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Further studies of the synthesis of 1-naphthols and 4-hydroxy-5,6-dimethylbenzothiophene by protonation of $Cp(CO)_2W{\equiv}CTol$ and $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$ in the presence of alkynes and carbon monoxide *

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Abstract

The previously reported (K.E. Garrett et al., *J. Am. Chem. Soc.*, 111 (1989) 8383) preparation of a naphthol derivative by protonation of $Cp(CO)_2W{\equiv}CTol$ in the presence of $MeC{\equiv}CMe$ has been extended to a variety of other alkynes ($EtC{\equiv}CEt$, $HC{\equiv}C^nPr$, $HC{\equiv}C^iPr$, $HC{\equiv}C^tBu$, $MeC{\equiv}C^nPr$, $MeC{\equiv}C^iPr$). Naphthols were produced in each case with the terminal alkynes giving complete regioselectivity for the isomer with the alkyne hydrogen substituent located adjacent to the hydroxy group of the naphthol. This is exactly opposite to the regiochemistry typically observed for Dötz-type benzannulation reactions using $(CO)_5Cr{=}C(OR)R'$ complexes. Also reported is the crystal structure of the thiophene-substituted carbyne complex $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$ and its reaction with $MeC{\equiv}CMe$ to form 4-hydroxy-5,6-dimethylbenzothiophene.

Introduction

An important application of transition metal carbene complexes in organic synthesis is that developed by Dötz and co-workers involving the combination of alkynes, CO and carbene ligands to yield naphthol derivatives, eq. 1 [1–3], with the assembly of the product occurring as indicated in I. This reaction has been extensively explored since its discovery in 1975, and many of the factors which

* Dedicated to Professor F.G.A. Stone on the occasion of his 65th birthday.

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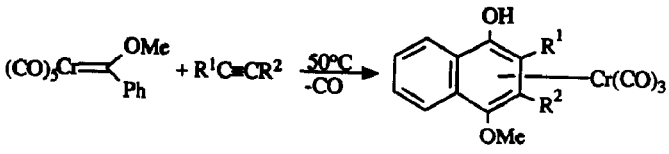
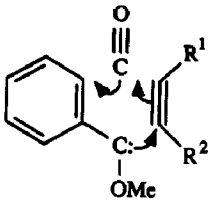


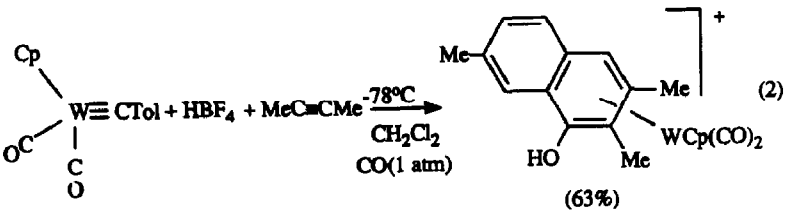
(1)



I

control yields and selectivity of products are now relatively well understood. With the chromium carbene complex $(CO)_5Cr{=}C(OR)R'$, the regiochemistry of the reaction is such that terminal alkynes always give a naphthol product having the hydrogen substituent from the alkyne located adjacent to the original carbene carbon (R^2 in eq. 1) [4–6]. A similar selectivity is obtained with internal alkynes which preferentially form the naphthol product having the smaller of the alkyne substituents adjacent to the carbene carbon, with the regioselectivity ranging from ~ 66–100% [4–6].

We recently reported that a Dötz-type reaction occurs when $Cp(CO)_2W{\equiv}CTol$, **1**, is protonated in the presence of MeC≡CMe and CO, eq. 2, by a pathway involving the initial formation of the electrophilic carbene complex $[Cp(CO)_2W{=}CHTol]^+$, **2**



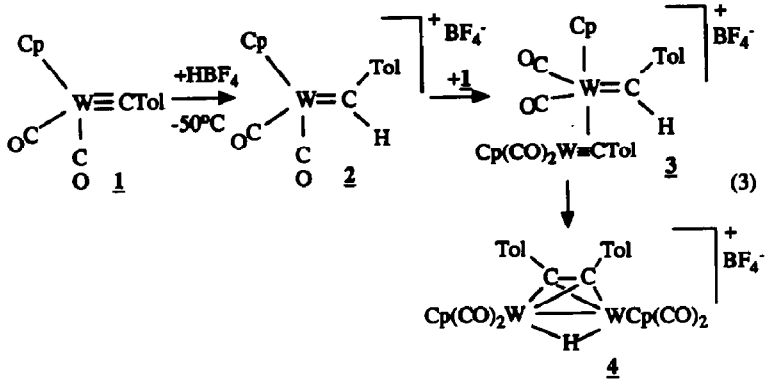
(2)

(63%)

[7]. The impetus for that study was a report by Stone and coworkers who showed that protonation of $Cp(CO)_2W{\equiv}CTol$ at $-50\,^{\circ}C$ led to the formation of binuclear complex **4** by a mechanism proposed to proceed via carbene complex **2**, eq. 3 [8]. We report herein a more extensive evaluation of the range of alkynes that can be employed in reaction 2 and particularly the regiochemistry of alkyne incorporation. The significant finding is that the regiochemistry of alkyne incorporation is exactly opposite to that previously noted for $(CO)_5Cr{=}C(OR)R'$ complexes [4–6]. Also described are the synthesis and protonation reactions of the thiophene substituted carbyne complex $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$.

Results

Protonation of carbyne complex **1** in the presence of a variety of alkynes has been found to lead to the formation of naphthol complexes analogous to that shown in eq. 2. In the present study, no attempt was made to characterize these initially



formed complexes, but rather solutions of these species were stirred in air for 24 h to release the free naphthols which were then isolated and spectroscopically characterized. Table 1 lists the alkynes which have been found to produce naphthols by this method and the yields of the products obtained. Each of the naphthols were characterized by ^{1}H NMR and high resolution mass spectrometry. In their ^{1}H NMR spectra, they each showed a singlet for H^8 in the δ 7.7–7.9 region and doublets near δ 7.6 and 7.2 (J(HH) = 6.6–9.0 Hz) respectively assigned to the coupled protons H^6 and H^5 (see drawing). The H^4 and H^2 protons appeared as singlets near δ 7.2

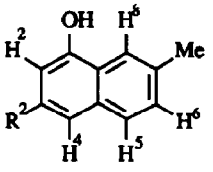
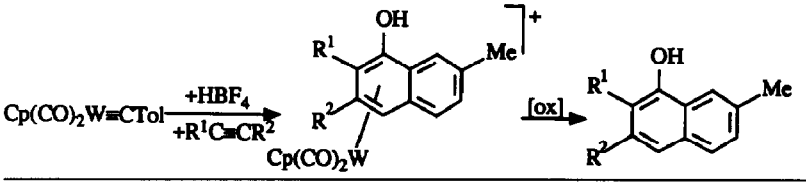


Table 1

Yields of free naphthols obtained from the reaction [a]



Alkyne	Product			Isolated yield (%)
		R^1	R^2	
MeC≡CMe [b]	**5**	Me	Me	62
EtC≡CEt	**6**	Et	Et	34
HC≡C^{n}Pr	**7**	H	^{n}Pr	34
HC≡C^{i}Pr	**8**	H	^{i}Pr	67
HC≡C^{t}Bu	**9**	H	^{t}Bu	49
MeC≡C^{n}Pr	**10a**	Me	^{n}Pr	33
	10b	^{n}Pr	Me	28
MeC≡C^{i}Pr	**11a**	Me	^{i}Pr	49
	11b	^{i}Pr	Me	16

[a] The reaction was conducted in CH_2Cl_2 at −78°C under 1 atm CO followed by evaporation of solvent, washing with Et_2O, dissolution in CH_2Cl_2 and stirring in air for 24 h. [b] Ref. 7.

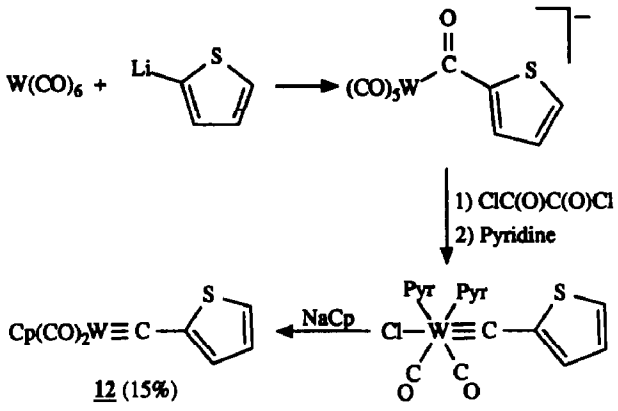
and 6.7, respectively. The latter resonance was absent in the naphthol products prepared from internal alkynes, confirming its assignment as a proton arising from the alkyne. In addition to the alkynes listed in Table 1, protonation of $Cp(CO)_2W{\equiv}CTol$ in the presence of $PhC{\equiv}CPh$, $PhC{\equiv}CH$, $^tBuC{\equiv}CMe$, $Me_3SiC{\equiv}CSiMe_3$, $EtOCC{\equiv}CH$, and $MeO_2CC{\equiv}CCO_2Me$ was examined. As noted in our earlier study [7], protonation of $Cp(CO)_2W{\equiv}CTol$ in the presence of $PhC{\equiv}CPh$ led to the formation of an η^3-vinylcarbene complex which did not further transform into a naphthol product. Complex reaction mixtures were formed when $Cp(CO)_2W{\equiv}CTol$ was protonated in the presence of the other alkynes listed above, but no evidence was obtained for naphthol products.

The most significant finding in this study is the regiochemistry observed in the reaction. This is most striking for the terminal alkynes which gave only a single regioisomer of the naphthol products **7–9** with the hydrogen substituent of the alkyne located adjacent to the hydroxy group. This is exactly opposite the well-established regiochemistry for the Dötz-type reactions of the chromium carbene complexes $(CO)_5Cr{=}C(OR)R'$ [4–6]. This stereochemistry is indicated by the singlet observed for the naphthol hydrogen H^2 in the ^1H NMR spectra of the products. If the alkyne had added with the opposite regiochemistry to put the alkyl substituent adjacent to the hydroxy group, then coupling between the alkyne proton and H^4 should have been observed, analogous to the 6.6–9.0 Hz coupling observed between the adjacent hydrogens H^6 and H^5.

As illustrated in Table 1, a slight preference for the isomer with the smaller substituent located adjacent to the hydroxy group was found for the naphthols produced from the internal but asymmetrical alkynes $MeC{\equiv}C^nPr$ and $MeC{\equiv}C^iPr$. This regiochemistry was indicated by a NOE ^1H NMR experiment which showed that irradiation of the δ 2.70 propyl $CH_2CH_2CH_3$ resonance of the minor isomer of **10 (10b)** gave enhancement of both the methyl and OH resonances at δ 2.32 and δ 5.12, as it would if the n-propyl group were located between these substituents. The NOE enhancement patterns observed when the OH and H^4 protons were irradiated were also consistent with the assigned regiochemistry. As with terminal alkynes, the regiochemistry found for internal alkynes is opposite that previously reported for the Dötz-type reactions with $(CO)_5Cr{=}C(OMe)Ar$ complexes where regioselectivities for products with the bulky substituents adjacent to the hydroxy group range from 2 : 1 to 100% [4,5].

Preparation and protonation of $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$ in the presence of $CH_3C{\equiv}CCH_3$ to form 4-hydroxy-5,6-dimethylbenzothiophene

We sought to extend the methodology of eq. 2 to carbyne complexes bearing other aromatic substituents. Particularly interesting was the thiophene-substituted carbyne complex **12.** This species was previously unknown but was readily generated in this study by the methodology shown in Scheme 1. The complex was isolated in low overall yield from $W(CO)_6$ and was spectroscopically (see Experimental) and crystallographically characterized. An ORTEP drawing is shown in Fig. 1 and relevant crystallographic information is set out in Tables 2–4. The W≡C distance of 1.828(10) Å in this molecule is similar to those found in the related carbyne complexes $Cp(CO)_2W{\equiv}CSiPh_3$ (1.81 Å) [9a], $Cp(CO)_2W{\equiv}CTol$ (1.82(2) Å) [9b], and



Scheme 1.

$Cp(CO)(PPh_3)W{\equiv}CSPh$ (1.807(10) Å) [9c], and the structure of **12** is otherwise similar to these three compounds.

Protonation of **12** in the presence of MeC≡CMe led immediately to the formation of the annulation product **13**, eq. 4. Unlike protonation of $Cp(CO)_2W{\equiv}CTol$/alkyne mixtures which give naphthol complexes initially, no evidence of an intermediate complex possessing **13** coordinated to a metal fragment was obtained. The organic **13** was spectroscopically characterized. It showed a parent ion at $m/z = 178.0451$ (calcd. 178.2484), and its IR, ^1H. and ^{13}C NMR spectra are consistent with its formulation (see Experimental). Unlike $Cp(CO)_2W{\equiv}CTol$, no other alkynes (PhC≡CPh, PhC≡CMe, PhC≡CH, $^iPrC{\equiv}CMe$) were found to give reactions equivalent to that shown in eq. 4, although annulation reactions like this have been observed for complexes within the $(CO)_5Cr{=}C(OMe)(2\text{-}C_4H_3X)$, (X = O, S) family [10–12].

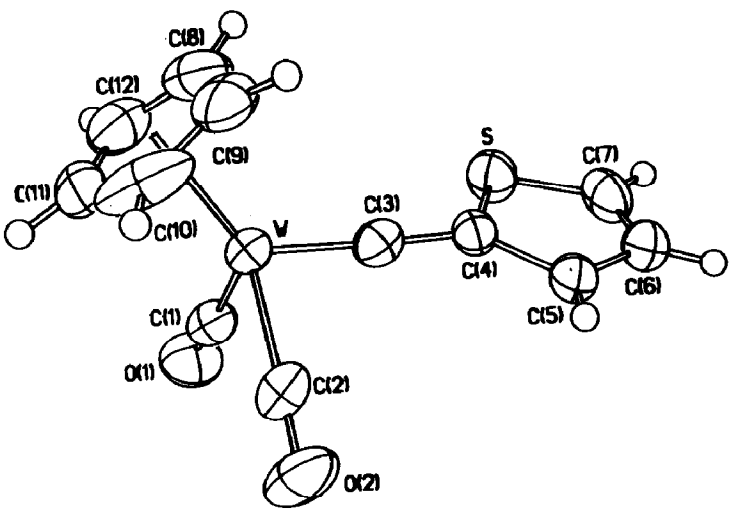
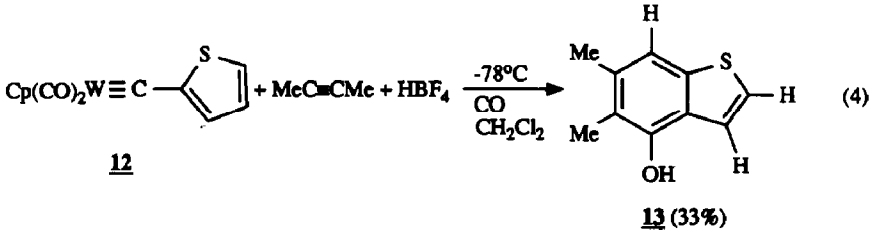


Fig. 1. An ORTEP drawing for $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$, **12**.

Table 2

Crystallographic data for $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$, **12**

(a) *crystal parameters*	
Formula	$C_{12}H_8O_2SW$
form. wt.	400.09
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	13.398(3)
b, Å	6.063(1)
c, Å	14.797(3)
β, deg	92.27(2)
V, Å^3	1201.1(4)
Z	4
crystal dimensions, mm	0.42×0.48×0.48
crystal, color	red
D(calc), g/cm^3	2.213
μ(Mo-K_α), cm^{-1}	103.1
temp, °C	22
T_{max}/T_{min}	2.457
(b) *data collection*	
diffractometer	Nicolet R3m
monochromator	graphite
scan technique	Wyckoff
radiation	Mo-K_α ($\lambda = 0.71073$ Å)
2θ scan range, deg	5–48
data collected	$\pm h, +k, +l$
reflections collected	2173
independent reflections	1886
R_{merg}, %	4.2
independent reflections observed $F_o \geq 5\sigma(F_o)$	1566
stds. reflections	3 std/197 reflections
variation in stds., %	±1
(c) *data reduction and refinement*	
$R(F)$, %	3.58
$R(wf)$, %	3.79
Δ/σ (max)	0.07
$\Delta(\rho)$, eÅ^{-3}	0.84
N_0N_v	10.7
GOF	1.01



12 **13** (33%) (4)

Table 3

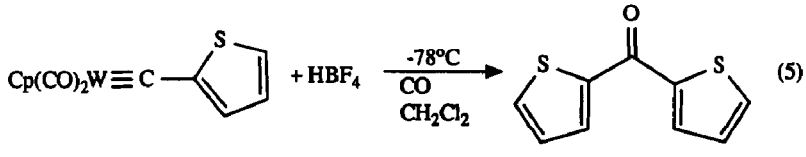
Atomic coordinates ($\times 10^4$) and isotropic thermal parameters ($Å^2 \times 10^3$) for $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$, **12**

	x	*y*	*z*	U^a
W	1928.5(2)	1793.4(5)	896.8(2)	55.1(2)
S	4184(3)	6721(6)	1598 (3)	82 (1)
O(1)	1158(7)	5396(14)	−436 (5)	98 (3)
O(2)	2698(8)	−654(16)	−797 (7)	114 (4)
C(1)	1451(8)	4045(18)	50 (7)	68 (3)
C(2)	2430(7)	227(17)	−166 (7)	73 (3)
C(3)	3137(7)	3183(15)	1025 (7)	66 (3)
C(4)	4069(7)	4208(16)	1167 (6)	59 (3)
C(5)	5094(4)	3026(10)	929 (4)	72 (2)
C(6)	5822(8)	4886(21)	1198 (7)	79 (4)
C(7)	5424(10)	6736(20)	1543 (8)	86 (5)
C(8)	1340(13)	1761(22)	2368 (9)	102 (6)
C(9)	1759(11)	−257(31)	2227 (9)	114 (6)
C(10)	1137(15)	−1248(19)	1538 (10)	131 (8)
C(11)	397(10)	289(33)	1339 (8)	113 (6)
C(12)	564(11)	2055(23)	1840 (9)	96 (5)

[a] Equivalent isotropic *U* defined as one third of the trace of the orthogonalized U_{ij} tensor

Protonation of $Cp(CO)_3W{\equiv}C(2\text{-}C_4H_3S)$ in the absence of alkynes

A surprising product was obtained in a control experiment when carbyne complex **12** was protonated under a constant purge of CO but in the absence of added alkyne. Obtained in modest yield from this reaction was the thienylketone **14**, eq. 5. This species was spectroscopically characterized. It showed a parent ion at $m/z = 193.9844$ (calcd. 193.8860) and a strong ν(CO) band at 1617 cm^{-1} in its IR spectrum. Its ^1H NMR and ^{13}C NMR spectra are consistent with its formulation, and its 87 °C melting point is in agreement with the reported value (87–88 °C) [13]. When the reaction was carried out under a ^{13}CO atmosphere, the IR spectrum of the product **14** showed a strong ν(CO) band at 1608 cm^{-1} and a much weaker band at 1617 cm^{-1}, indicating that exogenous CO is largely incorporated into the product. Tractable products were not obtained when complex **12** was refluxed in hexane for 8 h under a CO atmosphere, nor when complex **12** was protonated with HBF_4 under an N_2 atmosphere. This is quite an unexpected product, and we cannot confidently offer a mechanism to explain its formation.



(5)

12 **14** (21%)

Discussion

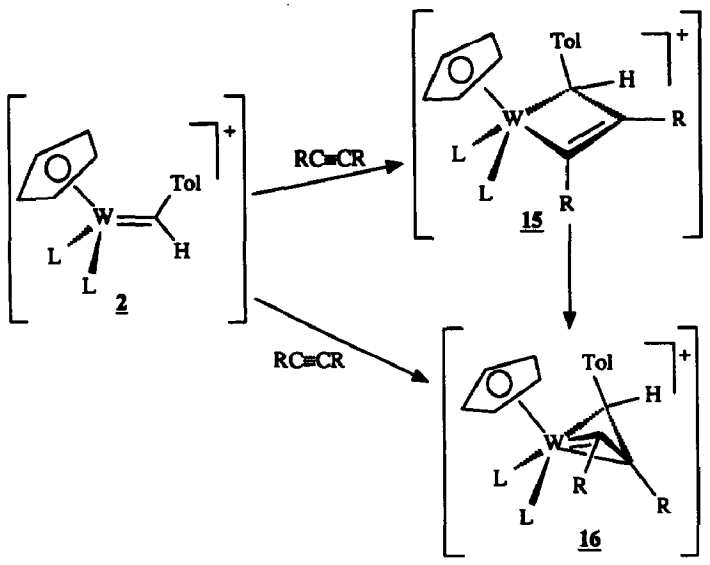
As previously discussed in Ref. 7, the first step in the reactions reported herein is likely protonation of the carbyne carbon of $Cp(CO)_2W{\equiv}CTol$ to form the electrophilic carbene complex $[Cp(CO)_2W{=}CH(Tol)]^+$, **2**, although this species has not

Table 4

Selected bond distances (Å) and angles (deg) for $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$, **12**

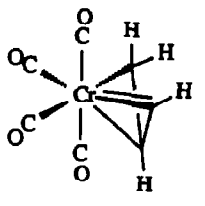
Bond distances			
W–C(1)	1.944(11)	W–C(2)	2.977(11)
W–C(3)	1.828(10)	W–C(8)	2.345(14)
W–C(9)	2.347(15)	W–C(10)	2.346(15)
W–C(11)	2.361(14)	W–C(12)	2.349(15)
S–C(4)	1.657(10)	S–C(7)	1.667(14)
O(1)–C(1)	1.149(13)	O(2)–C(2)	1.146(15)
C(3)–C(4)	1.403(13)	C(4)–C(5)	1.601(11)
C(5)–C(6)	1.533(13)	C(6)–C(7)	1.351(17)
C(8)–C(9)	1.365(23)	C(8)–C(12)	1.289(21)
C(9)–C(10)	1.424(22)	C(10)–C(11)	1.383(23)
C(11)–C(12)	1.316(22)	CNT–W	2.047(13)
Bond angles			
C(1)–W–C(2)	86.5(4)	C(1)–W–C(3)	90.6(4)
C(2)–W–C(3)	88.7(4)	C(1)–W–C(8)	119.4(5)
C(2)–W–C(8)	150.7(4)	C(3)–W–C(8)	103.6(5)
C(1)–W–C(9)	150.7(5)	C(2)–W–C(9)	117.4(5)
C(3)–W–C(9)	105.8(5)	C(8)–W–C(9)	33.8(5)
C(1)–W–C(10)	132.1(5)	C(2)–W–C(10)	96.7(5)
C(3)–W–C(10)	137.1(5)	C(8)–W–C(10)	56.2(5)
C(9)–W–C(10)	35.3(5)	C(1)–W–C(11)	100.5(5)
C(2)–W–C(11)	111.2(5)	C(3)–W–C(11)	157.6(4)
C(8)–W–C(11)	54.0(5)	C(9)–W–C(11)	56.5(5)
C(10)–W–C(11)	34.2(6)	C(1)–W–C(12)	95.2(5)
C(2)–W–C(12)	143.3(4)	C(3)–W–C(12)	127.9(5)
C(8)–W–C(12)	31.9(5)	C(9)–W–C(12)	55.5(5)
C(10)–W–C(12)	55.8(5)	C(11)–W–C(12)	32.4(5)
C(4)–S–C(7)	93.7(6)	W–C(1)–O(1)	178.6(9)
W–C(2)–O(2)	178.0(9)	W–C(3)–C(4)	177.2(8)
S–C(4)–C(3)	122.3(7)	S–C(4)–C(5)	115.4(6)
C(3)–C(4)–C(5)	122.4(8)	C(4)–C(5)–C(6)	99.0(6)
C(5)–C(6)–C(7)	116.9(9)	S–C(7)–C(6)	115.0(9)
W–C(8)–C(9)	73.2(8)	W–C(8)–C(12)	74.2(9)
C(9)–C(8)–C(12)	110.9(13)	W–C(9)–C(8)	73.0(9)
W–C(9)–C(10)	72.3(8)	C(8)–C(9)–C(10)	104.8(13)
W–C(10)–C(9)	72.4(9)	W–C(10)–C(11)	73.5(8)
C(9)–C(10)–C(11)	105.2(13)	W–C(11)–C(10)	72.3(9)
W–C(11)–C(12)	73.3(9)	C(10)–C(11)–C(12)	108.9(12)
W–C(12)–C(8)	73.9(9)	W–C(12)–C(11)	74.3(8)
C(8)–C(12)–C(11)	110.1(13)		

been directly observed (see eq. 3). This species must then react with alkynes to form η^3-vinylcarbene intermediates on the way to the naphthol products as detailed in Ref. 7. Evidence for the importance of η^3-vinylcarbene complexes in this chemistry came from the observed formation of the η^3-vinylcarbene complex **16** upon protonation of $Cp(CO)_2W{\equiv}CTol$ in the presence of $PhC{\equiv}CPh$, Scheme 2 [7]. As indicated in the scheme, we originally considered that the η^3-vinylcarbene complex **16** may have formed via the intermediacy of the metallacyclobutene complex **15**. However, a recent theoretical analyses by Hofmann indicates that this reaction, and the related Dötz reactions, may instead proceed via the direct formation of the η^3-vinylcarbene



Scheme 2.

complex without the involvement of a metallacyclobutene intermediate [14]. Hofmann, for example, showed through a molecular orbital analysis that the η^3-vinylcarbene complex **17** is ~ 26 kcal/mol more stable than the planar metallacyclobutene complex **18**.



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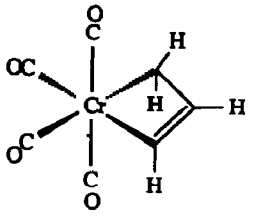

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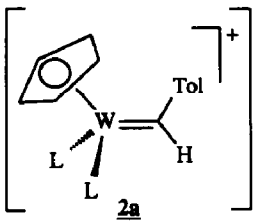
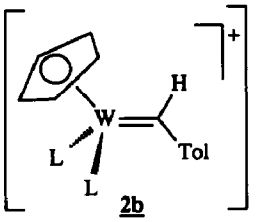
The regiochemistry of the reactions reported herein are consistent with Hofmann's suggestion that the η^3-vinylcarbene complex forms via direct cycloaddition of the alkyne to the electrophilic carbene complex **2**. First, it is known from the earlier study [7] that the reaction of PhC≡CPh with **2** proceeds via the *synclinal* rotomer **2a** rather the the *anticlinal* rotomer **2b**. The two possible orientations in which the alkyne can approach the *synclinal* rotomer **2a** are illustrated in **A** and **B** below where R_S and R_L respectively represent small and large alkyne substituents. The sterically favored orientation is clearly **A** with the larger alkyne substituent located away from the bulky cyclopentadienyl and tolyl groups. This orientation would lead directly to an η^3-vinylcarbene complex with the initial carbyne carbon bound to the alkyne carbon bearing the larger substituent. This would in turn lead to a naphthol product with the smaller substituent bound to the carbon adjacent to the CO derived hydroxy group, exactly as observed in this study.



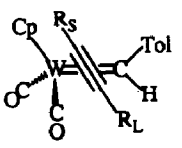
2a

synclinal

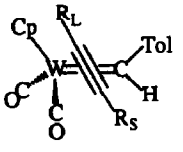


2b

anticlinal

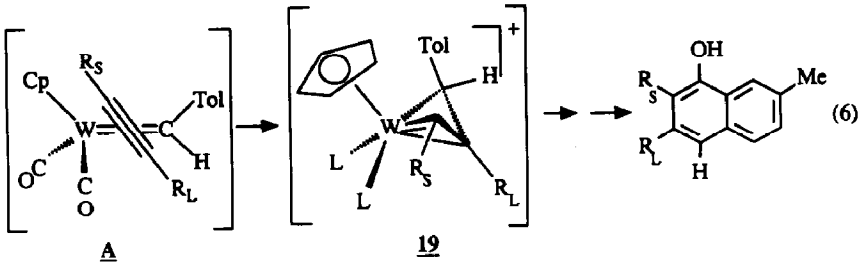


A



B

(R_S= Small R, R_L= Large R)



Experimental

General

The compounds $Cp(CO)_2W{\equiv}CTol$ [15] and 2-thienyllithium [16] were prepared by literature procedures. Solvents were dried by refluxing over Na/benzophenone ketyl (tetrahydrofuran (THF), Et_2O) or CaH_2 (CH_2Cl_2, pentane, hexane) and were freshly distilled prior to use. All manipulations were performed using standard Schlenk techniques. IR spectra were recorded on an IBM FTIR-32 spectrometer operated in the absorbance mode, NMR spectra were obtained on a Bruker AM 300 FT NMR spectrometer, and mass spectra were recorded on an AEI-MS9 mass spectrometer. Elemental analyses were obtained from Galbraith Laboratories, Inc. Knoxville, TN.

Reaction of $Cp(CO)_2W{\equiv}CTol$ with HBF_4 and alkynes to form free naphthols. A $-78°$C CH_2Cl_2 (20 mL) solution of $Cp(CO)_2W{\equiv}CTol$ (0.05 g; 0.12 mmol) and the appropriate alkyne (0.2 mL) was stirred under a constant purge of CO while 1 equiv. (0.015 mL) of $HBF_4 \cdot Et_2O$ was added. The orange solution immediately turned red. After warming to room temperature, the solvent was removed under

vacuum and the residues were washed with Et_2O, dissolved in CH_2Cl_2, and stirred for 24 h in air, during which time the color changed from red to dark brown. The reaction mixture was filtered through 3 cm of silica gel and chromatographed on a silica gel TLC plate eluting with 50% CH_2Cl_2/hexane to yield the corresponding naphthol. In addition to purifying the compounds, this separated the regioisomers of **10** and **11**.

6: MS: Found: $m/z = 214.1331$ $C_{15}H_{18}O$ calcd.: $m/z = 214.1358$ (M^+). ^1H NMR ($CDCl_3$): δ 7.79 (s, 1H), 7.65 (d, 1H, J(HH) = 8.36 Hz), 7.24 (m, 2H), 5.20 (s, 1H, O*H*), 2.81 (q, 2H, J(HH) = 7.99 Hz, CH_2), 2.78 (q, 2H, J(HH) = 7.99 Hz, CH_2), 2.51 (s, 3H, CH_3), 1.31 (t, 3H, J(HH) = 7.45, CH_3), 1.23 (t, 3H, J(HH) = 7.60, CH_3).

7: MS Found: $m/z = 200.1203$ $C_{14}H_{16}O$ calcd.: $m/z = 200.1202$ (M^+). ^1H NMR ($CDCl_3$): δ 7.85 (s, 1H), 7.62 (d, 1H, J(HH) = 8.39 Hz), 7.27 (d, 1H, J(HH) = 6.6 Hz), 7.17 (s, 1H), 6.64 (s, 1H), 5.19 (s, 1H, O*H*), 2.64 (t, 2H, J(HH) = 7.2 Hz, CH_2), 2.49 (s, 3H, CH_3), 1.68 (m, 2H, J(HH) = 7.6 Hz, CH_2), 0.94 (t, 3H, J(HH) = 7.3 Hz, CH_3).

8: MS; Found: $m/z = 200.1181$. $C_{14}H_{16}O$ calcd.: $m/z = 200.1201$ (M^+). ^1H NMR ($CDCl_3$): δ 7.84 (s, 1H), 7.63 (d, 1H, J(HH) = 8.4 Hz), 7.27 (d, 1H, J(HH) = 8.4 Hz), 7.19 (s, 1H), 6.70 (s, 1H), 5.21 (s, 1H, O*H*), 2.95 (sep, 1H, J(HH) = 7.0 Hz, C*H*(CH_3)$_2$), 2.49 (s, 3H, CH_3), 1.28 (d, 6H, J(HH) = 7.0 Hz, CH(CH_3)$_2$).

9: Found: $m/z = 214.1340$. $C_{15}H_{18}O$ calcd.: $m/z = 214.1358$ (M^+). ^1H NMR ($CDCl_3$): δ 7.86 (s, 1H), 7.69 (d, 1H, J(HH) = 9.0 Hz), 7.34 (s, 1H), 7.31 (d, 1H, J(HH) = 9.0 Hz), 6.90 (s, 1H), 5.20 (s, 1H, O*H*), 2.52 (s, 3H, CH_3), 1.38 (s, 9H, C(CH_3)$_3$).

10a: MS: Found: $m/z = 214.1354$. $C_{15}H_{18}O$ calcd.: $m/z = 214.1358$ (M^+). ^1H NMR ($CDCl_3$): δ 7.78 (s, 1H), 7.57 (d, 1H, J(HH) = 8.0 Hz), 7.22 (d, 1H, J(HH) = 8.0 Hz), 7.20 (s, 1H), 5.09 (s, 1H, O*H*), 2.72 (t, 2H, J(HH) = 7.8 Hz, CH_2CH$_2$CH$_3$), 2.49 (s, 3H, CH_3), 2.42 (s, 3H, CH_3), 1.59 (m, 2H, CH$_2$CH_2CH$_3$), 1.03 (t, 3H, J(HH) = 7.4 Hz, CH$_2$CH$_2$CH_3).

10b: MS: Found: $m/z = 214.1336$. $C_{15}H_{18}O$ calcd.: $m/z = 214.1358$ (M^+). ^1H NMR ($CDCl_3$): δ 7.77 (s, 1H), 7.59 (d, 1H, J(HH) = 8.0 Hz), 7.22 (d, 1H, J(HH) = 8.0 Hz), 7.19 (s, 1H), 5.12 (s, 1H, O*H*), 2.70 (t, 2H, J(HH) = 7.7 Hz, CH_2CH$_2$CH$_3$), 2.49 (s, 3H, CH_3), 2.32 (s, 3H, CH_3), 1.64 (m, 2H, CH$_2$CH_2CH$_3$), 0.99 (t, 3H, J(HH) = 7.5 Hz, CH$_2$CH$_2$CH_3).

11a: MS: Found: $m/z = 214.1308$. $C_{15}H_{18}O$ calcd.: $m/z = 214.1358$ (M^+). ^1H NMR ($CDCl_3$): δ 7.76 (s, 1H), 7.63 (d, 1H, J(HH) = 7.3 Hz), 7.26 (d, 1H, J(HH) = 7.3 Hz), 7.21 (s, 1H), 5.07 (s, 1H, O*H*), 3.21 (sep, 1H, J(HH) = 6.9 Hz, C*H*(CH_3)$_2$), 2.49 (s, 3H, CH_3), 2.36 (s, 3H, CH_3), 1.29 (d, 6H, J(HH) = 6.9 Hz, CH(CH_3)$_2$).

11b: MS: Found: $m/z = 214.1308$. $C_{15}H_{18}O$ calcd.: $m/z = 214.1358$ (M^+). ^1H NMR ($CDCl_3$): δ 7.69 (s, 1H), 7.56 (d, 1H, J(HH) = 8.3 Hz), 7.21 (d, 1H, J(HH) = 8.3 Hz), 7.18 (s, 1H), 5.21 (s, 1H, O*H*), 3.42 (sep, 1H, J(HH) = 6.8 Hz, C*H*(CH_3)$_2$), 2.49 (s, 3H, CH_3), 2.45 (s, 3H, CH_3), 1.45 (d, 6H, J(HH) = 7.3 Hz, CH(CH_3)$_2$).

Synthesis of $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$, 12. Freshly made 2-thienyllithium (1 mL, 13.7 mmol of thiophene) was added to a Et_2O solution of $W(CO)_6$ (3.0 g, 8.5 mmol) and allowed to stir at room temperature for 12 h. The solvent was removed under

vacuum yielding the yellow acyl complex Li[$(CO)_5WC\{O\}(2\text{-}C_4H_3S)$]. This species was dissolved in CH_2Cl_2 (50 mL), and the solution was cooled to −78°C. One equiv of oxalyl chloride (0.74 mL) was added, and the solution was stirred for 30 min, after which time 4 equiv (3 mL) of pyridine was added. *Caution must be taken to vent the reaction flask when the oxalyl chloride and pyridine are added since a substantial amount of CO is released.* After warming to room temperature, the solvent was removed under vacuum and the brown residues were extracted with hexane. The hexane was concentrated, and the resulting solution was chromatographed at −30°C on an alumina column eluting with 2:1 CH_2Cl_2/pentane. Removal of the solvent yielded $Cl(pyr)_2(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$ as a yellow solid. To a CH_2Cl_2 (100 mL) solution of this complex (2.51 g, 4.75 mmol) was then added 1.1 equiv (2.4 mL) of NaCp (2 *M* in THF). The reaction mixture was allowed to stir for 18 h at room temperature, the solution was concentrated, and an equal volume of pentane was added. The resulting solution was filtered through Celite and chromatographed at −30°C on alumina eluting with 1:1 CH_2Cl_2/pentane. This gave a single orange band which upon removal of solvent left complex **12** as an orange microcrystalline solid in 15% yield (based on $W(CO)_6$).

12: Anal. Found: C, 34.19; H, 1.82. $C_{12}H_8O_2SW \cdot \frac{1}{2}CH_2Cl_2$ calcd.: C, 33.97; H, 2.05%. IR (CH_2Cl_2): ν(CO) = 1985 (m), 1917 (s) cm^{-1}. ^1H NMR (CD_2Cl_2): δ 5.70 (s, 5H, Cp), 6.87 (dd, 1H, $^1J(HH) = 4.9$ Hz, $^2J(HH) = 3.7$ Hz, H^2), 7.22 (dd, 1H, $^1J(HH) = 3.7$ Hz, $^2J(HH) = 1.1$ Hz, H^3), 8.81 (dd, 1H, $^1J(HH) = 4.9$ Hz, $^2J(HH) = 1.5$ Hz, H^1). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ 92.2 (Cp), 127.1 (C_γ), 128.7 (C_β), 130.7 (C_δ), 137.9 (C_α), 221.2 (*C*O), 281.2 (W≡*C*). MS (EI): $m/z = 400$ (M^+), 372 ($M^+ - CO$), 344 ($M^+ - 2\ CO$), 317 ($M^+ - C_4H_3S$).

Protonation of $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$ in the presence of $CH_3C{\equiv}CCH_3$ to form $C_{10}H_{10}OS$, 13. A −78°C CH_2Cl_2 (20 mL) solution of $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$ (0.107 g; 0.267 mmol) and $CH_3C{\equiv}CCH_3$ (0.40 mL; 5.11 mmol) was stirred under a constant purge of CO while 1 equiv. (0.04 mL) of $HBF_4 \cdot Et_2O$ was added by syringe. The orange solution immediately turned brown. After warming to room temperature, the reaction mixture was filtered through 5 cm of silica gel, and the volume of solvent was reduced on a rotory evaporator. Chromatography on a silica TLC plate using 50% CH_2Cl_2/hexane as eluant gave a single colorless band of **13** which was isolated as a white microcrystalline solid in 33% yield (0.016 g; 0.88 mmol).

13: MS: Found: $m/z = 178.0451$ (M^+). $C_{10}H_{10}OS$ calcd.: $m/z = 178.2484$ (M^+). IR (KBr): ν(OH) = 3327 (s) cm^{-1}. ^1H NMR ($CDCl_3$): δ 2.32, 2.36 (s, 3H, CH_3), 4.97 (s, 1H, O*H*), 7.23 (d, 1H, $J(HH) = 5.5$ Hz, H_b), 7.28 (s, 1H, H_c), 7.32 (d, 1H, $J(HH) = 5.5$ Hz, H_a). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 20.9 (CH_3), 115.9, 119.1 (C_6, C_7), 123.8 (C_3), 127.9 (C_5), 133.2 (C_2), 133.5 (C_1), 142.9 (C_8), 179.9 (C_4).

Protonation of $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$ in the presence of CO. A −78°C CH_2Cl_2 (20 mL) solution of $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$ (0.195 g; 0.488 mmol) was stirred under a constant purge of CO while 1 equiv. (0.07 mL) of $HBF_4 \cdot Et_2O$ was added by syringe. The orange solution immediately turned brown. After warming to room temperature, the reaction mixture was filtered through 5 cm of silica gel, and the volume of solvent was reduced on a rotory evaporator. Chromatography on a silica TLC plate using 50% CH_2Cl_2/hexanes as eluant gave a single colorless band of **14** which was isolated as a white microcrystalline solid in 21% yield (0.02 g; 0.103 mmol).

14: MS: Found: $m/z = 193.9844$ (M^+). $C_9H_6OS_2$ calcd.: $m/z = 193.8860$ (M^+). IR (CH_2Cl_2): ν(CO) = 1617 (s) cm^{-1}, ν(CC) = 1516 (m) cm^{-1}. ^1H NMR ($CDCl_3$): δ7.17 (dd, 2H, ^1J(HH) = 5.0 Hz, ^2J(HH) = 3.9 Hz, H_2), 7.68 (dd, 2H, ^1J(HH) = 5.0 Hz, ^2J(HH) = 1.1 Hz, H_3), 7.89 (dd, 2H, ^1J(HH) = 3.8 Hz, ^2J(HH) = 1.3 Hz, H_1). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 127.9 (C_c), 133.2 (C_a), 133.5 (C_d), 142.8 (C_b), 178.8 (*C*O).

*Crystal structure determination of $Cp(CO)_2W{\equiv}C(2\text{-}C_4H_3S)$, **12**.*

Crystallographic data are summarized in Table 2. Crystals were mounted on glass fibers and determined to belong to the monoclinic system. Systematic absences uniquely determined the space group as $P2_1/c$. Corrections for absorption were applied using an empirical absorption tensor from an expression relating F_o and F_c. (Hope, Håkon, Moezzi, B. University of California at Davis.)

The structure was solved from a Patterson synthesis, and completed from subsequent difference Fourier syntheses. Refinement of a complete isotropic model revealed anomalies in the thermal parameters for S and C(5) and in C(4)–C(5) bond distance resulting from rotational disorder in the thiophene ring around the C(3)–C(4) axis. The amount of S character in C(5), and vice versa, was determined by incrementally varying a common thermal parameter for S and C(5) while refining their occupancies until values were obtained that produced the same value for X in the equations:

$$\frac{X(6) + (1 - X)16}{6} = \text{C(5) occupancy}$$

$$\frac{X(16) + (1 - X)6}{16} = \text{S occupancy}$$

By these means, the occupancies for the C(5) and S sites were found to 1.79 and 0.70, respectively; these values indicate an only slight site preference of 52%. These occupancies were then fixed, and all non-hydrogen atoms were refined as the anisotropic thermal parameters. All hydrogen atoms were treated as idealized, isotropic contributions.

All computations used the SHELXTL (5.1) program library (G. Sheldrick, Nicolet XRD, Madison, WI). Atomic coordinates are given in Table 3, and bond distances and angles in Table 4. A complete set of crystallographic data including structure factors may be obtained upon request from one of us (A.L.R.).

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