Mechanisms by which Alkynes React with CpCr(CO)₃H. Application to Radical Cyclization
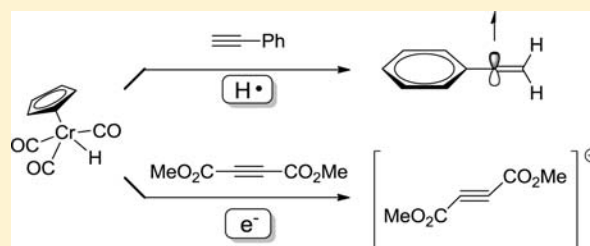
Deven P. Estes, Jack R. Norton,* Steffen Jockusch, and Wesley Sattler

Department of Chemistry, Columbia University, 3000 Broadway, New York, New York 10027, United States
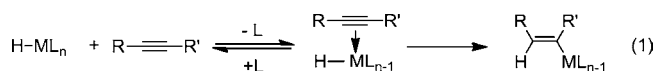
S *Supporting Information*

ABSTRACT: The reaction of CpCr(CO)₃H with activated alkynes in benzene has been examined. The kinetics of these reactions have been studied with various alkynes, along with the stereochemistry with which the alkynes are hydrogenated. The hydrogenation of phenyl acetylene and diphenyl acetylene with CpCr(CO)₃H has been shown to occur by a hydrogen atom transfer (HAT) mechanism. The reaction of CpCr(CO)₃H with dimethyl acetylenedicarboxylate (DMAD) produced hydrogenated products as well as phenyl substitution from reaction with solvent. On the basis of kinetic data, it is thought that the reaction of DMAD may proceed via a single electron transfer (SET) as the rate-determining step. The radical anion of dimethylfumarate was observed by EPR spectroscopy during the course of the reaction, supporting this claim. The aromatic 1,6 eneyne (**8**) gave cyclized products in 78% yield under catalytic conditions (35 psi H₂), presumably by the 5-exo-trig cyclization of the vinyl radical arising from H• transfer. Using a cobaloxime catalyst (**12**) hydrogenation was completely eliminated to yield 100% cyclized products.
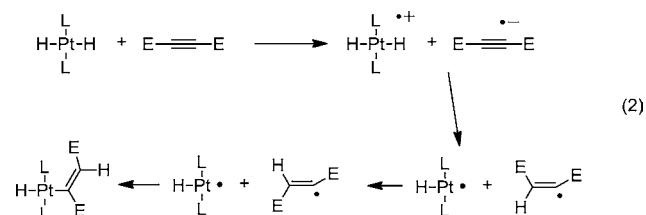
INTRODUCTION

A variety of mechanisms have been proposed for the reactions of alkynes with transition-metal hydrides. The most common of these (eq 1) involves coordination of the alkyne to the metal,

$$H\text{-}ML_n + R\text{---}R' \underset{+L}{\overset{-L}{\rightleftharpoons}} \begin{matrix} R\text{---}R' \\ | \\ H\text{---}ML_{n-1} \end{matrix} \longrightarrow \begin{matrix} R \quad R' \\ \diagup \diagdown \\ H \quad ML_{n-1} \end{matrix} \quad (1)$$

followed by its insertion into the M–H bond.[1] This mechanism results in syn addition of the M–H to the triple bond, and gives a Z-alkene after protolytic cleavage of the M–C bond.

However, there are a number of reports of the anti addition of M–H to alkynes, resulting in E-olefins after protonolysis.[2] Several mechanisms have been offered to explain this, one of which involves radicals. Clark has proposed that the platinum dihydride in eq 2 transfers first an electron and then a proton to

$$\begin{matrix} L \\ | \\ H\text{-}Pt\text{-}H \\ | \\ L \end{matrix} + E\text{---}E \longrightarrow \begin{matrix} L \\ | \\ H\text{-}Pt\text{-}H \\ | \\ L \end{matrix}^{\bullet+} + E\text{---}E^{\bullet-}$$

$$(2)$$

an electron-poor alkyne, producing a vinyl radical; isomerization of that radical, coordination, and reductive elimination give an E-olefin.[2b]

Transition-metal hydrides with weak metal–hydrogen bonds have been shown to donate H• to appropriately activated C=C bonds, giving carbon-centered radicals.[3] While originally

used to effect hydrogenation, this reaction has also been used in the catalysis of chain transfer during radical polymerizations,[4] and in the initiation of radical cyclizations.[5] However, H• transfer to C≡C, forming vinyl radicals, has seldom been observed.[2h,i] Ungváry reported, on the basis of CIDNP evidence, the transfer of H• to phenylacetylene during hydroformylation by HCo(CO)₄.[2i] Gridnev and Wayland also observed trans selectivity in the reaction of cobalt porphyrin hydrides with various alkynes and assumed a radical mechanism.[2h] One expects HAT to C≡C to be slower than transfer to C=C because alkynes react with radicals more slowly than olefins do.[6]

We have recently shown that, under H₂, CpCr(CO)₃H *catalyzes* the transfer of H• and effects the cyclization of various dienes by a radical mechanism.[5a] We next considered the possibility of using vinyl radicals generated by HAT to alkynes. Despite the fact that alkynes react more slowly, vinyl radicals are less stable, and should cyclize faster, than the RO₂C(Me)-CR• radicals we have been making (by H• transfer to acrylates), minimizing the formation of hydrogenated products. We have demonstrated here that it is possible to form vinyl radicals from HAT to some alkynes, while others react by different mechanisms. We have also shown that we can cyclize an appropriate *enyne* by a radical mechanism.

EXPERIMENTAL SECTION

All manipulations were performed under an argon atmosphere using standard Schlenk or inert atmosphere box techniques. NMR spectra

were taken on either a Bruker 300, 400, or 500 MHz spectrometer. IR spectra were taken with a Perkin-Elmer Spectrum 2000 FT-IR spectrometer. Gas chromatography was performed on a HP-5890A gas chromatograph utilizing a DB-5 column with He as the carrier gas. X-ray diffraction data were collected on a Bruker Apex II diffractometer. Crystal data, data collection and refinement parameters are summarized in the Supporting Information (SI) (Table S1). The structures were solved using direct methods and standard difference map techniques, and were refined by full matrix least-squares procedures on F^2 with SHELXTL (Version 6.1).[7] Benzene and THF were distilled from Na/benzophenone ketyl and stored over 3 Å molecular sieves. Benzene-d_6 (Cambridge Isotope Laboratories) was dried by distillation from CaH$_2$ and then deoxygenated by three freeze−pump−thaw cycles. All liquids were dried by distillation from CaH$_2$ and then deoxygenated by three freeze−pump−thaw cycles and stored under an argon atmosphere. Phenylacetylene, phenylacetylene-d_1, methyl propiolate, diphenylacetylene, dimethyl acetylenedicarboxylate, and di-*tert*-butyl acetylenedicarboxylate were purchased from commercial sources.

Materials. CpCr(CO)$_3$H and CpCr(CO)$_3$D were synthesized by known procedures and sublimed prior to use.[8] Methyl propiolate-d_1,[9] dimethylphenylmaleate,[10] and the cobaloxime **12**[11] were also synthesized by literature procedures.

(3-(2-Ethynylphenyl)prop-1-ene-1,1-diyl)dibenzene (8). To a solution of 2-bromo-phenylethynyltrimethylsilane (1.58 mmol) in THF (16 mL) was added ^{n}BuLi (1.74 mmol, 1.1 equiv) at −78 °C and stirred for 20 min. CuCN (71 mg, 0.79 mmol) was then added to the solution and the temperature raised to −20 °C for 20 minutes after which time the solution turned from yellow to pale pink. The solution was returned to −78 °C, and 3-bromo-1,1-diphenyl-prop-1-ene (431 mg, 1.58 mmol in 1 mL THF) was added dropwise, and the mixture was brought to room temperature slowly and stirred overnight. The reaction was quenched with NH$_4$Cl, extracted with ether (50 mL, 3 times), and dried with MgSO$_4$ and the solvent was removed.

To this crude mixture in 5 mL of 10:1 THF/H$_2$O was added dropwise a solution of 0.45 g of tetrabutylammonium fluoride dissolved in 2 mL of the same solvent mixture at 0 °C. This was stirred for 12 h and worked up in the same manner as before. This was then isolated (clear oil, 199 mg, 43% yield) from a silica column using a 4% toluene in hexane mixture as mobile phase (R_f = 0.19). ^{1}H NMR (300 MHz, CDCl$_3$, δ), 7.49−7.13 (m, 14H, ArH), 6.27 (t (*J* = 7.5 Hz), 1H, =C−H), 3.66 (d (*J* = 7.5 Hz), 2H, CH$_2$) 3.19 (s, 1H, ≡C−H). ^{13}C NMR (100 MHz, CDCl$_3$, δ) 143, 142.7, 142.4, 139.8, 132.9, 130.0, 129.0, 128.6, 128.3, 128.1, 127.4, 127.1, 127.04, 127.00, 126.0, 121.6, 82.2, 81.3, 34.5. IR (neat) 3293 (≡C−H stretch), 2104 (C≡C stretch), 1598 (ring stretch), 700 (≡C−H bend). MS (APCI) 295 [M + 1]$^+$.

Procedure for Cyclizations. *Caution! All reactions under gas pressure should be properly shielded!* A solution of (3-(2-ethynylphenyl)-prop-1-ene-1,1-diyl)dibenzene (**8**) (0.187 mmol) and CpCr(CO)$_3$H (0.014 mmol) in benzene (0.5 mL) was added to a Fischer−Porter reactor that was subsequently charged with an appropriate pressure of H$_2$. This reaction was then heated with vigorous stirring until the reaction was over, during which time the green color changed to brown and then to greenish-gray once the starting material had been consumed (no color change observed with cobaloxime **12**). For details of compound isolation see SI.

2-Benzhydryl-3-methyl-1H-indene (10). ^{1}H NMR (300 MHz, CDCl$_3$, δ) 7.30−7.16 (m, 14H, ArH), 5.53 (s, 1H, CPh$_2$H), 3.19 (q (*J* = 1.9 Hz), 2H, CH$_2$), 2.08 (t (*J* = 1.9 Hz), 3H, CH$_3$) (long-range coupling confirmed by COSY). ^{13}C NMR (75 MHz, CDCl$_3$) 146.9, 143.75, 143.0, 135.2, 129.2, 128.4, 128.0, 126.4, 124.4, 123.4, 118.8, 50.2, 39.8, 10.8 IR (neat) 3056, 3024 (sp^2 C−H stretch), 2962, 2918(sp^3 C−H stretch) cm^{-1} MS (APCI) 167 [CH(Ph)$_2$]$^+$, 295 [M − 1]$^+$, 329 [M + 33]$^+$

(3-(2-Ethylphenyl)prop-1-ene-1,1-diyl)dibenzene (9). ^{1}H NMR (300 MHz, CDCl$_3$, δ) 7.41−7.16 (m, 14H, ArH), 6.20 (t (*J* = 7.5 Hz), 1H, =C−H), 3.47 (d (*J* = 7.5 Hz), 2H, CH$_2$−CH=), 2.54 (q (*J* = 7.5 Hz), 2H, CH$_2$−CH$_3$), 1.12 (t (*J* = 7.5 Hz), 3H, CH$_3$). ^{13}C NMR (100 MHz, CDCl$_3$, δ) 142.50, 142.25, 142.19, 139.88, 138.59, 129.90,

129.04, 128.40, 128.28, 128.12, 127.96, 127.36, 127.17, 127.02, 126.40, 125.99, 33.12, 25.70, 14.96. IR (neat) 3060, 3023 (sp^2 C−H stretch), 2962, 2922, 2852 (sp^3 C−H stretch), MS (APCI) 299 [M + 1].

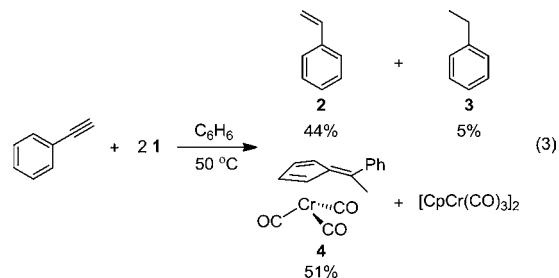*2-(Diphenylmethylene)-1-methyl-2,3-dihydro-1H-indene (11).* ^{1}H NMR (300 MHz, CDCl$_3$, δ) 7.37−7.14 (m, 14H, ArH), 4.14 (q (*J* = 7.0 Hz), 1H, C−H), 3.81 (AB system (*J* = 21 Hz, Δν = 263.7 Hz), 2H, inequivalent CH$_2$ pair) 1.08 (d (*J* = 7.0 Hz), 3H, CH$_3$). ^{13}C NMR (125 MHz, CDCl$_3$, δ) 147.6, 144.3, 143.0, 142.5, 141.1, 136.3, 129.5, 129.0, 128.5, 128.2, 126.71, 127.66, 126.60, 124.4, 123.8, 43.6, 37.9, 21.4 IR (neat) 3079, 3056, 3020 (sp^2 C−H stretch), 2962, 2922, 2860 (sp^3 C−H stretch) cm^{-1}. MS (FAB) 295 [M − 1]

Kinetic Measurements. Stock solutions (C$_6$D$_6$) of both CpCr-(CO)$_3$H and the appropriate alkyne were added separately to a J-Young NMR tube and frozen in two layers with appropriate concentrations to achieve a 10-fold excess of alkyne. This was kept frozen until the experiment began, when it was quickly melted, mixed, and inserted into the probe of a 500 MHz NMR spectrometer which had been equilibrated to 50.0 (±0.5)°C using an ethylene glycol chemical shift thermometer. Spectra were taken every 3 min, and the intensity of the hydride resonance (δ −5.6) was compared with that of an internal standard (hexamethylcyclotrisiloxane). Reactions were monitored through at least three half-lives and fit to a first-order exponential. The product peaks from the reaction with DMAD were fit to the model in Scheme S1 (SI) using *Kintecus* kinetic modeling software.[12] Reported rate constants other than that for phenylacetylene are the average of three kinetic runs.

EPR Measurements. X-band EPR spectra were taken on a Bruker EMX spectrometer at ambient temperature in benzene in 4 mm J-Young style tubes (concentrations of organic reactants were ∼1 M). *g* values were calculated by comparison with an internal sample of TEMPO (*g* = 2.00623).[13] EPR simulations were done with Bruker's Simphonia software.[14] EPR spectra not included in the text can be found in the SI.

■ RESULTS AND DISCUSSION

Unactivated alkynes such as TMSC≡CH and 1-octyne proved unreactive. However, aryl alkynes, such as phenylacetylene, are readily consumed by CpCr(CO)$_3$H (**1**). The reaction of phenylacetylene (0.044 M) with 2 equiv of **1** (0.088 M) yields the products shown in eq 3. The major products are styrene

(44%), ethylbenzene (5%), and the organometallic complex **4** (51%). Crystals of **4** were identified by X-ray crystallography as the fulvene complex (Figure 1); its structure is similar to that of known fulvene complexes[15] (see SI for structural parameters).

The observation of **4** made us question whether H• transfer was occurring. In order to determine whether the addition of M−H was syn or anti we treated phenylacetylene-d_1 with **1**. We obtained *cis*- and *trans*-styrene-d_1 in a 1:1 ratio, consistent with the mechanism in Scheme 1. Donation of an H• to the terminal carbon of phenylacetylene will give the vinyl radical **5**, which is linear.[16] Transfer of a second H• from **1** will not be affected by the position of the deuterium, so there will be a 1:1 *E*:*Z* (**7**:**6**) ratio for the resulting styrene-d_1. The same result has been reported by Ungváry for the reaction of phenylacetylene-d_1 with HCo(CO)$_4$.[2i]
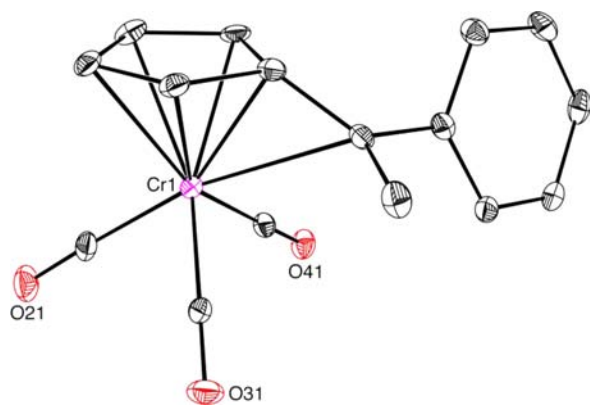
Figure 1. X-ray structure of **4** (20% ellipsoids, hydrogens omitted for clarity).
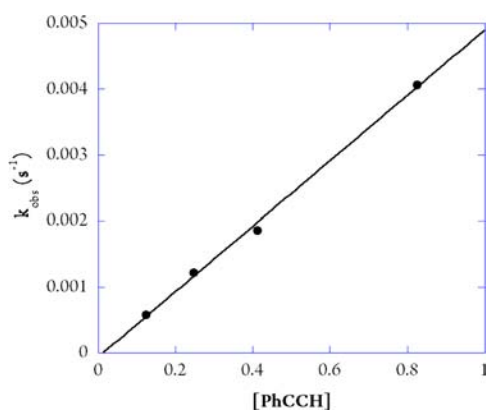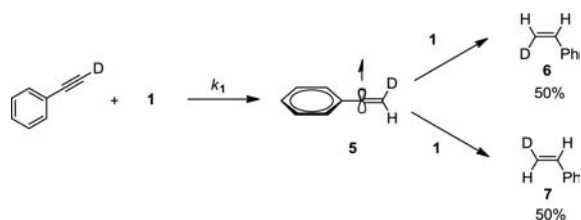

Figure 2. Kinetics of HAT from **1** to phenyl acetylene.

Scheme 1

Further evidence for a radical mechanism is offered by comparing the rate constant for phenylacetylene/**1** with that for styrene/**1**. When we treat **1** (0.012 M) with a 10-fold excess of phenylacetylene (≥0.124 M), the amounts of **3** and **4** that form are very small, i.e., the yield of styrene is greater than 95%. The disappearance of **1** is first order, and k_{obs} is linear in [PhC≡CH] (Figure 2), showing the rate law to be that in eq 4.

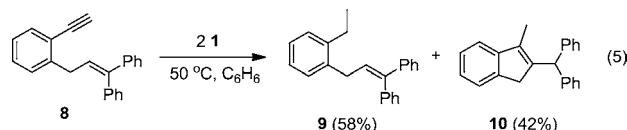$$-\frac{d[\mathbf{1}]}{dt} = 2k_1[\mathbf{1}][PhC\equiv CH] \qquad (4)$$

The resulting rate constant (k_1) ((2.5 ± 0.1) × 10^{-3} M^{-1} s^{-1}) for HAT to PhC≡CH is 6 times slower than k_H for HAT from **1** to styrene.[3b] The ratio is very similar to that (1:6) for the addition of the ^{t}Bu radical to PhC≡CH/PhCH=CH$_2$.[6] The similarity in the rate constant ratio strongly supports our description of eq 3 as a H• transfer process.
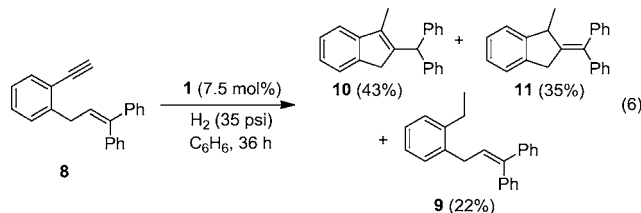
The CrH/CrD isotope effect cannot be measured accurately because of the competition between back transfer and hydrogenation after the initial H• transfer. With CpCr(CO)$_3$D,

for example, back transfer of H• competes not only with back transfer of D• but also with addition of a second D•; both styrene and phenylacetylene-d_1 are products. Addition of excess CpCr(CO)$_3$• favors exchange over hydrogenation and allows estimation of k_H/k_D as 0.2—substantially inverse.
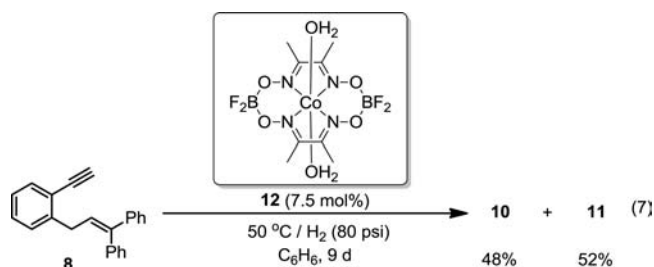
In view of the fact that **1** does transfer H• to phenyl-acetylene, we designed a substrate that could be cyclized by that reaction. The ease of transfer to phenylacetylene suggested the enyne **8**. (Our previous work[3b] showed that HAT to 1,1-diphenyl-1-propene was very slow.) When we treated **8** with a stoichiometric amount (2 equiv) of **1**, we obtained the indene product **10** in 42% yield, with the balance being the hydrogenated product **9**.

Under H$_2$ pressure in the presence of a catalytic amount of **1**, **10** was formed in 43% yield along with 22% of **9** and 35% of the double bond isomer **11**, for a total of 78% cyclized material.
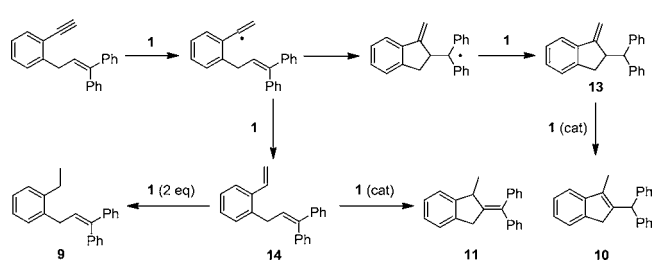

With our recently discovered cobaloxime catalyst **12**, **8** gives only **10** and **11** in 48% and 52% yields, respectively (eq 7).[17] This is expected since the cobalt hydride is created in situ in very small concentrations, making this catalyst good at suppressing hydrogenation.

The mechanism is probably that shown in Scheme 2. The vinyl radical produced by the initial H• transfer cyclizes to make **13**. A second H• transfer, from **1** to the methylene in **13**, then isomerizes the double bond in **13** to an internal position,

Scheme 2

giving **10**; the fact that no **13** accumulates implies that isomerization to **10** is fast. The same vinyl radical which made **13** can also react with **1** to form styryl compound **14**, which can further hydrogenate to form **9** or cyclize to form **11**.

In order to study the effect of substitution we next studied diphenylacetylene. Treating PhC≡CPh with **1** gave only the expected hydrogenation products, *E*- and *Z*-stilbene, as observed by GC, with no further hydrogenation.

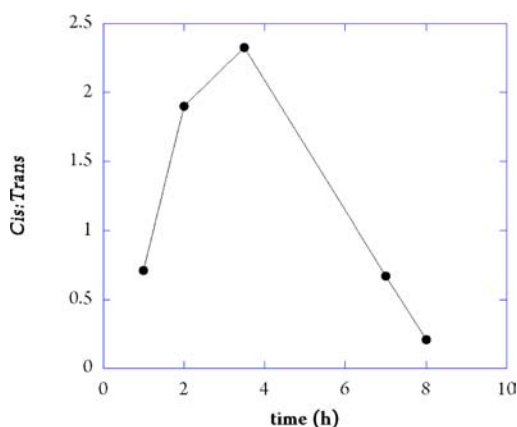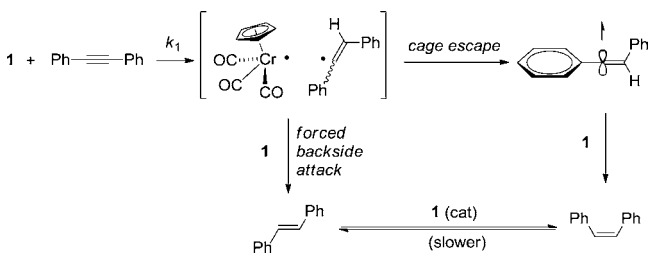**Figure 3.** Time dependence of cis/trans ratio in diphenyl acetylene hydrogenation.

The rate constant for HAT ($k_1 = (1.4 \pm 0.3) \times 10^{-4}$ M^{-1} s^{-1}) was approximately 20 times smaller than that of PhC≡CH, similar to the pattern seen for substituted alkenes.[3b] This trend strongly suggests that the key step is HAT.

The cis/trans ratio was not constant over the course of the reaction, beginning with a slight preference for trans, then favoring cis formation, but ending with predominantly trans (Figure 2).

We propose the mechanism in Scheme 3 to explain this variation over time. The initial product of the HAT from
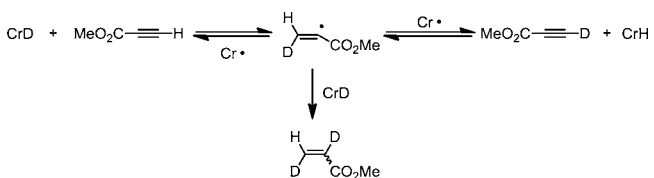
Scheme 3

CpCr(CO)$_3$H to PhC≡CPh is presumably a radical cage, with the Cr remaining near the hydrogen it has just transferred; the second CpCr(CO)$_3$H will prefer to approach the *caged* vinyl radical on the side away from the first Cr (and the H), and will give predominantly trans (*E*) product. Later, when the lower [**1**] permits cage escape, the *free* vinyl radical will prefer approach on the same side as the first hydrogen and give largely *Z*-stilbene. Eventually cis/trans isomerization, catalyzed by reversible H● transfer, will move toward the largely *E* equilibrium mixture (the thermodynamic ratio is known[18] to be 99.8:0.2).

REACTION OF CPCR(CO)$_3$H WITH ELECTRON-POOR ALKYNES

Treating methyl propiolate (0.0365 M) with stoichiometric **1** (2 equiv) produced methyl acrylate (39%) as well as small oligomers (confirmed by mass spectrometry and ^{1}H NMR) of the methyl propiolate. Larger concentrations (0.58 M) of propiolate gave lower yields of acrylate, presumably because the amount of oligomerization increases.

When we treat **1**-d_1 with excess methyl propiolate, only hydrogenation occurs. When we carry out this reaction in the presence of excess CpCr(CO)$_3$● (**15**) (in equilibrium with the dimer [CpCr(CO)$_3$]$_2$[19]) H/D exchange is observed at the start of the reaction, showing the intermediacy of a vinyl radical (Scheme 4). (We have found the addition of the metalloradical
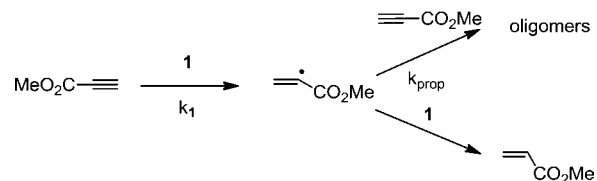
Scheme 4

15 to be a useful general method for observing H/D exchange in the absence of other reactions.) The vinyl radical will *not* be linear, but will invert rapidly,[16a] and both cis and trans acrylate esters will be formed (a cis/trans of 1.4:1 is observed).
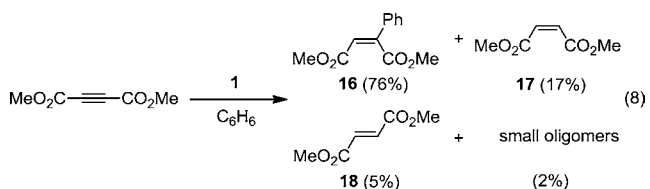
In the presence of a large excess of methyl propiolate, the reaction is first order in **1**. Given the small chain length of the oligomers and assuming rapid chain propagation, the rate law for Scheme 5 will be the same as that for phenyl acetylene (eq

Scheme 5

4), with $k_1 = (3.2 \pm 0.3) \times 10^{-4}$ M^{-1} s^{-1}. The overall mechanism is that in Scheme 5; after rate-determining HAT, the vinyl radical either hydrogenates by reaction with **1** or adds to propiolate to make an oligomer.

Treating dimethyl acetylenedicarboxylate with **1** (eq 8) gave **16** as the major product (76%) in addition to **17** (17%), **18**

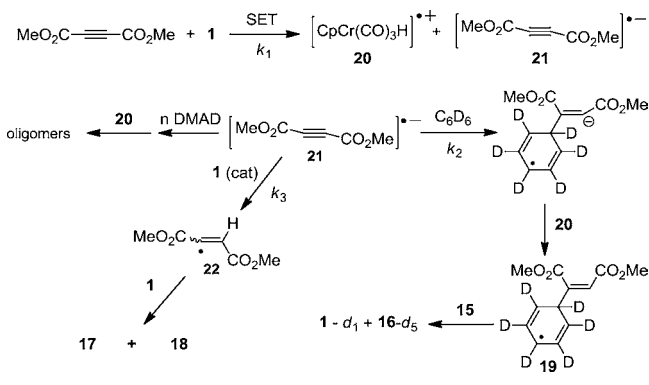(5%), and oligomers as big as tetramers (2%) as minor products. There was a 4:1 preference for the cis hydrogenation product **17** over the trans product **18**.

The appearance of **16** makes a HAT mechanism seem less likely. No phenyl-substituted product was seen with methyl propiolate, implying that the reactivity is very different. While attack on benzene by vinyl radicals is known,[20] it is generally

intramolecular and occurs more readily for unstabilized vinyl radicals (although more reactive radicals such as HO• readily attack benzene).[21] A SET mechanism (similar to that of Clark[2b]) could explain the presence of **16** (Scheme 6).

Scheme 6

The ratio of **17** to **18** remains constant throughout the reaction, but the ratio of **16** to the sum of **17** and **18** increases as the reaction continues. This variation in product ratio excludes a HAT (giving **17** and **18**) parallel to SET (giving **16**). Indeed, it proved impossible to simulate the kinetics[12] on this basis.

The initial reaction is probably formation of an ion pair **20**/**21** (Tilset and Parker have made cation **20** electrochemically, in a quasi-reversible fashion, and found it to be very acidic.[22]) After escape, the free radical anion **21** (which is probably in a trans-bent form[23]) will react with either benzene, **1**, or DMAD (the predominant species). With benzene, **21** will give **19** and eventually **16**. With **1**, **21** will be protonated to the vinyl radical **22** (presumably nonlinear, cf. the radical from methyl propiolate above). With DMAD, **21** will give oligomers (vide infra). There is literature precedent for the attack of anion radicals ($SO_4^{-\bullet}$,[24] $HPO_4^{-\bullet}$,[25] and $O^{-\bullet24c}$) on aromatic compounds (including benzene) and for the formation of oligomer from **21** and DMAD.[26]

The mechanism in Scheme 6 was used to fit the concentration profiles of **16**, **17**, and **18** using *Kintecus* kinetic modeling software[12] (see SI for full details and fits). The rate constants k_1, k_2, and k_3 were optimized respectively as $(9.9 \pm 0.2) \times 10^{-3}$ M^{-1} s^{-1}, (12.5 ± 0.3) s^{-1}, and (850 ± 10) M^{-1} s^{-1}. The rate constant k_1 for electron transfer to DMAD is over 30 times *greater* than the rate constant k_1 for HAT to methyl propiolate.

Electron transfer from inorganic reductants such as iodide and thiocyanate has been observed to be 2000 times faster to DMAD than to methyl propiolate.[26] Irreversible reduction potentials[27] are available for many alkynes, even though they do not tell us the thermodynamics of electron transfer to these alkynes. Table 1 shows the reduction potential and the HAT rate constant for each alkyne studied. A plot of these irreversible potentials vs the rate constants k_1 (Figure 4) offers a strong argument for a change in mechanism between phenylacetylene and DMAD.

In order to further study the reaction of DMAD with **1**, we followed the reaction by EPR spectroscopy at room temperature. The EPR spectra produced during the course of the reaction are shown in Figure 5 as a function of time. The first signal to appear (radical c) is a triplet of septets ($a_1 = 1.0$ G

Table 1. k_1 Values and Reduction Potentials of Alkynes

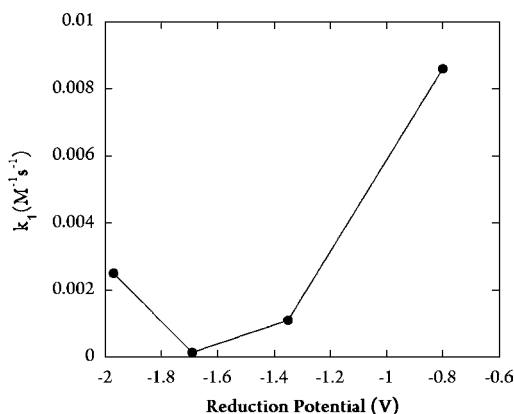| Alkyne	$k_1 (\times 10^3)(M^{-1}s^{-1})$	Reduction Potential (V)
≡—Ph	$2.5(\pm 0.1)$	-1.97
≡—CO$_2$Me	$0.32(\pm 0.03)$	-1.35
Ph—≡—Ph	$0.14(\pm 0.03)$	-1.69
MeO$_2$C—≡—CO$_2$Me	$9.9(\pm 2)$	-0.8

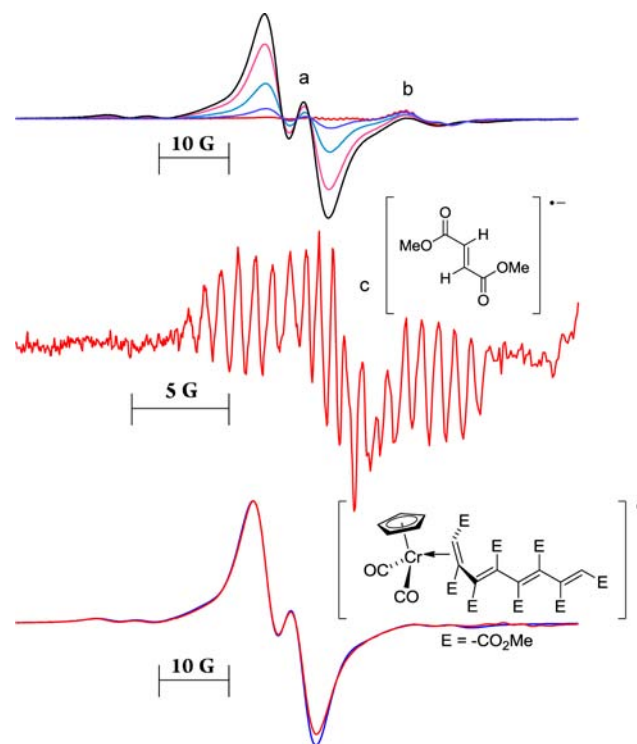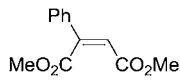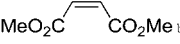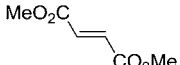**Figure 4.** Rate constants (k_1) vs alkyne reduction potential.

Figure 5. EPR spectra from reaction of DMAD with **1**. (Top) Stacked spectra over time. (Middle) Signal attributed to the fumarate radical anion (spectrum obtained by scaled subtraction of other signals). (Bottom) Doublet signal attributed to the oligomer spin adduct (Simulation in blue).

(6H), a_2 = 5.4 G (2H), Figure 5 middle) which has a g value of 2.0044. When the reaction is run with $\mathbf{1}$-d_1, the larger triplet coupling fades (see SI for EPR spectra). When the methyl esters are replaced with ^{t}Bu esters, the septet coupling disappears. These data match the EPR spectrum of the dimethyl fumarate radical anion, previously reported in liquid ammonia at -50 °C.[28] Observation of the dimethyl fumarate radical anion supports our claim that electron transfer from $\mathbf{1}$ to electron-poor alkenes and alkynes is possible. This signal is not observed when $\mathbf{1}$ reacts directly with dimethyl fumarate, most likely due to its poor solubility in benzene.

Two more major EPR signals appear over the course of the reaction. The first (signal b) is a broad singlet with a g value of 1.9990 whose appearance coincides with the disappearance of the fumarate radical anion. The second (signal a) is a broad doublet with a g value of 2.0093 which persists after the reaction is over. This second signal shows coupling to one proton (which disappears when the reaction is run with $\mathbf{1}$-d_1) and satellites due to coupling to one chromium atom (^{53}Cr I = $^3/_2$, 9.55% abundance). Appearance of this radical corresponds to disappearance of the previous radical. Simulated parameters for all Cr-centered radicals are given in Table 2.

Table 2. Spin Adducts of CpCr(CO)$_3$• with Alkenes

Alkene	g^a	a_H (G)	a_{Cr} (G)
Signal a	2.0093	4.95 (d)	14.85
Signal b^b	1.9990	--------	--------
Ph / MeO$_2$C / CO$_2$Me	2.0095	6.60 (d)	14.45
MeO$_2$C / CO$_2$Me $_{b,c}$	--------	5.1 (t)	--------
MeO$_2$C / CO$_2$Me $_c$	--------	4.6 (t)	14.7

^{a}Referenced to TEMPO.[13] ^{b}^{53}Cr satellites were too low in intensity to obtain an accurate a value. ^{c}Since their multiplicity automatically ruled them out as candidates for the identity of a and b, their g value was not determined.

Compound $\mathbf{15}$ is known to form complexes (so-called "spin adducts") with alkenes under ambient conditions (thought to occur by substitution of CO) that have similar ^{53}Cr coupling and g values to that of both these radicals.[29] Assignment as spin adducts makes sense given the amount of $\mathbf{15}$ which is being produced in this reaction. However, spin adducts with $\mathbf{16}$, $\mathbf{17}$, and $\mathbf{18}$ do not match the observed spectra (see Table 2).

The assignment of signal b as a spin adduct with solvent, similar to the one seen with toluene,[29] is tentative but reasonable. An oligomer could displace benzene to create the final signal. Since only one of the double bonds could be coordinated at a time, binding to an end group would give rise to a doublet due to coupling with only one vinyl proton. This signal was reproduced with low intensity from a mixture of $\mathbf{15}$ with DMAD laced with trace oligomer impurity (see SI). Under the conditions of the EPR experiment (1.35 M DMAD),

oligomers are one of the major products and thus more likely to form a spin adduct with $\mathbf{15}$.

CONCLUSIONS

In conclusion we have shown that transition-metal hydrides with weak M−H bonds can react with activated alkynes by different mechanisms, (1) H• transfer or (2) electron transfer. H• transfer can be used to effect the catalytic cyclization of an appropriate eneyne. Electron transfer gives radical anions reactive enough to add to benzene.

ASSOCIATED CONTENT

S **Supporting Information**

Synthetic details, compound characterization, kinetic traces, crystallographic information file (CIF), X-ray structural parameters, and EPR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

jrn11@columbia.edu

Notes

The authors declare no competing financial interest.

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