dination shifts $\Delta(\nu_{CC})$ and $\Delta(\delta_{C_{alk}})$ indicate variations in C≡C bond order and therefore reflect composite changes in forward donation and back acceptance from the alkyne moiety. To further probe the relative importance of these two factors on the coordination shifts, the variations in $\Delta(\delta_{C_{alk}})$ vs. $\Delta G^{\ddagger}$ and $\Delta(\nu_{CC})$ vs. $\Delta G^{\ddagger}$ were investigated (Figure 4). The figure nicely shows the inverse relation between $\Delta G^{\ddagger}$ and $\Delta\delta$ and $\Delta\nu_{CC}$ which is due to the apparent anomaly in $\Delta\delta$ (vide supra). It also establishes that, despite the nonuniform changes between Fe/Ru and Ru/Os, there is a good linear relationship between these properties as the metal is changed. Clearly this implies that, as long as our assumption about the dependence of $\Delta G^{\ddagger}$ on metal–alkyne π-component is valid, at least in this class of compounds π-back-bonding also dominates changes affecting ν_{CC} and $\delta_{C_{alk}}$.

It is perhaps not totally unexpected that the small changes in $\Delta(\nu_{CC})$, $\Delta(\delta_{C_{alk}})$, and $\Delta G^{\ddagger}$ on going from Fe to Ru correspond also to the lesser stability of **2b** compared to that of **2a**. Similarly, $Ru(CO)_4(\eta^2\text{-olefin})$ compounds are less stable than their iron analogues.[3d] Discontinuity in stability at the second-row transition metal is not confined to the Fe triad but appears to be a general phenomenon for metal π-complexes. For instance, Maitlis et al.[39] found that in the series of complexes $(Ph_3P)_2M(\eta^2\text{-}CF_3C_2CF_3)$, the stability decreased in the order Pt > Ni > Pd. Moreover, for this class of alkyne–transition-metal derivatives the variation in $\Delta(\nu_{CC})$, Pt > Ni > Pd, reflects exactly the stability sequence and implies that with these highly basic d^{10} $M(PPh_3)_2$ fragments metal d to π^*(alkyne) back-bonding dominates the metal–alkyne interactions. This is clearly not the case with $M(CO)_4(\eta^2\text{-BTMSA})$ compounds. Here, due to the presence of the electron acceptor $M(CO)_4$ metal carbonyl fragment and the electron-rich bis(trimethylsilyl)acetylene, both σ- and π-components of the metal–alkyne interaction appear to play an important role in determining the overall thermodynamic stability of the bond.

Acknowledgment. We wish to thank the Natural Sciences and Engineering Research Council of Canada and the University of Alberta for financial support of this work and Johnson Matthey for generous loan of osmium tetraoxide.

Registry No. **1b**, 15696-40-9; **1c**, 15243-33-1; ^{13}CO-enriched **2a**, 109088-06-4; **2b**, 109088-05-3; ^{13}CO-enriched **2b**, 109088-07-5; **2c**, 109088-04-2; BTMSA, 14630-40-1; $Fe(^{13}CO)_5$, 16997-09-4; $Ru_3(^{13}CO)_{12}$, 104469-63-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms and derived positional and thermal parameters for the hydrogen atoms for **2c** (2 pages); a listing of observed and calculated structure amplitudes for **2c** (12 pages). Ordering information is given on any current masthead page.

Trans Insertion of Activated, Symmetrically Disubstituted Acetylenes into the Metal–Hydrogen Bond of Bis(cyclopentadienyl)metal Hydrides of Rhenium, Tungsten, and Molybdenum

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The insertion reactions of Cp_2ReH and Cp_2WH_2 with $MeO_2CC{\equiv}CCO_2Me$ were reinvestigated. The kinetically controlled products are $Cp_2M[\eta^1\text{-}(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)]$ (M = Re, **1a**; M = WH, **2a**) which can thermally isomerize to the more stable *E* isomers (M = Re, **1b**; M = WH, **2b**). Cp_2ReH inserts $NCC{\equiv}CCN$ to form $Cp_2Re[\eta^1\text{-}(Z)\text{-}C(CN){=}CH(CN)]$ (**5a**). Upon irradiation **5a** gives a photostationary mixture of **5a** and the *E* isomer **5b** (ratio 1:2). Pure **5b** thermally reverts to **5a** in the dark while irradiation affords the same isomeric mixture as above. The crystal structures of **1a** and **1b** were determined. For **1a**: space group $P2_1/c$ (No. 14), a = 915.5 (3) pm, b = 764.9 (2) pm, c = 2085.5 (1) pm, β = 92.10 (1)°, Z = 4; R = 0.041, R_w = 0.050. For **1b**: space group $P2_1/c$ (No. 14), a = 2169.5 (9) pm, b = 888.1 (1) pm, c = 1683.1 (8) pm, β = 111.36 (3)°, Z = 8; R = 0.042, R_w = 0.047. **2a** shows rotational isomerism about the metal–alkenyl bond with $\Delta G^{\ddagger}$ = 62.8 ± 0.5 kJ/mol at 298 K. The stereochemistry of the alkenyl group can be determined from the $^3J(^{13}C\text{–}^1H)$ coupling constants. For the *Z* isomers (e.g., **1a** and **5a**) the cis coupling constant ranges from 8.5 to 10 Hz while the trans constants of the *E* isomers (e.g., **1b** and **5b**) lie between 14 and 16 Hz.

Introduction

The insertion of acetylenes into metal–hydrogen bonds represents one of the fundamental processes of organometallic chemistry.[1-4] Insertion reactions may proceed in a cis or a trans manner.[2-4] This is exemplified in eq 1 for the most simple case of symmetrical disubstituted acetylenes which may give alkenyl complexes of *Z* or *E* stereochemistry. Several authors have pointed out that the determination of the product stereochemistry is not trivial.[2,5,6] Furthermore, the reaction stereochemistry can

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(1) Collman, J. P.; Hegedus, L. S. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1980.

(2) Otsuka, S.; Nakamura A. *Adv. Organomet. Chem.* **1976**, *14*, 245.

(3) For a recent review of the literature see: Barlage, W. Dissertation, Technical University of Aachen, 1985.

(4) Bianchini, C.; Innocenti, P.; Masi, D.; Meli, A.; Sabat, M. *Organometallics* **1986**, *5*, 72. Amaudrut, J.; Leblanc, J.-C.; Moïse, C.; Sala-Pala, J. *J. Organomet. Chem.* **1985**, *295*, 167.

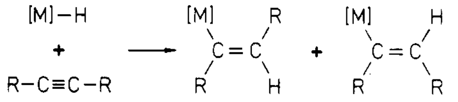
0276-7333/87/2306-1924$01.50/0

Table I. Crystallographic Data, Data Collection Parameters, and Refinement Parameters

	1a	1b
formula	$C_{16}H_{17}O_4Re$	$C_{16}H_{17}O_4Re$
fw	459.51	459.51
space group	$P2_1/c$ (No. 14)	$P2_1/c$ (No. 14)
a, pm	915.5 (3)	2169.5 (9)
b, pm	764.9 (2)	888.1 (1)
c, pm	2085.5 (1)	1683.1 (8)
β, deg	92.10 (1)	111.36 (3)
V, nm^3	1.459	3.020
Z	4	8
d(calcd), g cm^{-3}	2.09	2.02
cryst size, mm^3	0.45 × 0.3 × 0.1	0.15 × 0.12 × 0.05
μ(Mo Kα),[a] cm^{-1}	84.5	81.7
radiatn (λ, pm)	Mo Kα (71.073)	Mo Kα (71.073)
monochromator	graphite	graphite
temp, °C	20	20
scan mode (θ range, deg)	ω–2θ (1–35)	ω–2θ (1–35)
no. of unique reflcns obsd	3605	3882[b]
N_o, no. of unique reflcns[c]	2962	3693
N_p, no. of params refined	190	379
goodness of fit[d]	1.64	5.73
R[e]	0.041	0.042
R_w[f]	0.050	0.047
w^{-1}	$(\sigma^2(I) + (pF_o^2)^2/4F_o^2$ ($p = 0.05$)	1

[a] No absorption correction was applied. [b] $I > 2\sigma(I)$. [c] $I > 3\sigma(I)$. [d] $[\sum w(|F_o| - |F_c|)^2/(N_o - N_p)]^{1/2}$. [e] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [f] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

only be discussed if the product stereochemistry is known and if the alkenyl complexes formed in eq 1 are kinetically controlled products.



(1)

In this paper we consider insertion reactions of bent metallocene hydrides with activated, symmetrically disubstituted acetylenes. The first example of these reactions was discovered by Dubeck and Schell when they treated $MeO_2CC{\equiv}CCO_2Me$ (DMAC) with Cp_2ReH.[7,8] This reaction represents one of the rare cases where the primary product can be isomerized to the alternative stereoisomer. This allows us to distinguish between the kinetically and the thermodynamically controlled isomeric product.

Dubeck and Schell considered the DMAC insertion of Cp_2ReH to be a cis insertion.[7] Later, the DMAC insertion of Cp_2MoH_2 was described and again cis insertion was assumed.[9] On the other hand, the insertion reactions of hexafluoro-2-butyne (HFB) with Cp_2ReH, Cp_2MoH_2, and Cp_2WH_2 give trans insertion products as evidenced by ^{19}F NMR spectra.[10] In a previous study we have already shown by means of X-ray diffraction work that the DMAC insertion of Cp_2MoH_2 does in fact give a trans insertion product.[11] We now present a reinvestigation of the DMAC insertion reactions of Cp_2ReH and Cp_2WH_2 and a study of the reaction of dicyanoacetylene (DCA) with Cp_2ReH. We wish to show by means of combined application of X-ray crystallography and ^{13}C NMR spectroscopy that bent metallocene hydrides insert activated, symmetrically disubstituted acetylenes by a trans insertion process in all cases.

Scheme I

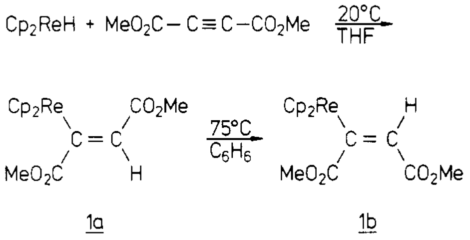


Table II. Non-Hydrogen Atoms Coordinates for 1a

atom	x	y	z	B_{eq}[a]
Re	0.23449 (2)	0.00358 (3)	0.16208 (1)	2.370 (3)
O(1)	−0.1273 (6)	−0.1934 (9)	0.1718 (3)	4.9 (1)
O(2)	−0.1434 (6)	−0.0244 (7)	0.0860 (3)	3.9 (1)
O(3)	0.3556 (6)	−0.2906 (9)	0.0447 (3)	6.1 (1)
O(4)	0.1993 (6)	−0.4423 (8)	−0.0181 (3)	4.1 (1)
C(1)	0.0825 (7)	−0.1578 (9)	0.1076 (4)	2.8 (1)
C(2)	0.0972 (7)	−0.2795 (9)	0.0612 (4)	3.1 (1)
C(3)	−0.0688 (8)	−0.1309 (9)	0.1272 (4)	3.1 (1)
C(4)	0.2335 (8)	−0.333 (1)	0.0313 (4)	3.5 (1)
C(5)	−0.291 (1)	0.021 (1)	0.1035 (5)	5.5 (2)
C(6)	0.321 (1)	−0.514 (1)	−0.0506 (4)	4.7 (2)
C(11)	0.310 (1)	−0.006 (1)	0.2634 (4)	4.5 (2)
C(12)	0.4134 (9)	−0.086 (1)	0.2274 (4)	4.0 (2)
C(13)	0.349 (1)	−0.236 (1)	0.1988 (4)	4.7 (2)
C(14)	0.204 (1)	−0.242 (1)	0.2203 (4)	5.2 (2)
C(15)	0.178 (1)	−0.098 (1)	0.2598 (4)	5.0 (2)
C(21)	0.1151 (8)	0.243 (1)	0.1258 (4)	3.7 (2)
C(22)	0.2369 (9)	0.291 (1)	0.1675 (4)	4.3 (2)
C(23)	0.3646 (9)	0.235 (1)	0.1374 (4)	3.9 (2)
C(24)	0.3275 (9)	0.149 (1)	0.0788 (4)	3.8 (2)
C(25)	0.1741 (9)	0.158 (1)	0.0721 (4)	3.6 (1)

[a] The anisotropic thermal parameters are given in the form of their isotropic equivalents; in 10^4 pm^2.

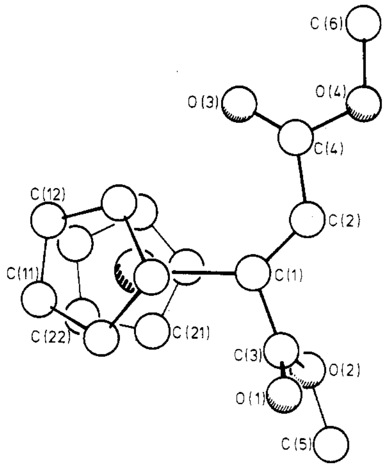


Figure 1. Molecular structure of $Cp_2Re[\eta^1\text{-}(Z)\text{-}C(CO_2Me){=}CH(CO_2Me)]$ (**1a**).

Results

Reaction of Cp_2ReH with $MeO_2CC{\equiv}CCO_2Me$. The insertion product **1a** was prepared from Cp_2ReH and

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[6] Blackmore, T.; Bruce, M. I.; Stone, F. G. A. *J. Chem. Soc., Dalton Trans.* **1974**, 106.

[7] Dubeck, M.; Schell, R. A. *Inorg. Chem.* **1964**, *3*, 1757.

[8] The only earlier examples of an acetylene insertion of a hydrido transition–metal complex is the reaction of $MnH(CO)_5$ with $F_3C{-}C{\equiv}C{-}CF_3$: Treichel, P. M.; Pitcher, E.; Stone, F. G. A. *Inorg. Chem.* **1962**, *1*, 511.

[9] Nakamura, A.; Otsuka, S. *J. Am. Chem. Soc.* **1972**, *94*, 1886.

[10] Nakamura, A.; Otsuka, S. *J. Mol. Catal.* **1975/1976**, *1*, 285.

[11] Herberich, G. E.; Hessner, B.; Okuda, J. *J. Organomet. Chem.* **1983**, *254*, 317.

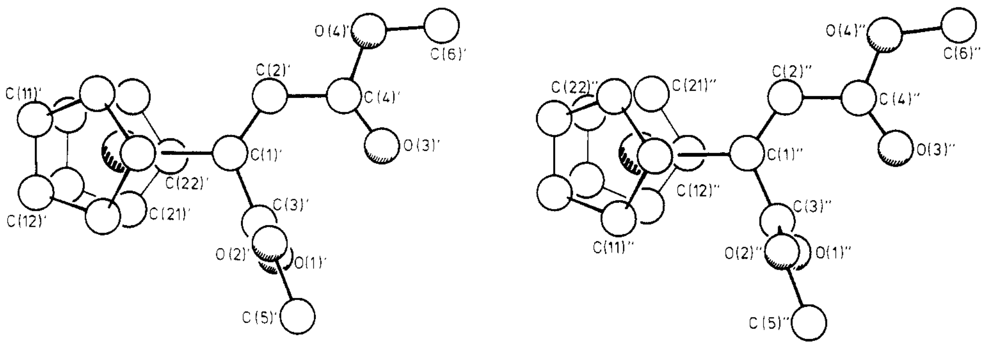


Figure 2. Molecular structure of $Cp_2Re[\eta^1$-(*E*)-$C(CO_2Me){=}CH(CO_2Me)]$ (**1b**) with two independent molecules **1b′** and **1b″**.

Scheme II

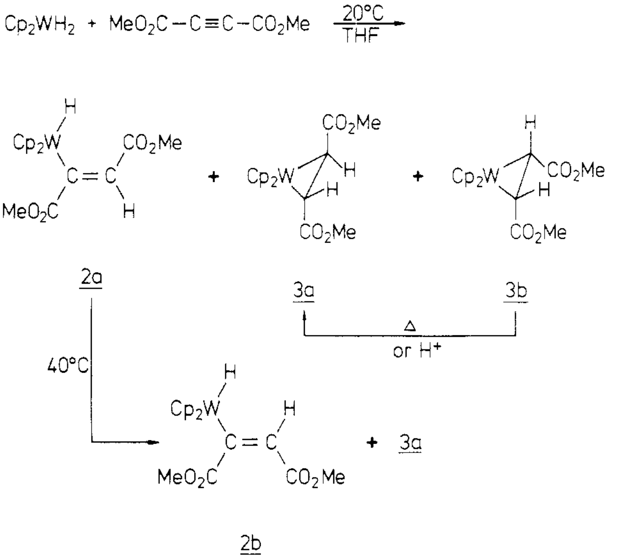


Table III. Non-Hydrogen Atom Coordinates for the Molecules 1b′ and 1b″ of Compound 1b

atom	*x*	*y*	*z*	B_{eq}[a]
		Molecule **1b′**		
Re(1′)	0.08027 (2)	0.18464 (7)	0.38896 (3)	2.527 (9)
O(1′)	0.0542 (5)	0.276 (1)	0.1635 (6)	3.7 (2)
O(2′)	0.1545 (5)	0.166 (1)	0.2209 (6)	3.9 (2)
O(3′)	0.1720 (5)	0.508 (2)	0.2070 (7)	4.4 (3)
O(4′)	0.2080 (5)	0.661 (1)	0.3215 (6)	4.4 (3)
C(1′)	0.1203 (6)	0.313 (2)	0.3105 (8)	3.1 (3)
C(2′)	0.1540 (6)	0.444 (2)	0.3340 (8)	3.1 (3)
C(3′)	0.1052 (7)	0.249 (2)	0.2240 (10)	3.5 (3)
C(4′)	0.1779 (6)	0.535 (2)	0.2806 (8)	3.2 (3)
C(5′)	0.1429 (9)	0.092 (2)	0.1396 (10)	4.9 (4)
C(6′)	0.2335 (10)	0.756 (2)	0.2732 (13)	6.4 (5)
C(11′)	0.1310 (8)	0.047 (2)	0.5019 (10)	4.7 (4)
C(12′)	0.1033 (7)	−0.052 (2)	0.4341 (10)	4.0 (4)
C(13′)	0.1339 (8)	−0.025 (2)	0.3709 (10)	4.0 (4)
C(14′)	0.1809 (7)	0.087 (2)	0.4067 (9)	3.5 (3)
C(15′)	0.1810 (7)	0.131 (2)	0.4863 (10)	3.8 (4)
C(21′)	−0.0258 (7)	0.214 (2)	0.3014 (9)	3.4 (3)
C(22′)	0.0025 (6)	0.356 (2)	0.3186 (9)	3.3 (3)
C(23′)	0.0233 (7)	0.382 (2)	0.4104 (11)	4.3 (4)
C(24′)	0.0092 (8)	0.252 (2)	0.4468 (10)	4.1 (4)
C(25′)	−0.0237 (7)	0.152 (2)	0.3787 (11)	4.2 (4)
		Molecule **1b″**		
Re(1″)	0.42106 (2)	0.31990 (8)	0.31260 (3)	2.76 (1)
O(1″)	0.4421 (5)	0.227 (1)	0.1068 (7)	4.4 (3)
O(2″)	0.3492 (5)	0.359 (1)	0.0768 (6)	3.8 (2)
O(3″)	0.3142 (7)	0.023 (2)	0.0373 (7)	6.1 (3)
O(4″)	0.2825 (6)	−0.137 (1)	0.1168 (7)	4.9 (3)
C(1″)	0.3778 (6)	0.195 (2)	0.1949 (7)	2.9 (3)
C(2″)	0.3410 (7)	0.071 (2)	0.1858 (8)	3.5 (3)
C(3″)	0.3939 (7)	0.254 (2)	0.1238 (9)	3.5 (3)
C(4″)	0.3120 (7)	−0.011 (2)	0.1064 (9)	4.0 (4)
C(5″)	0.3642 (8)	0.428 (2)	0.0083 (10)	4.7 (4)
C(6″)	0.2489 (13)	−0.231 (2)	0.0432 (14)	7.8 (7)
C(11″)	0.3697 (7)	0.534 (2)	0.2496 (9)	3.4 (3)
C(12″)	0.1398 (7)	0.423 (2)	0.2396 (9)	3.7 (3)
C(13″)	0.3236 (7)	0.376 (2)	0.3222 (10)	4.1 (4)
C(14″)	0.3725 (8)	0.454 (2)	0.3842 (9)	4.5 (4)
C(15″)	0.4036 (10)	0.554 (2)	0.3445 (11)	5.5 (4)
C(21″)	0.4750 (7)	0.116 (2)	0.3821 (9)	3.7 (3)
C(22″)	0.4941 (8)	0.244 (2)	0.4355 (10)	4.8 (4)
C(23″)	0.5250 (7)	0.344 (2)	0.3976 (12)	4.8 (4)
C(24″)	0.5272 (6)	0.284 (2)	0.3210 (10)	3.8 (4)
C(25″)	0.4978 (7)	0.142 (2)	0.3117 (11)	4.2 (4)

[a] See footnote *a* in Table II.

DMAC at room temperature (Scheme I) as described by Dubeck and Schell.[7] When **1a** is heated in benzene solution at 75 °C, a slow thermal isomerization takes place to produce the alkenyl complex **1b**; the platinum catalyst mentioned in the original literature is unnecessary.

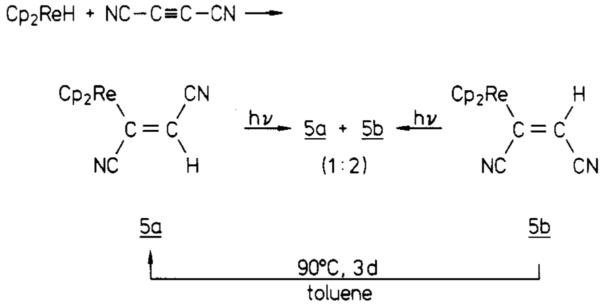
The structure of both isomers **1a** and **1b** was determined by single-crystal X-ray diffraction work (Tables I–III; Figures 1 and 2). This work shows unambiguously that the primary insertion product **1a** is the *Z* isomer while the thermodynamically more stable **1b** is the *E* isomer. Thus the reaction of Cp_2ReH with DMAC is a trans insertion process. These findings correct the stereochemical assignments of the original literature.[7]

Reaction of Cp_2WH_2 with $MeO_2CC{\equiv}CCO_2Me$. The systems Cp_2WH_2/DMAC and Cp_2MoH_2/DMAC are more complex because the insertion products can rearrange to form alkene complexes. When Cp_2WH_2 is treated with DMAC at room temperature, an alkenyl complex, **2a**, and two isomeric alkene complexes, **3a** and **3b**, are formed (Scheme II). Complex **2a**, which has already been observed by Nakamura and Otsuka,[9] possesses the *Z* configuration as shown by its ^{13}C NMR spectrum (see below). The fumaric ester complex **3a** (symmetry C_2) and the maleic ester complex **3b** (symmetry C_s) are easily distinguished by means of their ^1H NMR spectra; **3a** possesses two chemically equivalent Cp rings, while **3b** has two inequivalent Cp rings and hence gives two Cp signals of equal intensity in its ^1H NMR spectrum.

The (*Z*)-alkenyl compound **2a** slowly rearranges at slightly elevated temperatures to give small amounts of the *E* isomer **2b** together with the fumaric ester complex **3a** as the main product. Traces of **2b** may also be found in the Cp_2WH_2/DMAC reaction mixture. We conclude that the reaction of Cp_2WH_2 with DMAC is again a trans insertion process.

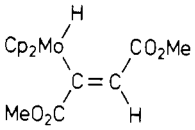
The maleic ester complex **3b** thermally isomerizes to the more stable fumaric ester complex **3a**. This isomerization is strongly catalyzed by traces of acid or by alumina during chromatography; as a consequence, we have not been able to isolate **3b**. Careful thermolysis of the (*E*)-alkenyl complex **2b** in C_6D_6 above 60 °C again gives the fumaric ester

Scheme III



complex **3a**; only traces of the expected product with the original cis disposition of the ester groups, the maleic ester complex **3b**, can be seen in the ^{1}H NMR spectrum.

Comparatively little is known about the Cp_2MoH_2/DMAC system. The reaction of Cp_2MoH_2 with DMAC gives the (*Z*)-alkenyl complex **4**[9,11] and as a byproduct a fumaric ester complex analogous to **3a**.[9] No other products can be detected by means of ^{1}H NMR control.[12]



4

Reaction of Cp_2ReH with NCC≡CCN. Cp_2ReH readily inserts dicyanoacetylene (DCA) to give the (*Z*)-alkenyl complex **5a** (Scheme III). Irradiation of **5a** in toluene affords a photostationary mixture of **5a** and the *E* isomer **5b** in a 1:2 ratio. The two isomers can be separated by chromatography on alumina. Pure (*E*)-alkenyl complex **5b** upon irradiation in toluene produces the same photostationary mixture as above. When **5b** in toluene is heated in the dark at 90 °C, slow isomerization takes place and quantitative conversion to the *Z* isomer **5a** is observed within 3 days.

The configurations of the two isomers **5a** and **5b** follow from their ^{13}C NMR spectra (see below). We note that the primary insertion product is again the *Z* isomer. In this case, however, the primary insertion product is also the thermodynamically more stable isomer.

X-ray Structural Results. Crystals of **1a** and of **1b** are van der Waals crystals. The asymmetric unit contains one molecule in the case of **1a** and two independent molecules **1b′** and **1b″** in the case of compound **1b**. Each molecule consists of a bent metallocene fragment and an alkenyl moiety. Important data are collected in Tables IV and V.

The bent metallocene fragments in **1a**, **1b′**, and **1b″** do not show unusual features. The Re–C(Cp) distances are similar to those found earlier, e.g., in $Cp_2Re–CHMe–O–ZrCp_2Me$ (224 pm)[13] and in $CpRe(\eta^4–C_5H_5Me)Me_2$ (224 pm).[14] The bending angle θ[15] of the $ReCp_2$ fragments is rather large as in other d^4 bent metallocene complexes.[13,16,17] The observation of large bending angles has been attributed to strong donor ability of the ligands[18,19] and to steric influences.[13,16b,20]

The Re–C(1) bond length (ranging from 215.0 (7) to 216.3 (6) pm) is well-characterized by our work. This bond

Table IV. Selected Bond Distances and Bond Angles for 1a, 1b′, and 1b″

	1a	**1b′**	**1b″**
(a) Bond Distances (pm)			
$Re–C(Cp)_{min}$	220.0 (6)	218.4 (8)	219.7 (7)
$Re–C(Cp)_{max}$	226.8 (6)	227.3 (7)	229.6 (7)
$Re–C(Cp)_{av}$	223.3	223.7	225.2
$C(Cp)–C(Cp)_{min}$	137.2 (10)	138.4 (9)	137.2 (10)
$C(Cp)–C(Cp)_{max}$	143.6 (10)	146.5 (10)	150.5 (10)
$C(Cp)–C(Cp)_{av}$	141.1	141.2	142.5
Re–C(1)	215.3 (6)	215.0 (7)	216.3 (6)
C(1)–C(2)	135.2 (8)	135.7 (10)	133.3 (9)
C(1)–C(3)	147.4 (8)	148.3 (9)	146.0 (9)
C(3)–O(1)	119.1 (7)	122.5 (7)	120.4 (8)
C(3)–O(2)	135.1 (7)	131.3 (8)	137.4 (8)
O(2)–C(5)	145.5 (8)	145.8 (8)	144.2 (8)
C(2)–C(4)	147.4 (8)	143.8 (9)	144.9 (9)
C(4)–O(3)	118.9 (7)	122.2 (8)	122.1 (8)
C(4)–O(4)	135.2 (8)	135.2 (8)	133.0 (8)
O(4)–C(6)	143.6 (8)	141.4 (10)	145.4 (9)
(b) Bond Angles (deg)			
Re–C(1)–C(2)	133.9 (4)	124.7 (5)	124.7 (4)
Re–C(1)–C(3)	111.7 (4)	114.0 (5)	114.5 (5)
C(2)–C(1)–C(3)	114.4 (5)	121.2 (6)	120.8 (6)
C(1)–C(3)–O(1)	128.0 (6)	123.2 (6)	127.8 (7)
C(1)–C(3)–O(2)	111.5 (5)	111.1 (6)	112.6 (6)
O(1)–C(3)–O(2)	120.5 (6)	125.6 (7)	119.5 (7)
C(3)–O(2)–C(5)	116.0 (6)	115.2 (6)	115.4 (6)
C(1)–C(2)–C(4)	127.1 (5)	125.3 (6)	124.3 (6)
C(2)–C(4)–O(3)	128.8 (6)	126.5 (7)	126.5 (7)
C(2)–C(4)–O(4)	108.6 (5)	111.4 (6)	111.8 (6)
O(3)–C(4)–O(4)	122.6 (6)	122.1 (6)	121.5 (7)
C(4)–O(4)–C(6)	115.6 (5)	114.7 (6)	119.3 (6)

Table V. Definition of Best Planes and Interplanar Angles (deg) for 1a, 1b′, and 1b″

		1a	**1b′**	**1b″**
plane A ≡ [C(11)⋯C(15)]	θ^a	146.2	146.8	145.7
plane B ≡ [C(21)⋯C(25)]				
plane C ≡ [Re(A),[b] Re, Re(B)]	∠(C,D)	86.7	84.2	93.0
plane D ≡ [Re, C(1), C(2)]				
plane E ≡ [O(1), C(3), O(2)]	∠(D,E)	98.9	85.7	90.8
plane F ≡ [O(3), C(4), O(4)]	∠(D,F)	6.6	4.1	5.0

[a] Bending angle $\theta = 180° - \angle(A,B)$. [b] Projection of Re atom onto plane A.

Table VI. ^{1}H NMR Data[a]

compd	Cp	CH═	CO_2CH_3	WH
1a[b]	4.20	6.72	3.45	
1b[b]	4.04	6.61	3.37, 3.61	
2a[c,d]	4.28, 4.40	6.63 (9),[e] 6.78 (10)[e]	3.37,[f] 3.41[f], 3.42[f]	−11.22 (65),[e] −12.77 (72)[e]
2b[c]	4.11	6.56 (7.5)[e]	3.35, 3.69	−12.11 (69.5)[e]
3a[b]	4.17	2.83 (5.5)[e]	3.47	
3b[b]	3.83, 4.49	2.18 (6.1)[e]	3.58	
5a[g]	3.88	6.10		
5b[g]	3.69	5.71		

[a] δ in ppm, Me_4Si as internal standard; all signals are singlets; satisfactory integration values were obtained. [b] C_6D_6, ambient temperature. [c] $C_6D_5CD_3$, 213 K. [d] Two conformational isomers. [e] $J(^{183}W–^1H)$ in Hz. [f] Relative intensities 3:3:6. [g] $C_6D_5CD_3$, ambient temperature.

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Table VII. ^{13}C **NMR Data**[a]

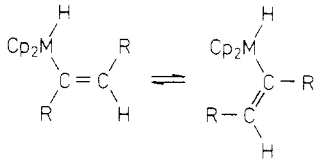
compd		Cp	^{1}C	^{2}C	^{3}C	^{4}C	OMe
1a[b,c]	(M = Re)	73.1 dqn[d] (182; 7)	148.8 d (4)	131.8 d (156)	176.8 dq (9; $3._5$)	168.1 qn ($3._5$)	50.2, 50.6 q (146)
2a[b,e]	(M = WH)	80.1 dqn[d] (182; $6._5$)	148.4 t (5)	130.5 d (146)	178.3 dm ($9._5$)	167.5 qn ($3._5$)	50.5, 50.7 q (147)
		80.8 dqn[d] (182; $6._5$)	160.6 t (6)	137.0 d (155)	180.3 dm ($\leq 9._5$)[f]	169.8 qn ($3._5$)	50.8, 51.3 q (147)
4[b,g]	(M = MoH)	84.5 dqn[d] (181; $6._5$)	168.3 d (3)	128.7 dd (153; 2)	178.5 dm ($8._5$)	177.4 m[h]	50.7, 51.0 q (144)
		85.4 dqn[d] (181; $6._5$)	170.2 d (4)	133.9 dd (155; 3)	180.8 dm ($8._5$)	180.1 m[h]	51.1, 51.4 q (144)
1b[c,i]	(M = Re)	72.7 dqn[d] (182; $6._5$)	154.4 s br	132.8 d (166)	176.8 dq (14; 4)	164.0 qn (4)	50.3, 50.7 q (146)
2b[c,i]	(M = WH)	80.0 dqn[d] (182; $6._5$)	159.7 d[j] (7)	137.8 dd (167; $3._5$)	178.9 dq (15; $3._5$)	163.0 qn ($3._5$)	50.2, 50.5 q (146)
5a[k,l]	(M = Re)	74.7 dqn[d] (182; 7)	131.1 d (6)	127.4 d (172)	124.9 d (9)	120.4 d (4)	
6[k,l]	(M = MoH)	86.1 dqn[d] (181; $6._5$)	160.1 dd (8; 8)	128.3 dd (170; 3)	125.5 d (10)	120.6 d (5)	
5b[m,n]	(M = Re)	74.3 dqn[d] (183; $6._5$)	131.0[o]	124.1 d (180)	123.5 d (16)	117.7 d (5)	

[a] δ in ppm relative to internal Me_4Si, in parentheses $J(^{13}C-^1H)$ in Hz; br = broad, s = singlet, d = doublet, t = triplet, q = quartet, qn = quintet, m = multiplet. [b] $Cp_2M[\eta^1-(Z)-^1C(^3CO_2Me)=^2CH(^4CO_2Me)]$. [c] $C_6D_5CD_3$, ambient temperature. [d] $^3J(^{13}C-^1H) \approx {}^2J(13C-^1H)$; cf. ref 24. [e] $C_6D_5CD_3$, 203 K; two conformational isomers. [f] Calculated from the half-width of the signal. [g] $(CD_3)_2CO$, 213 K; two conformational isomers. [h] Not resolved. [i] $Cp_2M[\eta^1-(C)-^1C(^3CO_2Me)=CH(^4CO_2Me)]$. [j] $J(^{183}W-^{13}C)$ = 86 Hz. [k] $Cp_2M[\eta^1-(Z)-^1C(^3CN)=^2CH(^4CN)]$. [l] $(CD_3)_2CO$, ambient temperature. [m] $Cp_2M[\eta^1-(E)-^1C(^3CN)=^2CH(^4CN)]$. [n] $CDCl_3$, ambient temperature. [o] Slightly broadened.

length is slightly shorter than Re–C(sp^2) distances in rhenium aryl compounds (typically 218–220 pm[21]) and much longer than Re–C(sp^2) distances (195–197 pm[22]) in rhenium carbene complexes.

The olefinic plane D (cf. Table V) through the atoms Re, C(1), and C(2) nearly coincides with the pseudoequatorial plane of the bent metallocene group. The prominent structural feature of the alkenyl moiety is the orientation of the ester groups (planes E and F) relative to the olefinic plane. While the ester group in the β-position is approximately coplanar with the vinyl metal grouping, the ester group in the α-position is nearly perpendicular to the olefinic plane. This preferential conformation is common to maleic and fumaric ester derivatives with bulky metallo substitutents at C(1).[11,22c,23]

Spectral Data and Stereochemical Criteria. Relevant ^{1}H and ^{13}C NMR data are collected in Tables VI and VII. The (*Z*)-alkenyl complexes **2a** and **4** show a doubling of all ^{1}H and ^{13}C signals at low temperatures. This kind of behavior has first been observed for the closely related complexes $Cp_2MH[\eta^1-(Z)-C(CF_3)=CH(CF_3)]$ (M = Mo, W) and is caused by rotational isomerism (eq 2).[9,10] In the case of **2a** line-shape analysis of the 270-MHz ^{1}H NMR Cp signals (in $C_6D_5CD_3$, temperature range −20 to +40 °C) yielded $\Delta G^‡ = 62.8 \pm 0.5$ kJ/mol at 298 K while the isomer ratio was found to be 0.46/0.54. For the less crowded *E* isomer **2b** no line doubling could be found (^{1}H NMR, 270 MHz, in $C_6D_5CD_3$, −60 °C).



(2)

The important problem is the determination of the alkene configuration.[2,5] It is well-established within the realm of organic chemistry that the powerful Karplus dihedral angle relationship for proton–proton coupling may be extended into a Karplus-like relationship for $^3J(^{13}C-^1H)$ coupling constants,[25] that means especially that $^3J(^{13}C-^1H)$ trans coupling constants are significantly larger than comparable cis coupling constants (cf. Figure 3).

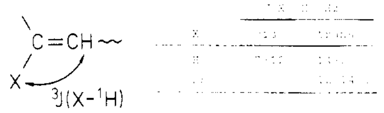
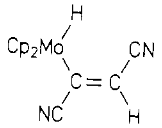


Figure 3. Typical values of vicinal coupling constants $^3J(^1H-^1H)$ and $^3J(^{13}C-^1H)$ for cis and trans disposition of the coupling nuclei.

These notions may be applied to organometallic complexes provided proton-coupled spectra of sufficient quality can be obtained. In the alkenyl complexes considered here the $^3J(^{13}C-^1H)$ cis coupling constant ranges from 8.5 to 10 Hz (**1a**, **2a**, **4**, **5a**, **6**) while the trans constants lie between 14 and 16 Hz (**1b**, **2b**, **5b**). The ranges observed are disjoint and close to the upper limit of the corresponding ranges established for organic compounds.[25] Taken together with the structure determinations for **1a** and **1b** these cis/trans assignments are unambiguous and straightforward. We note in passing that only few other $^3J(^{13}C-^1H)$ data of transition metal η^1-alkenyl complexes are known.[26]



6

There are indications of alternative stereochemical criteria from our NMR data. The $^3J(^{183}W-^1H)$ coupling constant for the trans coupling in **2a** (9 and 10 Hz for the two isomers) is larger than for the cis coupling in **2b** (7.5 Hz), as expected. Analogous though more pronounced differences of $^3J(^{195}Pt-^1H)$ coupling constants provide a well-established stereochemical criterion for (η^1-alkenyl)platinum complexes.[27,28] It should also be noted that the

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olefinic ${}^1J({}^{13}C-{}^1H)$ coupling constants in the [η^1-(*Z*)-CR=CHR] complexes are smaller (*R* = CO_2Me, 146–156 Hz for **1a**, **2a**, and **4**; R = CN, 170–172 Hz for **5a** and **6**) than in the corresponding *E* isomers (*R* = CO_2Me, 166 and 167 Hz for **1b** and **2b**; *R* = CN, 180 Hz for **5b**). The differences are larger than those usually observed for nonorganometallic ethylene derivatives[29] and are of complex origin.[29]

Discussion

The insertion reactions of activated, symmetrically disubstituted acetylenes (HFB, DMAC, DCA) with Cp_2ReH, Cp_2MoH_2, and Cp_2WH_2 give products of *Z* stereochemistry in all cases. In the case of HFB this has convincingly been established by the original work.[10] In the cases of DMAC and DCA the product configurations are now clarified (this work and ref 11). For complex **6** (readily prepared from Cp_2MoH_2/DCA)[12,30] and its tungsten analogue[30] an earlier study had used extensive comparisons of proton chemical shifts and proton–proton coupling constants to suggest the same *Z* configuration for these compounds;[30] furthermore a ${}^4J({}^1H-{}^1H)$ long-range coupling of 1.1 Hz has been correlated with the *Z* configuration of **6**.[30b] However, this method of assignment is less clear and less reliable than the stereochemical proofs of this paper.

We now have three pairs of configurational isomers (**1a**/**1b**, **2a**/**2b**, and **5a**/**5b**) where one isomer is unambiguously recognized as the kinetically controlled product. In each case the primary product is the *Z* isomer (**1a**, **2a**, **5a**) while the stereochemistry of the thermodynamically controlled products (**1b**, **2b**, **5a**) depends on individual product properties. Thus in these three cases trans insertion is rigorously established.

Various speculative mechanisms have been discussed for these reactions,[2,10,30a] although no kinetic data are available and few specifically mechanistic experiments have been described. Recent elegant work on the insertion reactions of activated acetylenes with *trans*-$PtH_2(PR_3)_2$ complexes has established a mechanism that consists (a) of an electron-transfer producing a caged radical pair and (b) of fast product formation involving proton transfer and radical combination.[28] The observed trans reaction stereochemistry is a straightforward consequence of this mechanism. Such a mechanism is likely also to be operative in the insertion reactions of the coordinatively saturated metallocene hydrides considered here. By contrast, coordinatively unsaturated metallocene hydrides as, e.g., Cp_2ZrHCl[31] and $(C_5Me_5)_2MH_2$ (M = Zr, Hf),[26b,32] give stereospecific cis insertion of acetylenes.

Experimental Section

General Procedures. Reactions were carried out under an atmosphere of dinitrogen by means of conventional Schlenk techniques. Pentane and hexane were distilled from Na/K alloy; benzene, toluene, and etheral solvents were distilled from sodium benzophenone ketyl. Methylene chloride was dried over P_4O_{10} and distilled. Alumina for chromatography (Woelm) was heated in a high vacuum at 300 °C and deactivated (7% H_2O, deoxygenated) after cooling. Melting points were measured in sealed capillaries and are uncorrected. Elemental analyses were performed by Analytische Laboratorien, D-5270 Gummersbach 1 Elbach, FRG.

NMR spectra were recorded on a Bruker WH 270 PFT-spectrometer (${}^1H$, 270 MHz; ${}^{13}C$, 67.88 MHz), a Bruker WP 80 PFT-spectrometer (${}^1H$, 80 MHz; ${}^{19}F$, 75.26 MHz), and a JEOL NM-C-60-HL CW-spectrometer (${}^1H$, 60 MHz). The digital resolution was <0.5 Hz/point for ${}^1H$ and ${}^{19}F$ spectra and <1.0 Hz/point for ${}^{13}C$ spectra. Electron-impact (70 eV) mass spectra were run on a Varian MAT CH5-DF spectrometer. Infrared spectra were recorded on a Perkin-Elmer 580 spectrometer and calibrated against the 1601 cm^{-1} band of polystyrene.

Materials. Cp_2ReH,[33,34] Cp_2WH_2,[35,36] and NCC≡CCN[37] were prepared as described in the literature. Samples of the molybdenum complexes **4**[9,11] and **6**[12,30] were provided by J. Okuda.[12] DMAC and $C_2(CONH_2)_2$ were available commercially and were used as received.

All rhenium and tungsten complexes prepared in this work are air-sensitive in solution; crystals of **1a**, **1b**, **3a**, **5a**, and **5b** can be handled in air without noticeable deterioration.

Reaction of Cp_2WH_2 with $MeO_2CC≡CCO_2Me$. DMAC (0.42 mL, 3.45 mmol) in THF (15 mL) was added dropwise to Cp_2WH_2 (1.09 g, 3.45 mmol) in THF (30 mL). The solution was stirred at room temperature for 2.5 h, filtered, and evaporated in vacuo to dryness. The residue was extracted with ether (50 mL) at 0 °C. The red soluble fraction yielded a mixture of **2a** and **2b** (ratio 4.3:1, 0.64 g, 41%) which could be separated by chromatography on alumina with CH_2Cl_2/Et_2O (10:1) at −25 °C. The light red, Et_2O-insoluble fraction consisted of **3a** and **3b** (ratio 2.5:1). Chromatography on alumina with toluene/THF (1:1) gave pure **3a**.

(a) **2a**: mp 93–94 °C; IR (cyclohexane, cm^{-1}) 1724.3 s, 1709.3 vs.

(b) **2b**: mp 108–108.5 °C; IR (cyclohexane, cm^{-1}) 1725.5 vs, 1709.7 s; MS (60 °C), *m/z* (I_{rel}) 458 (8, M^+), 314 (100, WCp_2^+). Anal. Calcd for $C_{16}H_{18}O_4W$: C, 41.94; H, 3.96. Found: C, 41.97; H, 3.99.

(c) **3a**: mp 229–233 °C dec; MS (160 °C), *m/z* (I_{rel}) 458 (38, M^+), 314 (100, WCp_2^+). Anal. Calcd for $C_{16}H_{18}O_4W$: C, 41.94; H, 3.96. Found: C, 41.71; H, 3.88.

Preparation of $Cp_2WH[\eta^1$-(*E*)-$C(CO_2Me)=CH(CO_2Me)]$ (2b). **2a** (0.70 g, 1.53 mmol) in benzene (40 mL) was kept at 40 °C for 18 h. Removal of the solvent in vacuo and extraction with Et_2O gave insoluble **3a** and a solution of **2b**. Crystallization from Et_2O/pentane (1:1) gave pure crystalline **2b** (0.112 g, 16%).

Reaction of Cp_2ReH with NCC≡CCN. A suspension of $C_2(CONH_2)_2$ (2 g, 18 mmol) and P_4O_{10} (15 g) in paraffin oil (20 mL) was heated in vacuo to 170 °C. The volatiles were condensed into a Schlenk tube containing Cp_2ReH (200 mg, 0.63 mmol) in CH_2Cl_2 (10 mL) at −196 °C. Warming to room temperature and chromatography of the dark red reaction mixture on alumina gave a yellow band of unreacted Cp_2ReH (eluent CH_2Cl_2/pentane (1:1)) and a red band (eluent CH_2Cl_2) which after a second chromatography afforded pure **5a** (97 mg, 39%).

5a: mp 185–186 °C; IR (KBr, cm^{-1}) 2205 s, 2178 s (CN); MS (65 °C), *m/z* (I_{rel}) 394 (93, M^+), 317 (100, $ReCp_2^+$). Anal. Calcd for $C_{14}H_{11}N_2Re$: C, 42.74; H, 2.82. Found: C, 42.90; H, 2.78.

Preparation of $Cp_2Re[\eta^1$-(*E*)-C(CN)=CH(CN)] (5b). **5a** (202 mg, 0.51 mmol) in toluene (50 mL) was irradiated for 2 days (medium-pressure mercury lamp, Duran glass vessel). Chromatography on alumina with CH_2Cl_2 gave a dark red solution; removal of the solvent and crystallization from CH_2Cl_2/hexane yielded dark red crystalline **5b** (87 mg, 43%). Elution with CH_2Cl_2/THF gave a second band containing **5a** (49 mg, 24%), identified by its ${}^1H$ NMR.

5b: mp 152.5 °C; IR (KBr, cm^{-1}) 2210 s, 2185 m (CN); MS (65 °C), *m/z* (I_{rel}) 394 (56, M^+), 317 (100, $ReCp_2^+$). Anal. Calcd for

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$C_{14}H_{11}N_2Re$: C, 42.74; H, 2.82. Found: C, 42.70; H, 3.10.

Irradiation of **5b** in toluene for 2 days as above afforded a mixture of **5a** and **5b** (ratio 1:2, determined by ^1H NMR). Complete conversion to **5a** was effected when the toluene solution of **5b** was heated to 90 °C for 3 days.

Crystal Structure Analysis of 1a. Dark red crystals of **1a** were obtained from solutions of **1a** in Et_2O at -60 °C. A platelet of suitable size was mounted in a glass capillary under nitrogen. Intensity data were collected on a CAD4 four-circle diffractometer (Enraf-Nonius, Delft, The Netherlands). Some decay (0.06%/h, total 9%) was observed; the decay correction[38] had little influence on the structural parameters. The structures were solved and refined by means of standard heavy-atom methods, alternating least-squares refinements, and difference Fourier calculations. All non-hydrogen atoms were refined anisotropically. No attempt was made to localize the hydrogen atoms experimentally; they were placed in calculated positions (d(C-H) = 95 pm, $B_{eq} = 5.0 \times 10^4$ pm^2). All calculations were performed on a VAX 11/730 computer using the SDP program system.[38] The maximum residual electron density in the final difference Fourier map was $<0.7 \times 10^{-6}$ e pm^{-3} outside the Re atom (distance from Re, $d >$ 140 pm).

Crystal Structure Analysis of 1b. Dark red crystals of **1b** were grown from benzene solutions by slow evaporation at ambient temperature. The data collection was done as in the case for **1a**. No decay or intensity fluctuations were observed. The structure was solved by standard methods as above. Calculations were performed on a PDP 11/45 computer. Units weights were used during refinement; more sophisticated weighting schemes were not tested, largely because of limitations of the computing facility. The final maximum residual electron density was $<0.5 \times 10^{-6}$ e pm^{-3} outside the Re atom ($d >$ 110 pm).

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Registry No. **1a**, 12092-03-4; **1b**, 12092-02-3; **2a**, 109279-69-8; **2b**, 12701-30-3; **3a**, 109011-49-6; **3b**, 109063-32-3; **5a**, 109011-50-9; **5b**, 109063-33-4; DMAC, 762-42-5; DCA, 1071-98-3; Cp_2WH_2, 1271-33-6; Cp_2ReH, 1271-32-5.

Supplementary Material Available: Tables of positional parameters for **1a** and general temperature factor expressions for **1a**, **1b′**, and **1b″** (3 pages); listings of structure factors for **1a** and **1b** (31 pages). Ordering information is given on any current masthead page.

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An Unexpected Carbon–Carbon Bond Formation in the Reaction between $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ and Hexafluorobut-2-yne. X-ray Crystal Structure of $[\{(\eta^5\text{-}C_5H_5)Co\}_2\{\mu\text{-}\eta^4,\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}C_4(CF_3)_4\}]\cdot 0.5CH_2Cl_2$

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Reaction of hexafluorobut-2-yne with $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$, in boiling toluene for 48 h, gives novel complexes $[(\eta^5\text{-}C_5H_5)Co\{\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}\}]$ and $[\{(\eta^5\text{-}C_5H_5)Co\}_2\{\mu\text{-}\eta^4,\eta^4\text{-}C_4(CF_3)_4C_{10}H_{12}C_4(CF_3)_4\}]$ resulting from cycloaddition of a cobaltacyclopentadiene intermediate to dicyclopentadiene. Decoordinations of the new ligands formed in the coordination sphere of the cobalt atoms are carried out by controlled-potential electrolyses. The dicobalt complex has been characterized by an X-ray diffraction study. Crystals are monoclinic of space group $P2/n$ with four molecules in a unit cell of dimensions a = 27.983 (7) Å, b = 9.248 (7) Å, c = 14.996 (9) Å, and β = 103.89 (3)°. The structure has been solved by direct methods and refined by full-matrix least squares to R (R') = 0.046 (0.062) for 2419 intensities.

Introduction

The ability of transition metals to promote cyclization reactions of alkynes with other organic molecules has attracted much attention in the last few years. In many cases, particularly with the low-valent metals, metallocyclopentadienes, formed by oxidative cyclization of two coordinated alkynes, are involved as intermediates.[1] In the course of our investigation of the (η^5-cyclopentadienyl)cobalt system,[2] we have found that the reaction of $[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ with hexafluorobut-2-yne gives novel high-membered rings bonded to cobalt centres. We propose a mechanism involving a cobaltacyclopentadiene as intermediate in the reaction.

Results and Discussion

$[Co(\eta^5\text{-}C_5H_5)(CO)_2]$ (**1**) (ca. 1.5 g) reacts with hexafluorobut-2-yne (ca. 2.8 g) in boiling toluene for 48 h to give complexes **3** (ca. 17%) and **4** (ca. 31%). Careful examination of the reaction mixture from which **3** and **4** were isolated (separation by column chromatography) revealed the presence of a third minor (ca. 3.5%) product (**2**) (Scheme I). More substantial yields of **2** are obtained

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