and methanesulfonyl chloride were passed through alumina prior to cycling the liquid through one freeze/degass/thaw cycle before use. Benzaldehyde and pivaldehyde reagents were distilled. Tp′W(CO)$_3$I[9] was prepared according to literature methods.

Infrared spectra were collected on a Mattson Polaris FT-IR. ^{1}H and ^{13}C NMR spectra were recorded on a Varian XL 400 (400-MHz) spectrometer. Analyses are by Galbraith Laboratories of Knoxville, TN, or by Oneida Research Service of Whitesboro, NY.

Tp′(CO)(I)W(PhC$\equiv$CCH$_3$) (1). An excess of 1-phenyl-1-propyne (1.50 mL, 11.98 mmol) was added to a red-brown THF solution of Tp′W(CO)$_3$I (6.12 g, 8.85 mmol). The reaction was allowed to reflux for 18 h. The solvent was removed and the oily solid was chromatographed on alumina. A green band was eluted with hexanes and methylene chloride. The solvents were removed and the powder was recrystallized from methylene chloride and hexanes to yield a green crystalline powder (5.62 g, 85%). IR (THF): ν_{CO} 1912 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.26–7.19, 6.69 (C$_6$H$_5$); 5.90, 5.89, 5.70 (3 s, Tp′C*H*); 3.54 (PhC$\equiv$C$\mathrm{C}H_3$); 2.89, 2.60, 2.52, 2.38, 1.70, 1.33 (6 s, Tp′$\mathrm{C}H_3$). ^{13}C NMR (CD$_2$Cl$_2$): δ 233.3 ($^1J_{WC}$ = 145 Hz, CO); 208.9 ($^1J_{WC}$ = 50 Hz, Ph*C*$\equiv$CMe); 206.5 ($^1J_{WC}$ = 12 Hz, $^2J_{HC}$ = 10 Hz, PhC$\equiv$*C*Me); 155.7, 155.3, 150.2, 146.0, 145.7, 144.5 (6 s, Tp′*C*-CH$_3$); 137.7, 129.0, 128.9, 128.8 (C_6H$_5$); 108.7, 108.4, 107.2, (Tp′*C*H); 22.8, 18.5, 18.2, 16.3, 13.0, 12.9, 12.8 (7 s, Tp′CH$_3$, $\equiv$CCH$_3$). Anal. Calcd for WC$_{25}$H$_{30}$N$_6$OBI: C, 39.92; H, 3.99; N, 11.18. Found: C, 39.06; H, 3.94; N, 10.77.

Tp′(CO)(I)W(PhC$\equiv$CCH$_2$CH$_3$) (2). This compound was prepared by two routes as described below: (a) Butyllithium (0.70 mL, 1.75 mmol) in hexane solution was added to a THF solution of Tp′(CO)(I)W(PhC$\equiv$CCH$_3$) (0.99 g, 1.32 mmol) at −78 °C. Methyl iodide (0.16 mL, 2.64 mmol) was added 3 min later through a layer of alumina to the resulting red solution, and the solution returned to green. The solution was allowed to warm to room temperature. The solvent was removed and the oil was chromatographed on alumina. A green band was eluted with methylene chloride. The solvent was removed and the oily solid was recrystallized from methylene chloride and hexanes to give dark green crystals (0.90 g, 89%). (b) Complex **2** can be synthesized independently by reacting free PhC$\equiv$CEt with Tp′W(CO)$_3$I as described above for **1**. IR (THF): ν_{CO} 1907 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.25–7.18, 6.62 (Ph); 5.91, 5.87, 5.73 (3 s, Tp′C-*H*); 4.39 (overlapping dq, 1 H, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 7.6 Hz, –C*H*HCH$_3$); 3.73 (overlapping dq, 1 H, $^2J_{HH}$ = 14.3 Hz, $^3J_{HH}$ = 7.7 Hz, –CH*H*CH$_3$); 2.91, 2.61, 2.54, 2.39, 1.71, 1.39 (6 s, Tp′$\mathrm{C}H_3$); 1.58 (t, $^3J_{HH}$ = 7.6 Hz, –CH$_2$$\mathrm{C}H_3$). ^{13}C NMR (CD$_2Cl_2$): δ 233.1 ($^1J_{WC}$ = 145 Hz, CO); 208.8 ($^1J_{WC}$ = 49 Hz, Ph*C*$\equiv$CEt); 209.6 ($^1J_{WC}$ = 12 Hz, PhC$\equiv$*C*Et); 155.6, 155.2, 150.1, 146.0, 145.6, 144.4 (6 s, Tp′*C*-CH$_3$); 138.1, 128.9, 128.7, 128.6, (Ph); 108.7, 108.3, 107.3 (3 s, Tp′*C*H); 30.6 (–*C*H$_2$CH$_3$); 18.6, 18.3, 16.5, 13.1, 12.8, 12.7 (Tp′*C*H$_3$, –CH$_2$*C*H$_3$). Anal. Calcd for WC$_{26}$H$_{32}$N$_6$OIB: C, 40.75; H, 4.18; N, 10.97. Found: C, 40.98; H, 4.49; N, 10.77.

Tp′(CO)(I)W(PhC$\equiv$CCHMeCH$_2$Ph) (3a). Butyllithium (0.40 mL, 1.00 mmol) in hexane solution was added to a THF solution of Tp′(CO)(I)W(PhC$\equiv$CCH$_2$CH$_3$) (0.30 g, 0.39 mmol) at −78 °C. Benzyl bromide (0.50 mL, 4.20 mmol) was added 3 min later through a layer of alumina to the resulting red solution; the color immediately returned to green. The reaction was stirred at room temperature for 1 h. The solvent was removed and the oil was chromatographed on alumina. A green band was eluted with methylene chloride. The solvent was removed, and the oil was recrystallized from methylene chloride and hexanes to form a green powder (0.16 g, 48%). IR (THF): ν_{CO} 1905 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.47–7.37, 6.34 (10 H, C$_6$H$_5$); 5.90, 5.79, 5.76 (3 s, Tp′C-*H*); 4.38 (m, C*H*CH$_3$CH$_2$Ph); 3.74 (dd, 1 H, $^3J_{HH}$ = 3.5 Hz, $^2J_{HH}$ = 13.5 Hz, CHCH$_3$C*H*HPh); 2.94, 2.58, 2.54, 2.38, 1.68, 1.52 (6 s, 3 H each, Tp′$\mathrm{C}H_3$); 2.60 (CHCH$_3$CH*H*Ph, coupling obscured by a methyl signal); 1.50 (d, 3 H, $^3J_{HH}$ = 6.6 Hz, CHCH_3CH$_2$Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ 233.4 (s, CO); 210.0, 208.0 (*C*$\equiv$*C*); 155.7, 155.3, 150.6, 146.5, 145.6, 144.4 (Tp′*C*-CH$_3$); 140.2, 138.6, 130.4, 129.2, 128.7, 128.3, 128.1, 126.8 (Ph); 108.7, 108.4, 107.4 (Tp′*C*-H); 44.7, 40.2 (*C*HCH$_3$*C*H$_2$Ph); 18.9, 18.8, 18.6, 16.7, 13.2, 12.9, 12.8 (Tp′*C*H$_3$, CH*C*H$_3$). Anal. Calcd for WC$_{33}$H$_{38}$N$_6$BOI: C, 46.31; H, 4.44: N, 9.82. Found: C, 46.57; H, 4.77; N, 9.86.

Tp′(CO)(I)W(PhC$\equiv$CCH(CH$_2$Ph)Me) (3b). Butyllithium (1.00 mL, 2.50 mmol) in hexane solution was added to a THF solution of Tp′(CO)(I)W(PhC$\equiv$CCH$_2$CH$_2$Ph) (1.30 g, 1.54 mmol) at −78 °C. Methyl iodide (0.40 mL, 6.42 mmol) was added 3 min later through a layer of alumina to the resulting red solution, and the solution color returned to green. The reaction was stirred at room temperature for 1 h, at which point the solvent was removed, and the oil was chromatographed on alumina. A green band was eluted with methylene chloride. The solvents were removed, and the powder was recrystallized from methylene chloride and hexanes, to yield a fine green powder (0.88 g, 66%). IR (THF): ν_{CO} 1908 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.32–7.19, 6.58 (10 H, C$_6$H$_5$); 5.88, 5.79, 5.78 (3s, Tp′C-*H*); 4.24 (sextet, $^3J_{HH}$ = 7.0 Hz, C*H*(CH$_2$Ph)CH$_3$); 3.26 (d, 2H, $^3J_{HH}$ = 7.0 Hz, CH(CH_2Ph)CH$_3$); 2.87, 2.57, 2.35, 2.37, 1.68, 1.54 (6 s, Tp′$\mathrm{C}H_3$); 1.48 (d, $^3J_{HH}$ = 7.1 Hz, CH(CH$_2$Ph)CH_3). ^{13}C NMR (CD$_2$Cl$_2$): δ 239.2 (s, CO); 209.4, 209.0 (*C*$\equiv$*C*); 155.6, 155.3, 150.7, 146.5, 145.6, 144.4 (Tp′*C*-CH$_3$); 140.8, 139.0, 129.7, 129.2, 128.8, 128.4, 126.8 (Ph); 108.6, 108.4, 107.3 (Tp′*C*-H); 46.1, 43.2 (*C*H(*C*H$_2$Ph)CH$_3$); 18.8, 18.3, 16.7, 13.1, 12.9, 12.8 (Tp′*C*H$_3$, CH(CH$_2$Ph)*C*H$_3$). Anal. Calcd for WC$_{33}$H$_{38}$N$_6$BOI: C, 46.31; H, 4.44; N, 9.82. Found: C, 45.87; H, 4.58; N, 9.53.

Tp′(CO)(I)W(PhC$\equiv$CCH$_2$CH$_2$Ph) (4). Butyllithium (1.50 mL, 3.75 mmol) in hexane solution was added to a THF solution of Tp′(CO)(I)W(PhC$\equiv$CCH$_3$) (2.00 g, 2.66 mmol) at −78 °C. Benzyl bromide (1.00 mL, 8.41 mmol) was added 3 min later through a layer of alumina to the resulting red solution; the solution color returned to green. The reaction was stirred for 1 h at room temperature. The solvent was removed and the powder was chromatographed on alumina. A green band was eluted with methylene chloride and toluene. The solvent was removed, and the powder was recrystallized from CH$_2$Cl$_2$ and hexanes to give a green-blue powder (1.80 g, 80%). IR (THF): ν_{CO} 1906 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.42–7.05, 6.20 (C$_6$H$_5$); 5.91, 5.87, 5.69 (3s, Tp′C*H*); 4.60, 4.04, 3.48, 3.02 (4 m, 1 H each, CH_2CH_2Ph); 2.94, 2.60, 2.51, 2.38, 1.72, 1.34 (Tp′$\mathrm{C}H_3$). ^{13}C NMR (CD$_2$Cl$_2$): δ 233.0 (s, CO); 209.7, 206.5 (2 s, *C*$\equiv$*C*); 155.7, 155.3, 150.3, 146.2, 145.7, 144.4 (Tp′*C*-CH$_3$); 142.0, 137.6, 129.5, 128.9, 128.8, 128.7, 128.5, 126.7 (Ph); 108.8, 108.4, 107.3 (Tp′*C*H); 39.1, 33.2 (*C*H$_2$*C*H$_2$Ph); 18.8, 18.3, 16.5, 13.2, 12.9 (Tp′*C*H$_3$). Anal. Calcd for WC$_{32}$H$_{36}$N$_6$BOI: C, 45.65; H, 4.27; N, 9.98. Found: C, 46.05; H, 4.53; N, 9.63.

Tp′(CO)(I)W(PhC$\equiv$CCHMeCH(OH)CMe$_3$) (5). Butyllithium (0.80 mL, 2.00 mmol) in hexane solution was added to a THF solution of

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Tp′(CO)(I)W(PhC≡CCH$_2$CH$_3$) (1.00 g, 1.30 mmol) at −78 °C. Pivaldehyde (0.80 mL, 7.36 mmol) was added 3 min later through a layer of alumina to the resulting red solution, and the color immediately returned to green. The reaction was quenched with 1.5 mL of dilute aqueous HCl, and the solution was allowed to warm to room temperature. The solvent was removed, and the oil was chromatographed on alumina. A green band was eluted with methylene chloride. The solvent was removed, leaving a powder which was recrystallized from CH$_2$Cl$_2$ and hexanes to give green crystals (0.80, 72%). IR (THF): ν_{CO} = 1901 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.15, 6.66 (5 H, C$_6$H$_5$); 5.92, 5.80, 5.78 (3 s, Tp′C-*H*); 4.41 (broad doublet, $^3J_{HH}$ = 2 Hz, CHCH$_3$C*H*(OH)CMe$_3$); 4.35 (q of d, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 2 Hz, C*H*CH$_3$CH(OH)CMe$_3$); 2.89, 2.58, 2.56, 2.39, 1.62, 1.52 (6 s, Tp′C*H*$_3$); 1.73 (d, $^3J_{HH}$ = 6.8 Hz, CHC*H*$_3$CH(OH)CMe$_3$); 1.51 (broad, CHCH$_3$CH(O*H*)CMe$_3$); 1.21 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (CD$_2$Cl$_2$): δ 233.2 ($^1J_{WC}$ = 146 Hz, *C*O); 213.2 ($^1J_{WC}$ = 45 Hz, ≡*C*Ph); 211.9 ($^1J_{WC}$ = 12.5 Hz, ≡*C*R); 155.6, 155.3, 150.3, 146.3, 145.8, 144.4 (Tp′*C*-CH$_3$); 138.9 (C$_{ipso}$); 128.7, 128.3, 127.9 (Ph); 108.6, 108.4, 107.4 (Tp′*C*-H); 75.9 ($^1J_{HC}$ = 145 Hz, *C*H(OH)CMe$_3$); 46.1 ($^1J_{HC}$ = 129 Hz, *C*HCH$_3$); 36.0 (*C*Me$_3$); 27.5 (C(*C*H$_3$)$_3$); 18.7, 18.6, 16.4, 15.4, 13.1, 12.9 (Tp′*C*H$_3$, CH*C*H$_3$). Anal. Calcd for WC$_{31}$H$_{42}$N$_6$BO$_2$I: C, 43.68; H, 4.93; N, 9.86. Found: C, 43.89; H, 4.96; N, 9.90.

Tp′(CO)(I)W(PhC≡CCHMeCH(OH)Ph) (6). Butyllithium (2.00 mL, 5.00 mmol) in hexane solution was added to a THF solution of Tp′(CO)(I)W(PhC≡CCH$_2$CH$_3$) (2.59 g, 3.38 mmol) at −78 °C. Benzaldehyde (1.20 mL, 11.80 mmol) was added 3 min later through a layer of alumina to the resulting red solution, and the color immediately returned to green. The reaction was quenched with 3 mL of dilute aqueous HCl, and the solution was allowed to warm to room temperature. The solvent was removed and the oil was chromatographed on alumina. A broad green band was eluted with THF. The solvent was removed and the oil was recrystallized from methylene chloride and hexanes, yielding dark green crystals (2.28 g, 77%). IR (THF): ν_{CO} 1907 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.56–7.02, 6.16 (Ph); 5.90, 5.80, 5.75 (3 s, Tp′C-*H*); 5.11 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 2.9 Hz, CHCH$_3$C*H*(OH)Ph); 4.63 (quintet, $^3J_{HH}$ = 6.8 Hz, C*H*CH$_3$CH(OH)Ph); 3.07 (d, $^3J_{HH}$ = 3.0 Hz, O*H*); 2.92, 2.58, 2.53, 2.38, 1.65, 1.53 (6 s, Tp′C*H*$_3$); 1.30 (d, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$CH(OH)Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ 233.5 (s, CO); 213.3, 208.1 (2 s, *C*≡*C*); 155.7, 155.3, 150.8, 146.9, 145.7, 144.5 (6 s, Tp′*C*-CH$_3$); 142.1, 138.3, 129.4, 128.5, 128.1, (Ph); 108.9, 108.5, 107.4 (Tp′*C*H); 77.5, 50.8 (2 s, *C*HCH$_3$*C*H)(OH)Ph); 18.9, 18.5, 16.8, 16.1, 13.2, 13.0, 12.9 (7 s, Tp′*C*H$_3$, −CH*C*H$_3$−). Anal. Calcd for WC$_{33}$H$_{38}$N$_6$BO$_2$I: C, 45.46; H, 4.36; N, 9.64. Found: C, 45.89; H, 4.54; N, 9.32.

Tp′(CO)(I)W(PhC≡CCHMeCH(OSO$_2$Me)Ph) (7). Methanesulfonyl chloride (0.20 mL, 2.58 mmol) was added to a pyridine solution of Tp′(CO)(I)W(PhC≡CCHCH$_3$CH(OH)Ph) (0.80 g, 0.92 mmol) at 0 °C. The reaction was allowed to reach room temperature and stirred for 12 h. The solvent was removed, and the resulting oil was chromatographed on alumina. A yellow band was eluted using hexanes and discarded. A broad green fraction was eluted with methylene chloride. The solvent was removed and the oil was recrystallized from CH$_2$Cl$_2$ and hexanes to give a green powder (0.64 g, 73%). IR (THF): ν_{CO} 1901 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.51–6.79, 5.36 (10 H, C$_6$H$_5$); 5.90, 5.79, 5.74 (3 s, Tp′C-*H*); 6.25 (d, $^3J_{HH}$ = 3.0 Hz, CHCH$_3$C*H*(OMs)Ph); 4.96 (dq, $^3J_{HH}$ = 6.7 Hz, $^3J_{HH}$ = 3.0 Hz, C*H*CH$_3$CH(OMs)Ph); 3.15, 2.95, 2.58, 2.53, 2.37, 1.61, 1.51 (7 s, Tp′C*H*$_3$, OSO$_2$C*H*$_3$); 1.55 (d, $^3J_{HH}$ = 6.7 Hz, CHC*H*$_3$CH(OMs)Ph). ^{13}C NMR (CD$_2$Cl$_2$): δ 233.0 (s, CO); 201.0, 212.0 (2 s, *C*≡*C*); 155.8, 155.0, 150.7, 146.9, 145.7, 144.5, (6 s, Tp′*C*-CH$_3$); 136.7, 135.8, 129.3, 129.1, 128.8, 128.7, 127.8 (Ph); 108.9, 108.5, 107.4 (3 s, Tp′*C*-H); 79.8, 48.5 (2 s, *C*HCH$_3$*C*H(OMs)Ph); 39.0 (s, OSO$_2$*C*H$_3$); 19.0, 17.9, 16.8, 14.0, 13.1, 12.9, 12.8 (7 s, Tp′*C*H$_3$, CH*C*H$_3$CH(OMs)Ph). Anal. Calcd for WC$_{34}$H$_{40}$N$_6$SBO$_4$I: C, 42.99; H, 4.21; N, 8.85. Found: C, 42.83; H, 4.30; N, 8.70.

Tp′(CO)(I)W(PhC≡CCMe═CHPh) (8). A THF solution of potassium *tert*-butoxide (0.05 g, 0.45 mmol) at 0 °C was added to a THF solution of Tp′(CO)(I)W(PhC≡CCHCH$_3$CH(OSO$_2$CH$_3$)Ph) (0.11 g, 0.12 mmol) also at 0 °C. The resulting auburn solution was stirred at room temperature for 1 h. The solvent was removed and the oily solid was chromatographed on alumina. The orange-yellow band was eluted with CH$_2$Cl$_2$ and hexanes. The solvent was removed and the solid was recrystallized from methylene chloride and hexanes to yield yellow-brown crystals (0.05 g, 51%). IR (THF): ν_{CO} 1914 cm^{-1}. ^{1}H NMR (CD$_2$Cl$_2$): δ 7.72 (s, CCH$_3$═C*H*Ph); 7.65–7.18, 6.68 (10 H, C$_6$*H*$_5$); 5.91, 5.84, 5.81 (3 s, Tp′C*H*); 2.94, 2.63, 2.60, 2.41, 1.63, 1.57 (Tp′C*H*$_3$); 2.61 (d, $^4J_{HH}$ = 1.2 Hz, CC*H*$_3$═CHPh). ^{13}C NMR (CD$_2$Cl$_2$): δ 236.0 (s, CO); 211.0, 206.0 (*C*≡*C*); 155.7, 155.0, 150.2, 146.4, 145.8, 144.5 (Tp′*C*-CH$_3$); 138.9, 137.8 (*C*CH$_3$*C*HPh); 137.7, 136.3, 130.2, 129.3, 129.2, 128.8, 128.7, 128.0 (Ph); 108.8, 108.4, 107.3 (Tp′*C*-H); 19.1, 18.9, 18.2, 16.8, 13.1, 12.9, (Tp′*C*H$_3$, C*C*H$_3$CHPh). Anal. Calcd for WC$_{33}$H$_{36}$N$_6$BOI: C, 46.42; H, 4.22; N, 9.84. Found: C, 46.30; H, 4.34; N, 9.58.

Table I

Crystallographic Data Collection Parameters for **6**	
molecular formula	WC$_{33}$H$_{38}$N$_6$BO$_2$I
formula weight, g/mol	872.26
crystal dimensions, mm	0.25 × 0.30 × 0.40
space group	$P2_1/n$
cell parameters	
a, Å	11.331 (3)
b, Å	15.257 (7)
c, Å	20.274 (7)
β, deg	97.44 (3)
volume, Å^3	3475.2 (22)
Z	4
density calcd, g cm^{-3}	1.667
Collection and Refinement Parameters	
radiation (wavelength, Å)	Mo Kα (0.70930)
monochromator	graphite
linear abs coeff, cm^{-1}	43.1
scan type	$\theta/2\theta$
background	25% of full scan width on both sides
θ limits, deg	45
h,k,l ranges	−12 12, 0 16, 0 21
total no. of reflections	4510
data with $I \geq 2.5\sigma(I)$	2911
R, %	6.3
R_w, %	7.3
GOF	1.98
no. of parameters	398
largest parameter shift	0.057

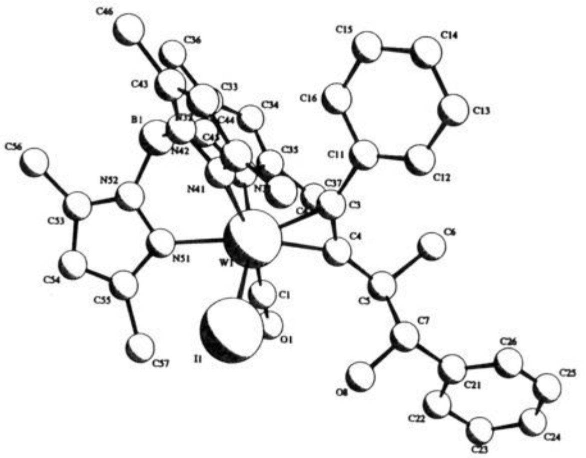

Figure 1. Pluto drawing showing complete atomic number scheme for Tp′(CO)(I)W(PhC≡CCHMeCH(OH)Ph), **6**.

X-ray Structure of Tp′(CO)(I)W(PhC≡CCHMeCH(OH)Ph) (6). Crystals of Tp′(CO)(I)W(PhC≡CCHMeCH(OH)Ph) were grown from hexane/methylene chloride. The crystal studied was monoclinic with space group $P2_1/n$ and unit cell dimensions a = 11.331 (3) Å, b = 15.257 (7) Å, c = 20.274 (7) Å, β = 97.44 (3)°, V = 3475.2 (22) Å^3, Z = 4, D_{calc} = 1.667 g cm^{-3}, λ(Mo Kα) = 0.70930 Å, μ = 43.1 cm^{-1}, and $F(000)$ = 1704.

The data were collected on an Enraf-Nonius CAD4 diffractometer (Mo Kα radiation) using the $\theta/2\theta$ scan mode. Details are presented in Table I. Of the 4510 reflections monitored, 2911 reflections with $I > 2.5\sigma(I)$ were used in the structure solution. Final agreement indices of R = 6.3% and R_w = 7.3% resulted with hydrogens placed in calculated positions; all other atoms were refined anisotropically. A Pluto drawing is shown in Figure 1.

Results and Discussion

Two carbonyl ligands in Tp′W(CO)$_3$I are easily displaced by phenyl propyne in refluxing THF solution to yield dark green crystals of Tp′(CO)(I)W(PhC≡CMe) (**1**) upon recrystallization. This monomeric d^4 alkyne adduct displays spectral behavior (detailed in the Experimental Section) associated with "four-electron donor" alkyne complexes.[10] The signals at 208.9 and

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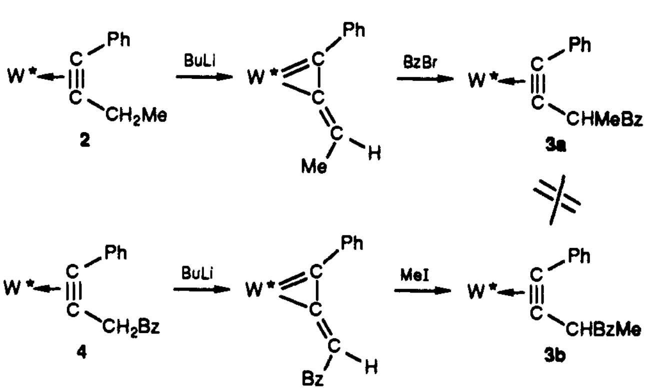
(10) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1.

Scheme I

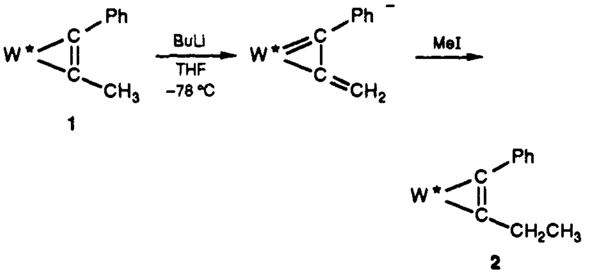


W* ≡ Tp′(CO)(I)W

BzBr ≡ PhCH$_2$Br

206.5 ppm in the ^{13}C NMR are assigned to the two alkyne carbons. These chemical shift values compare well with analogous signals of other four-electron donor internal alkyne complexes.

In a THF solution at −78 °C, the phenylpropyne complex **1** reacts with *n*-BuLi as evidenced by a color change from green to red. Quenching the reaction with methyl iodide yields the ethyl alkyne derivative **2** which can be synthesized independently by heating free phenylbutyne with Tp′W(CO)$_3$I. Presumably, the anionic η^2-allenyl complex, Li[Tp′(CO)(I)W(η^2-PhC=C=CH$_2$)], is the intermediate formed by deprotonation of the alkyne methyl substituent in this reaction (eq 4). The allenyl intermediate is very reactive and readily adds a proton to re-form the original alkyne.



(4)

W* = Tp′(CO)(I)W

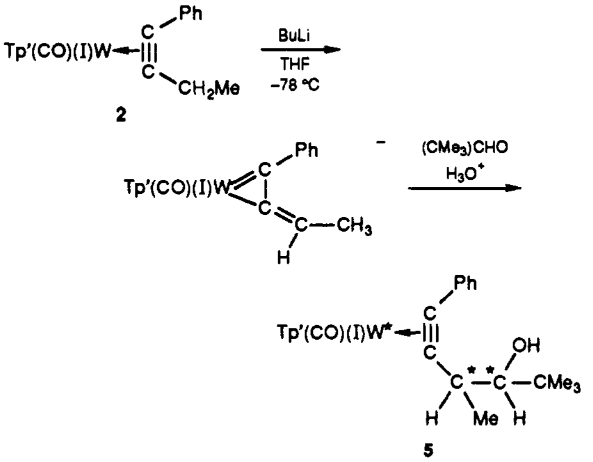
The ethyl alkyne derivative can be deprotonated at the methylene carbon, and addition of benzyl bromide (BzBr) to the resulting complex anion yields Tp′(CO)(I)W(PhC≡CCHMeBz) (**3a**) (Scheme I). Two chiral centers are present in the molecule, so diastereomers are possible. In order to confirm that the two possible isomers were generated as single diastereomers, we probed the diastereomer distribution of the crude reaction mixture. A ^{1}H NMR spectrum of the crude reaction mixture stripped to dryness and dissolved in CD$_2$Cl$_2$ prior to chromatography or recrystallization revealed only a single diastereomer. A COSY experiment on pure **3a** aided in the assignment of proton signals and located the second methylene proton, which is obscured by a Tp′ methyl signal, at 2.6 ppm.

The opposite diastereomer is formed by reversing the order of alkylations. Deprotonation of the alkyne in which the benzyl group is present, Tp′(CO)(I)W(PhC≡CCH$_2$CH$_2$Ph) (**4**), followed by addition of methyl iodide yields the opposite diastereomer, Tp′(CO)(I)W(PhC≡CCHBzMe) (**3b**) (Scheme I). Again, only a single diastereomer is evident in the ^{1}H NMR spectrum prior to chromatography and recrystallization.

Furthermore, pure **3a** and pure **3b** were combined to make two mixtures in ratios of 1:3 and 3:1 which were then passed through alumina columns separately. Elution with methylene chloride resulted in 1:3.06 and 2.93:1 mixtures of **3a**:**3b**. These results indicate that these diastereomers do not interconvert with each other nor do they separate under the experimental chromatography conditions we employed.

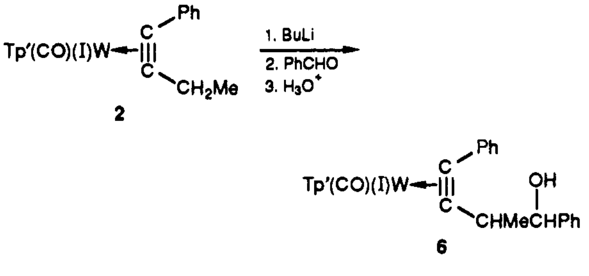
The C=CRH fragment of the anionic η^2-allenyl intermediate is surely planar, and evidently only a single *E*/*Z* isomer forms. Steric considerations must dictate that the electrophile, either MeI in the case of **3b** or BzBr in the formation of **3a**, approaches the allenyl intermediate preferentially from one side to yield a single diastereomer in each case. We have no information about the *E*/*Z* geometry of either allenyl intermediate, but since **3a** and **3b** are each generated separately as determined by ^{1}H NMR, it is clear that the facial selectivity in this system is excellent.

Aldehyde additions to the anionic η^2-allenyl complex, Li[Tp′(CO)(I)W(η^2-PhC=C=CHMe)], lead to alcohol products. Deprotonation of Tp′(CO)(I)W(PhC≡CCH$_2$CH$_3$), **2**, and reaction of the anionic η^2-allenyl intermediate with trimethylacetaldehyde at low temperature followed by an acid quench yields the alcohol product, Tp′(CO)(I)W(PhC≡CCHMeCH(OH)CMe$_3$) (**5**) (eq 5). A ^{1}H NMR spectrum of the crude product indicated the presence of a single diastereomer, an encouraging result given the presence of three chiral centers in the alcohol product. After chromatography and recrystallization a yield of 72% was realized.



(5)

Deprotonation of the 1-phenyl-but-1-yne complex, **2**, followed by addition to benzaldehyde gives an analogous alcohol product, **6** (eq 6).



(6)

Again three chiral centers are present in the molecule, so four potentially NMR distinguishable diastereomers could exist. ^{1}H NMR data for the crude product prior to recrystallization indicate the presence of two diastereomers in a 12:1 ratio. After recrystallization, only one diastereomer is detected by NMR of the dark green crystals.

The structure of the benzaldehyde addition product has been confirmed by a single-crystal X-ray analysis of a crystal selected from the major diastereomer product (Figure 1). The geometry of the metal alkyne fragment is typical of group VI d^4 monomers with a *cis*-(CO)M(RC≡CR) moiety.[10] Selected bond distances and angles are reported in Tables II and III, respectively. The alkyne lies roughly parallel to the metal carbonyl axis for well-known electronic reasons[11] (C$_1$WC$_3$C$_4$ torsion angle = 12.7°) and

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(11) (a) Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G. J.-J.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318. (b) Braterman, P. S.; Davidson, J. L.; Sharp, D. W. A. *J. Chem. Soc., Dalton Trans.* **1976**, 241. (c) Howard, J. A. K.; Stansfield, R. F. D.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1976**, 246.

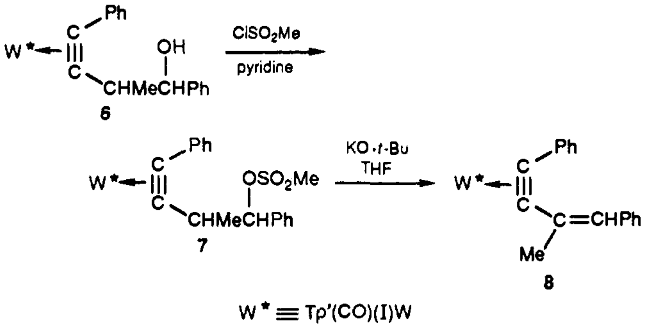
Table II. Selected Bond Distances (Å) for Tp′(CO)(I)W(PhC≡CCHMeCH(OH)Ph)

W(1)–I(1)	2.823 (2)	N(32)–C(33)	1.30 (2)
W(1)–C(1)	1.95 (2)	C(33)–C(34)	1.37 (3)
W(1)–C(3)	2.02 (2)	C(33)–C(36)	1.49 (3)
W(1)–C(4)	2.05 (2)	C(34)–C(35)	1.37 (3)
W(1)–N(31)	2.12 (2)	C(35)–C(37)	1.52 (3)
W(1)–N(41)	2.26 (1)	N(41)–N(42)	1.36 (2)
W(1)–N(51)	2.22 (2)	N(41)–C(45)	1.34 (2)
C(1)–O(1)	1.15 (2)	N(42)–C(43)	1.36 (2)
C(3)–C(4)	1.30 (3)	C(43)–C(44)	1.36 (3)
C(3)–C(11)	1.48 (3)	C(43)–C(46)	1.49 (3)
C(4)–C(5)	1.52 (3)	C(44)–C(45)	1.41 (3)
C(5)–C(6)	1.57 (3)	C(45)–C(47)	1.48 (3)
C(5)–C(7)	1.55 (3)	N(51)–N(52)	1.33 (2)
C(7)–O(8)	1.40 (3)	N(51)–C(55)	1.39 (3)
C(7)–C(21)	1.50 (3)	N(52)–C(53)	1.33 (2)
B(1)–N(32)	1.54 (3)	C(53)–C(54)	1.42 (3)
B(1)–N(42)	1.53 (3)	C(53)–C(56)	1.44 (3)
B(1)–N(52)	1.52 (3)	C(54)–C(55)	1.33 (3)
N(31)–N(32)	1.36 (2)	C(55)–C(57)	1.52 (3)
N(31)–C(35)	1.38 (3)		

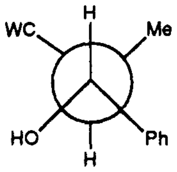
Table III. Selected Bond Angles (deg) of Tp′(CO)(I)W(PhC≡CCHMeCH(OH)Ph)

I(1)–W(1)–C(1)	91.5 (6)	N(31)–W(1)–N(51)	78.2 (6)
I(1)–W(1)–C(3)	105.2 (5)	N(41)–W(1)–N(51)	81.0 (5)
I(1)–W(1)–C(4)	98.5 (5)	W(1)–C(1)–O(1)	178 (2)
I(1)–W(1)–N(31)	163.6 (4)	W(1)–C(3)–C(4)	73 (1)
I(1)–W(1)–N(41)	86.2 (4)	W(1)–C(3)–C(11)	147 (1)
I(1)–W(1)–N(51)	86.4 (4)	C(4)–C(3)–C(11)	140 (2)
C(1)–W(1)–C(3)	108.8 (8)	W(1)–C(4)–C(3)	70 (1)
C(1)–W(1)–C(4)	72.4 (8)	W(1)–C(4)–C(5)	148 (1)
C(1)–W(1)–N(31)	93.3 (7)	C(3)–C(4)–C(5)	142 (2)
C(1)–W(1)–N(41)	168.1 (7)	C(4)–C(5)–C(6)	109 (2)
C(1)–W(1)–N(5)	87.2 (7)	C(4)–C(5)–C(7)	112 (2)
C(3)–W(1)–C(4)	37.3 (7)	C(6)–C(5)–C(7)	109 (2)
C(3)–W(1)–N(31)	88.0 (6)	C(5)–C(7)–O(8)	110 (2)
C(3)–W(1)–N(41)	83.1 (6)	C(5)–C(7)–C(21)	113 (2)
C(3)–W(1)–N(51)	159.6 (6)	O(8)–C(7)–C(21)	109 (2)
C(4)–W(1)–N(31)	97.9 (6)	C(3)–C(11)–C(12)	124 (2)
C(4)–W(1)–N(41)	119.5 (6)	C(3)–C(11)–C(16)	117 (2)
C(4)–W(1)–N(51)	159.1 (7)	C(7)–C(21)–C(22)	118 (2)
N(31)–W(1)–N(41)	85.8 (5)	C(7)–C(21)–C(26)	122 (2)

Scheme II



is tightly bound to tungsten (W–C3, 2.02 Å; W–C4, 2.05 Å). The conformation of the two chiral carbons in the solid state is staggered



with the hydroxy group anti to the methyl group ($C_6C_5C_7O_8$ torsion angle = 177°). The solution $^3J_{HH}$ value of 6.8 Hz linking C*H*MeC*H*Ph(OH) is also compatible with the anti disposition of these hydrogens found in the solid state.

Elimination of a molecule of water from the alcohol **6** to form the conjugated enyne product **8** was anticipated. However, it may be that the trans elimination geometry with H and OH anti to one another is unfavorable, as the molecule is reluctant to form the complexed enyne by elimination of water. In order to achieve elimination, the hydroxy proton was exchanged with a mesyl group by reacting **6** with methanesulfonyl chloride in pyridine to produce the isolable mesyl derivative **7** (Scheme II). Complex **7** was then reacted with potassium *tert*-butoxide in a THF solution to produce the conjugated enyne product Tp′(CO)(I)W(PhC≡CC(CH_3)=CHPh), **8**. In the ^1H NMR spectrum of **8**, a doublet with a coupling constant of 1.2 Hz was located at 2.61 ppm and assigned to the methyl group of the alkyne ligand. A two-dimensional (COSY) NMR experiment determined that the doublet at 2.61 ppm coupled to a signal at 7.72 ppm; this was assigned to the olefinic proton.

Conclusion

These regiospecific reactions demonstrate that propargylic anion equivalents can be readily generated from four electron donor alkynes. Subsequent alkyl additions to the propargylic anion are highly diastereoselective due to chirality at the tungsten center. Reaction of the propargylic anion with aldehyde reagents yields alcohol products. Work is in progress to define the scope of these alkyne elaboration reactions.

Acknowledgment. We gratefully acknowledge the National Science Foundation (CHE8907341) for support of this research.

Supplementary Material Available: Listings of atomic positions, thermal parameters, complete bond distances and angles, ORTEP diagram, and labeled figure (11 pages); tables of observed and calculated structure factors (15 pages). Ordering information is given on any current masthead page.