Regio- and Stereoselective Double Addition of Anionic C-Nucleophiles to Cobalt-Stabilized Acetylenedicarbaldehyde

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Though intrinsically unstable, Gorgues' acetylenedicarbaldehyde is an appealing, highly functional C4 synthon, which can be stabilized by η^2 complexation to a $Co_2(CO)_6$ unit. In contrast to the homologous dibenzoylacetylene complex, it can be used as a normal, doubly electrophilic, non-conjugated γ-dicarbonyl substrate toward alkyl-, aryl-, and alkynyllithium compounds or magnesium bromides; these anionic C-nucleophiles do not predominantly attack at the metal-carbonyl center. The 1,4-dialkyl- and 1,4-diphenylbut-2-yne-1,4-diol products are obtained with significant *meso*/dl diastereoselectivity (4–66% *de*), which can be explained by a simple model based on X-ray diffraction data and MM calculations. The alkyl- and arylmagnesium bromide reactants are more selective than their lithium counterparts.
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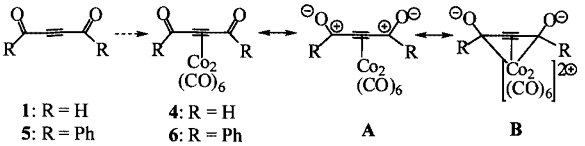
Introduction

Despite its potential strategic interest in retrosynthetic schemes of symmetrical functional targets, the instability of acetylene dicarbaldehyde **1**, though challenged by Gorgues, has limited its use in organic synthesis.[1] A stable $Co_2(CO)_6$ complex (**4**) has been prepared by Gorgues and Le Marouille from the $Co_2(CO)_6$ complex **3** of the diacetal **2**.[2,3] Reactions of **4** have been described with amines,[4] phosphorus ylides,[5] and enol ethers.[6] The numerous applications of the $Co_2(CO)_6$-activated substitution of *oxy*propyne derivatives (Nicholas reactions of propargylic alcohols, ethers, esters,[7] and acetals[8]) involve formally uncharged nucleophiles[9] (except borohydrides[10]) in either monopropargylic or bispropargylic versions.[6,11] Although $Co_2(CO)_6$ complexes of *oxo*propyne derivatives (alkynyl ketones and aldehydes) react with neutral nucleophiles (e.g., oxazaborolidine-BH_3 complexes,[12] silylenol ethers[6]), examples of addition of ligands of anionic C-nucleophiles, such as lithium enolates[13a] and very recently Grignard reagents,[13b] to acetylenic aldehydes are rare. Here, a parent study was undertaken with the bispropargylic dialdehyde complex **4** and the non-enolizable bispropargylic diketone complex **6**.

The possibility of 1,2- vs. 1,4-regiochemical competition in nucleophilic attacks of free diacylacetylenes **1** and **5** is a priori removed by complexation of the triple bond to $Co_2(CO)_6$. Nevertheless, the introduction of a new kind of electrophilic center in complexes **4** and **6** gives rise to a chemical competition between *organic carbonyl* groups (limit form A) and *metal carbonyl* groups (limit form B, Scheme 1). This ambiguity is accompanied by further questions regarding the mono/bis selectivity, and meso/dl stereoselectivity.



Scheme 1. Formal pairs of electrophilic sites of $Co_2(CO)_6$ complexes of diacylacetylenes.

Results

Complex **6** was readily prepared from dibenzoylacetylene **5** and $Co_2(CO)_8$.[6] While reaction of **6** with anionic alkyl- or alkynyllithiums produced intractable material, its reaction with ethylmagnesium bromide led to a mixture of decomplexation product **5**, reduced product **7a**,[14] and unchanged starting material **6**. Attempts to improve the selectivity by addition of $CeCl_3$ were unsuccessful.[15a] In the presence of $BF_3 \cdot OEt_2$, however, the reaction afforded a mixture of reduction product **7a** and acylation product **7b**.[16] The formation of **7a** is a consequence of the long-recognized reducing power of Grignard reagents.[15] A plausible mechanism for the formation of **7b** is proposed in Scheme 2. Actually, this observation is consistent with recent theoretical results on Nicholas' propargylic cations, which show

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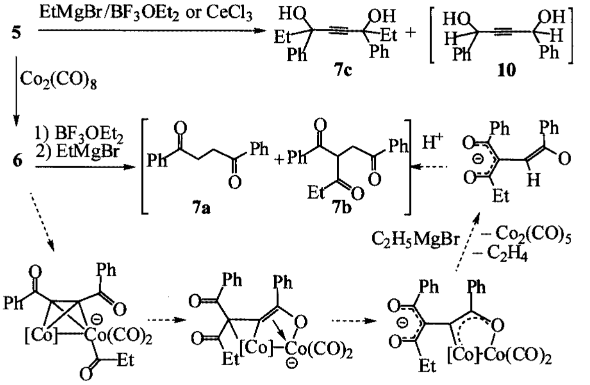
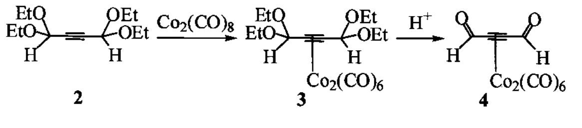
that whereas hard neutral nucleophiles are prone to react at the carbenium center, softer nucleophiles, such as carbanions, should react at the carbonylmetal center.[17] In comparison, free diketone **5** reacted with two equivalents of EtMgBr in the presence of either $BF_3{\cdot}OEt_2$ or $CeCl_3$ to afford the expected diethylation product **7c** (seemingly as a single diastereoisomer according to its ^{13}C NMR spectrum), along with reduction byproduct **10**.



Scheme 2. Synthesis and reactivity of the $Co_2(CO)_6$−dibenzoylacetylene complex with ethyl Grignard reagent. A plausible mechanism for the carbonylation/reduction of **6** to **7b** is proposed: After nucleophilic attack at a metal carbonyl and reductive elimination, the negative charge is stabilized in the β-diketonate fragment; reduction by the primary Grignard reagent[15b] brings about the loss of a $Co_2(CO)_5$ unit, as suggested in related processes.[6]

In contrast to the typical electronic and steric deactivation of the ketoyl functions in complex **6**, the study of the strain-free electrophilicity of the formyl functions in complex **4** deserved separate investigations. According to Gorgues and Meyer's reports,[2,3] diacetal **2** was prepared from acetylene dimagnesium bromide and diethylphenylorthoformate. This diacetal behaves as a normal alkyne ligand of transition metals.[18] In particular, **2** was readily converted into its $Co_2(CO)_6$ complex **3**. Formolysis of **3** afforded the dialdehyde complex **4** in quantitative yield.[2,3] (Scheme 3).



Scheme 3. Gorgues' synthesis of complex **4**.

Complex **4** exhibits spectroscopic properties of a classical "conjugated" aldehyde ($\nu_{HC=O}$ = 1671 cm^{-1}, δ_{CHO} = 10.30 ppm, δ_{CHO} = 191.3 ppm, $^1J_{C,H}$ = 187.1 Hz). Full X-ray diffraction data are consistent with partial data previously reported.[2] As in the case of **6**,[6] the crystal structure of **4** displays no hint of a possible $[Co{\cdots}C^+{-}O^-]$ interaction (Figure 1, Table 1).

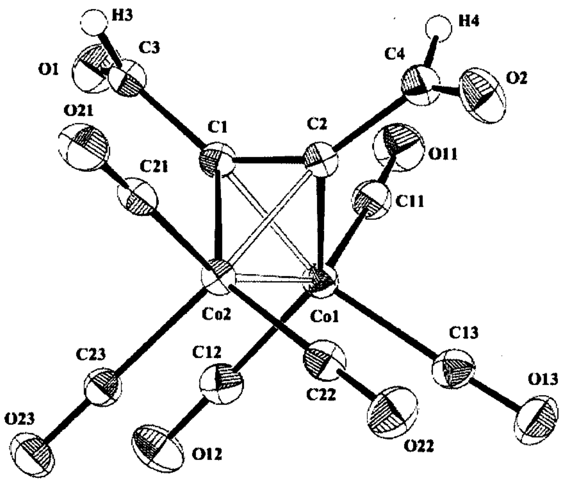


Figure 1. Detailed X-ray crystal structure of complex **4** (triclinic, P−1); selected bond lengths in Å and bond angles in degrees: Co(1)−C(1) = 1.924(3); Co(1)−C(2) =1.969(3); Co(1)−Co(2) = 2.4782(8); Co(2)−C(2) = 1.921(3); Co(2)−C(1) = 1.972(3); O(1)−C(3) = 1.198(4); O(2)−C(4) = 1.206(4); C(1)−C(2) = 1.359(4); C(1)−C(3) = 1.460(4); C(2)−C(4) =1.453(4); C(1)−C(2)−C(4) = 142.2(3); C(2)−C(1)−C(3) = 139.8(3); O(1)−C(3)−C(1) = 124.7(3); O(2)−C(4)−C(2) = 125.5(3).

While no selective electrophilicity is observed in complex **6**, regioselectivity is restored at the organic carbonyl centers in complex **4**. Indeed, two equivalents of various alkyl-, aryl- and alkynyllithium reactants added at the aldehyde functions of **4** to afford bisadducts **9a−e** in moderate yields, likely via the lithium salts of monoadducts **8a−e** (Scheme 4, Table 2). Although conversion of **4** to bisadduct **9** is far from quantitative (the RLi reactant is likely consumed in residual attack at metal carbonyl centers), monoaddition product **8** has been detected for alkyl nucleophiles only (R = Me, Et).

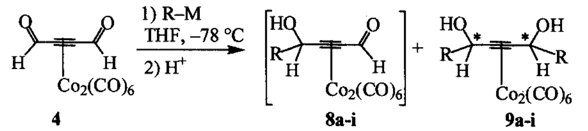
According to the ^1H NMR spectrum of the crude material, one of the epimers of **9a** was predominantly formed in 12% *de*. Crystallization from chloroform and analysis by X-ray diffraction allowed the assignment of a meso configuration to the major epimer of **9a** (Figure 2).[19]

The sp^3-hybridized carbanion of ethyllithium also reacted with **4** to give **9b** in 23% yield and 4% *de*. Again, X-ray diffraction studies (Figure 2) assigned a meso configuration to the major epimer of **9b**. The reaction, however, of *tert*-butyllithium with **4** did not yield the expected adduct **9c**, most likely because of steric hindrance.

In contrast, the sp^2-hybridized carbanion of phenyllithium reacted with **4** to produce **9d** in better isolated yield (37%) and stereoselectivity (54% *de*). Again, the meso configuration was assigned to the major epimer by X-ray crystallography (Figure 2). For comparison, an authentic sample of complex **9d** was prepared from $Co_2(CO)_8$ and 1,4-diphenylbut-2-yne-1,4-diol **10**, which was obtained by reaction of bis(trimethylsilyl)acetylene with two equivalents of benzaldehyde in the presence of catalytic amounts of KF and [18]crown-6.[20] The overall stereoselectivity of the latter method (*dl*:*meso*, 63:37) is reversed with respect to that

Table 1. Crystal data and structure refinement for complex **4** (Refinement method: Full-matrix least-squares on F^2)

Empirical formula	$C_{10}H_2Co_2O_8$	V (Å^3)	620.6(2)	R(int)	0.0325
Formula mass	367.98	Z	2	Completeness	
Temperature (K)	293(2)	ρ (g cm^{-3})	1.969	to $2\theta = 26.16$	91.6%
λ (Å)	0.71073	Abs. coef. μ(mm^{-1})	2.706	No of data	2275
Cryst. syst.	triclinic	F(000)	360	− restraints	0
Space group	P−1	θ range (deg)	2.15 to 26.16	− parameters	189
a (Å)	7.4070(10)	Index ranges	$-9 \le h \le 9$	R_1 [$I > 2\sigma(I)$]	0.0287
b (Å)	8.990(2)		$-11 \le k \le 11$	wR_2 [$I > 2\sigma(I)$]	0.0729
c (Å)	9.599(2)		$-11 \le l \le 11$	R_1 (all data)	0.0369
α (deg)	82.84(3)	Reflections		wR_2 (all data)	0.0797
β (deg)	83.54(3)	− collected	5743	ρ_{max} (e·Å^{-3})	0.362
γ (deg)	79.32(3)	− unique	2275	ρ_{min} (e·Å^{-3})	−0.362



Scheme 4. Nucleophilic addition to a protected acetylenedicarbaldehyde equivalent.

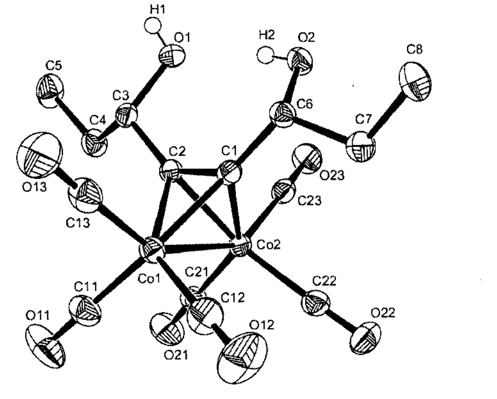
Table 2. Preparation of **9** from **4** and two equivalents of organolithium reactant

	RLi	**9**:**8**[a]	% *de*	% yield
a	MeLi	91:09	12[a]	22
b	EtLi	94:06	04[a]	23
c	*tert*-BuLi	–	–	–
d	PhLi	100:0	54[a]	37
e	PhC≡CLi	100:0	n.d.[b]	09
f	Me_3Si-C≡CLi	100:0	n.d.[c]	63
g	*rac*-(MeC_2)CPh(OMe)-C≡CLi (**11g**)	100:0	n.d.[d]	16
h	*rac*-(Me_3SiC_2)CPh(OMe)−C≡CLi (**11h**)	100:0	n.d.[d]	15
i	(Me_3SiC_2)CH(OTHP)−C≡CLi (**11i**)[e]	100:0	n.d.	15

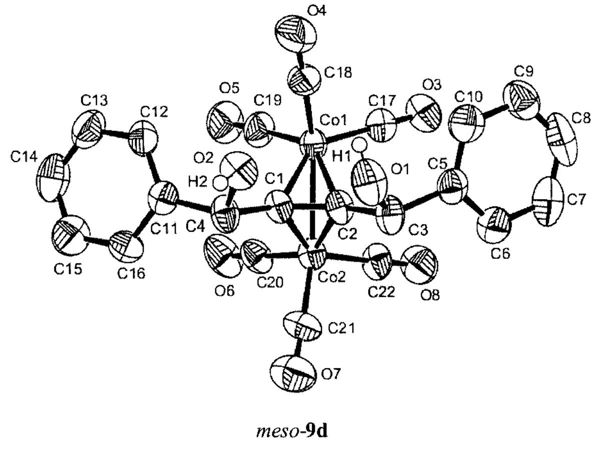
[a] Determined by ^{1}H NMR spectroscopy. [b] Integration of two slightly split signals in a resolved ^{13}C NMR spectrum afforded a rough estimate of 20 ± 10%. [c] Formal integrations of four split signals in a resolved ^{13}C NMR spectrum gave the same excesses of the main signals, 22%. [d] Signals of the a priori possible six diastereoisomers could not be resolved by NMR spectroscopy. [e] 50:50 mixture of racemic epimers.

of the former one (*dl:meso*, 23:77). Assuming that the stereochemistry of **10** was preserved during its complexation with $Co_2(CO)_6$, the preparation of free ligand **10** thus favored the dl epimer in 26% *de*.

sp-Hybridized carbanions also reacted with **4**. In accordance with the moderate nucleophilicity of acetylide reactants, reaction of **4** with PhC_2Li gave complex **9e** in rather low yield (9%). Stronger nucleophilicity, however, is restored in Me_3SiC_2Li, which afforded complex **9f** in 63% yield. The diastereoselectivity of the nucleophilic attack by acetetylides could not be determined in a reliable fashion. Indeed, because of the presence of paramagnetic impurities released from cobalt carbonyl units, it was not possible to resolve the two epimers of **9e** or **9f** by ^{1}H NMR spectroscopy. Moreover, despite several attempts, crystals of **9e**



meso-**9b**



meso-**9d**

Figure 2. X-ray-crystal structures of meso complexes **9b** and **9d**; selected bond lengths in Å and bond angles in degrees for **4** (triclinic, P−1); selected bond lengths in Å and bond angles in degrees. *meso*-**9b**: Co(1)−C(1) = 1.961(2); Co(1)−C(2) = 1.949(2); Co(1)−Co(2) = 2.4798(10); Co(2)−C(2) = 1.960(2); Co(2)−C(1) = 1.956(2); O(1)−C(3) = 1.441(3); O(2)−C(6) = 1.439(3); C(1)−C(2) = 1.348(3); C(2)−C(3) = 1.492(3); C(1)−C(6) =1.487(3); C(3)−C(4) = 1.520(3); O(1)−H(1) = O(2)−H(2) = 0.93(7); C(3)−C(5) =1.529(12); C(2)−C(1)−C(6) = 136.56(19); C(1)−C(2)−C(3) = 137.41(19); O(1)−C(3)−C(2) = 107.67(17); O(2)−C(6)−C(7) = 107.93(17). *meso*-**9d**: Co(1)−C(1) = 1.942(8); Co(1)−C(2) = 1.943(8); Co(1)−Co(2) = 2.4678(18); Co(2)−C(2) = 1.945(8); Co(2)−C(1) = 1.923(7); O(1)−C(3) = 1.406(11); O(2)−C(4) = 1.423(10); C(1)−C(2) = 1.328(11); C(2)−C(3) = 1.540(11); C(1)−C(4) =1.530(10); O(1)−H(1) = 0.70(3); O(2)−H(2) = 0.73(3); C(3)−C(4) =1.520(3); C(2)−C(1)−C(4) = 133.0(7); C(1)−C(2)−C(3) = 137.1(7); O(1)−C(3)−C(2) = 108.0(7); O(2)−C(6)−C(7) = 107.0(6).

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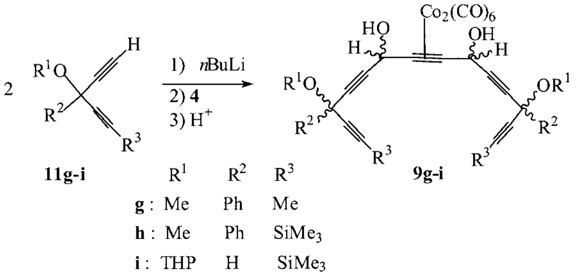
and **9f** were not suitable for X-ray crystal structure determination.

Symmetrical carbinol-skipped triynes and pentaynes are key intermediates for the synthesis of functional ring *carbo*mers of cycloalkanes or pericyclynes.[21] As a first application of the results above, tertiary and secondary carbinol-skipped pentayne complexes **9g**, **9h**, and **9i** were isolated in one step, albeit in moderate yields, by reaction of **4** with the lithium salts of diynes **11g**, **11h**, and **11i**, respectively (Table 2, Scheme 5).[22] The secondary carbinol-tetra-skipped pentayne complex **11i** was found to be particularly stable with respect to its tautomeric rearrangements. In all three cases, the signals of possible stereoisomers could not be assigned in NMR spectra and the stereoselectivity was not determined. It is noteworthy, however, that all carbon atoms of a given chemical type give sharp ^{13}C NMR resonances, but without resolved stereochemical fine structures; as previously noted for related structures, the remote dialkynyl stereogenic centers appear to be virtually independent.[21]



Scheme 5. Preparation of carbinol-skipped pentanyne complexes from lithium 1,4-heptadiynes and complex **4**.

Both the yields and diastereoselectivities of these reactions should depend on the countercation of the nucleophile. Indeed, we found that reactions of organomagnesium bromides with **4** gave compounds **9** with higher isolated yields and diastereoselectivities than do the corresponding reactions of organolithiums (Table 3). This feature is particularly interesting for alkyl nucleophiles, since the yields of **9a** and **9b** are both improved from ca. 20% to 80%, and their values of *de* are improved from 12% to 22% and from 4% to 60%, respectively. To a lesser extent, switching from PhLi to PhMgBr also resulted in improved yield and stereoselectivity in **9d** and **9e**. Thus, for sp^3- and sp^2-hybridized carbanions, the magnesium bromide salts are more selective at the aldehyde function than their lithium counterparts, but overall, however, are less reactive. Indeed, appreciable amounts of monoadducts **8** were obtained.

Table 3. Preparation of **9** from **4** and two equivalents of organomagnesium bromide reactant (compared with the preparation from the corresponding organolithium reactant)

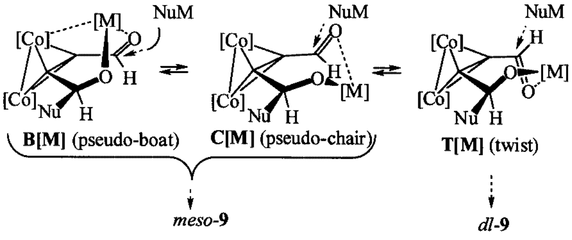
	RMgBr	% conversion[a]	9:8	% *de*[a]	% isolated yield
a	MeMgBr	100	87:13	22(12)	81 (22)
b	EtMgBr	100	73:27	60(04)	71 (23)
d	PhMgBr	100	88:12	66(54)	48 (37)
e	Ph-C≡CMgBr	100	52:48	n.d.[b]	16 (09)
f	Me_3Si-C≡CMgBr	62	67:33	n.d.	15 (63)

[a] Determined by ^1H NMR spectroscopy (see Exp. Sect. The values of *de* in brackets were obtained from reactions with lithium nucleophiles (see Table 2)). [b] Although the ^1H NMR spectra could not be resolved, the separation of the epimers by TLC allowed for the estimation: $36 < de \approx 68\%$ (see Exp. Sect.).

For *sp*-hybridized carbanions, the cation effect is much weaker. It is even reversed for trimethylsilylacetylide, which afforded **9f** in lower yield (15%) than did its lithium counterpart (63%), and even led repeatedly to the recovery of unchanged complex **4**.

Discussion

The origin of the stereochemical induction is tentatively proposed on the basis of a simple model. Let us first recall that the bending around the alkyne *sp*-carbon atoms brought about by $Co_2(CO)_6$ complexation (ca. 180° − 145° = 35°) draws the two reacting propargylic carbon atoms nearer. Whereas diacylacetylene complexes **4** and **6** display quasi-C_2 molecular symmetry in their crystals, *meso*-1,4-disubstituted but-2-yne-1,4-diol complexes **9a**, **9b**, and **9f** display quasi-C_s molecular symmetries. In the latter complexes, the short intramolecular HO···OH distances (ca. 2.70 Å) reveal intramolecular hydrogen bonding, which is evidenced further by the positions of the refined OH protons. In **9b**, for example, the values O−H = 0.93 Å, [H···O] =1.78 Å and [O−H···O] = 172.8°, are typical for hydrogen bonds. Replacement of the OH proton for M^+ (Li^+ or $MgBr^+$) gives a likely approximate structure for the metal salt of the primary monoaddition product **8**. In this structure, the cation acts as a Lewis acid for the second aldehyde function, thus closing a seven-membered metallacycle by a CH=O→[M] dative bond. Assuming that the first added nucleophile (e.g., ethylide) prefers a pseudo-equatorial orientation (anti to the triple bond), two kinds of conformations can be envisioned (Scheme 6): a quasi-C_s conformation (pseudo-chair **C[M]** or pseudo-boat **B[M]**) and a quasi-C_2 conformation (twisted, **T[M]**), which upon exo attack by the second nucleophile would lead to the meso and dl epimer of **9**, respectively.



Scheme 6. Putative conformations of the intermediate lithium salt of primary products **8**, and associated stereochemistries of the second nucleophilic attack by NuM. M = Li, MgBr. The first entered Nu group is assumed to lie in a pseudo-equatorial position.

To fit the experimental conditions closer, the model was refined by adding two THF ligands on lithium and one THF ligand on magnesium bromide. With this model, ESFF molecular mechanic calculations showed that in both cases [i.e., M = $Li(THF)_2$ and M = MgBr(THF)] the minimum-energy structures had quasi-C_s conformations, while no quasi-C_2 conformations exist as minima. The minimum C_s conformations are of the pseudo-boat type **B[M]** (Figure 3).

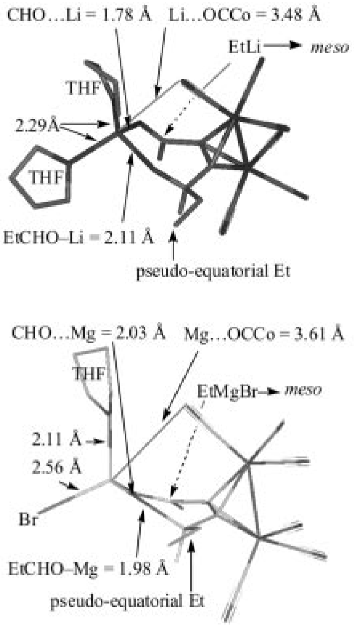


Figure 3 MM(ESFF) model for the intermediate resulting from the first attack of acetylene dicarbaldehyde complex **4** by EtLi [M = $Li(THF)_2$] and EtMgBr [M = MgBr(THF)]. [Co] = $Co(CO)_3$. In both cases, a single minimum conformation is found. They are of pseudo-boat type, **B[M]** (Scheme 6). These conformations account for the observed meso diastereoselectivity of the nucleophilic attack by the second equivalent of EtM.

Since the sterically favored exo attack of the remaining aldehyde function in the **B[M]** conformation would indeed provide a meso configuration for the bisaddition product **9**, the experimental meso stereoselectivity is explained simply by this model.

Conclusion

Complex **4** reacts quite efficiently with alkyl and aryl Grignard reagents. The lower reactivity of alkynyl nucleophiles has been challenged with Carreira's zinc reactant, but without success.[23] Nevertheless, though optimization of yields is required in a few cases, the present results show that use of this attractive, highly functional C_4 synthon is henceforth possible. These compounds are potentially valuable at three levels. Firstly, the introduced $Co_2(CO)_6$ metal core could be reused as an activator for a further Nicholas reaction of the primary 1,4-butyndiols products with *neutral* C-nucleophiles, such as enol ethers; overall retention of configuration of the asymmetric propargylic carbinol center would allow the preservation of the stereochemical information gained in the first addition step. Secondly, owing to the availability of various known methods for oxidative deprotection of Nicholas' cobalt complexes,[24] the triple bond of the symmetrical 1,4-difunctional but-2-yne derivatives could be used in further classical functionalization (e.g., semi-hydrogenation to cis-meso bisallylic diol derivatives). Thirdly, a cyclizing version of this methodology can be applied to the synthesis of five- and six-membered ring *carbo*mers of carbocycles, which will be reported shortly.[25]

Experimental Section

THF and diethyl ether were distilled over Na/benzophenone. Pentane and dichloromethane were distilled over P_2O_5. Commercial organomagnesium bromide and organolithium reactants were used: EtMgBr (3 M in diethyl ether), MeMgBr (3 M in diethyl ether), PhMgBr (3 M in ether), *n*BuLi (2.5 M in hexanes), MeLi (1.6 M in ether), and PhLi (1.6−1.8 M in cyclohexane/diethyl ether). Solutions of ethyllithium in diethyl ether were prepared according to a described procedure.[26] Alkyllithium solutions were titrated with 2,2,2′-trimethylpropionanilide.[27] Dibenzoylacetylene **5**,[28] its complex **6**,[6] and racemic 1-trimethylsilyl-3-hydroxy-3-phenylpenta-1,4-diyne **11h**,[21] were prepared according to described procedures. TLC was performed on a 60F254 silica gel phase. Mass spectra (DCI/NH_3) were recorded on a Nermag R10−10H apparatus. IR spectra were recorded on a Perkin−Elmer Spectrum GX FT-IR spectrometer using a CaF_2 cell. ^1H NMR spectra were recorded on Bruker AC 200, AM 250, and AMX 400 spectrometers at 200, 250, and 400 MHz, respectively; ^{13}C spectra were recorded at 50 MHz, 62.9, and 100 MHz, respectively. Positive chemical shifts at low field are expressed in ppm by internal reference to TMS. Samples of cobalt complexes for NMR spectroscopy were filtered through celite before recording their spectra.

Acetylenedicarbaldehyde Bis(diethyl acetal) Complex 3: A solution of 1,1,4,4-tetraethoxybut-2-yne **2** (3.56 g, 15.5 mmol) in diethyl ether (30 mL) was poured into a solution of dicobaltoctacarbonyl (5.30 g, 15.5 mmol) in diethyl ether (30 mL). After stirring for 3 h, the solution was filtered and the solvents were evaporated to dryness. Complex **3** was obtained as a brown oil (7.61 g, 95%). TLC (heptane/EtOAc, 7:3): $R_f = 0.50$. MS (DCI/NH_3): *m/z* = 534 ($[M + NH_4]^+$), 471 ($[MH - EtOH]^+$). IR ($CDCl_3$): $\nu_{sp3\text{-}CH} = 2980$ (m), 2931 (w), 2875 (w) cm^{-1}; $\nu_{C\equiv O} = 2097$ (s), 2060 (vs), 2034 (vs) cm^{-1}. ^1H NMR ($CDCl_3$, 250 MHz): $\delta = 1.22$ (t, 12 H, CH_3); 3.73 (q, 8 H, CH_2); 5.44 [s, 2 H, $CH(OEt)_2$] ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): $\delta = 13.95$ (q, $^1J_{C,H} = 125.9$ Hz, CH_3), 63.27 (dt-like, $^1J_{C,H} = 141.2$, $^2J_{C,H} = 3.9$ Hz, CH_2O), 91.68 (s, $C\equiv C$), 101.81 (d, $^1J_{C,H} = 161.5$ Hz, $CH(OEt)_2$], 199.47 [br s, $Co_2(CO)_6$] ppm.

Acetylenedicarbaldehyde Complex 4: Bis(diethyl acetal) complex **3** (7.60 g, 14.73 mmol) was dissolved in formic acid (120 mL) at 0 °C. After stirring for 2.5 h between 0 °C and room temp., the solution was filtered, evaporated, and dried under vacuum for 1.5 h. The red-brown residue was dissolved in CH_2Cl_2 and the solution was filtered through a small pad of silica gel. The filtrate was again evaporated, the residue dissolved in diethyl ether and the resulting solution filtered though celite. After evaporation, complex **4** was obtained as a red-orange microcrystalline solid (4.80 g, 89%). TLC (pentane/Et_2O, 9:1): $R_f = 0.52$. MS (DCI/NH_3): *m/z* = 386 ($[M + NH_4]^+$), 369 ($[MH]^+$). IR ($CDCl_3$): $\nu_{OC-H} = 2814$ (w) cm^{-1};

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$\nu_{\mathrm{C{\equiv}O}}$ = 2114 (s), 2081 (vs), 2057 (vs) cm^{-1}; $\nu_{\mathrm{HC=O}}$ = 1671 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 10.30 (s, C*H*O) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 85.88 (d, $^3J_{\mathrm{C,H}}$ = 36 Hz, *C*≡*C*-CHO), 191.30 (d, $^1J_{\mathrm{C,H}}$ = 187 Hz, *C*HO), 199.47 [s, $Co_2(\mathit{C}O)_6$] ppm. Recrystallization from CH_2Cl_2/pentane afforded crystals of **4** suitable for an X-ray structure determination.

Reaction of Complex 6 with EtMgBr: $BF_3{\cdot}OEt_2$ (0.097 mL, 0.77 mmol) was added by syringe into a solution of diketone complex **6** (0.200 g, 0.385 mmol) in diethyl ether (20 mL) at −78 °C. After stirring for 1.5 h, a solution of EtMgBr in diethyl ether (3 M, 0.256 mL, 0.77 mmol) was added by syringe. The resulting deep-red solution was kept at −15 °C for 17 h, then quenched with saturated aqueous NH_4Cl (20 mL). The organic layer was separated, washed with aqueous NH_4Cl and the solvents evaporated to dryness. Three products were identified in the ^{1}H NMR spectrum of the crude material: starting material **6** (73%), reduced product **7a** (5%), and acylated product **7b** (22%). The reddish residue (0.107 g) was chromatographed over silica gel eluting with pentane/diethyl ether mixtures of increasing polarity (starting at 95:5). After recovering unchanged **6**, triketone **7b** was obtained as a yellow oil (0.007 g, ca. 6%) containing 20% of reduced product **7a** (δ_{H} = 3.46 ppm).[14] TLC (pentane/Et_2O, 1:1): R_{f} = 0.72. MS (DCI/NH_3): *m*/*z* = 312 ($[M + NH_4]^+$), 295 ($[MH]^+$). IR ($CDCl_3$): $\nu_{\mathrm{EtC=O}}$ = 1723 (s) cm^{-1}; $\nu_{\mathrm{PhC=O}}$ = 1675 (s br) cm^{-1}; $\nu_{\mathrm{ArC=C}}$ = 1598 (m), 1581 (w), 1449 (m) cm^{-1}. ^{1}H NMR ($CDCl_3$, 400 MHz): δ = 1.07 (t, $^3J_{\mathrm{H,H}}$ = 7.2 Hz, 3 H, CH_3), 2.63 (second-order m, from the decoupling of the Me resonance at δ =1.07 ppm: $^2J_{\mathrm{H,H}}$ = 18.8 Hz, 2 H, O=C-CH*H*-Me), 2.56 (second-order m, from the decoupling of the Me resonance at δ = 1.07 ppm: $^2J_{\mathrm{H,H}}$ = 18.8 Hz, 2 H, O=C-C*H*H-Me), 3.62 (dd, $^2J_{\mathrm{H,H}}$ = 18.3, $^3J_{\mathrm{H,H}}$ = 6.2 Hz, 1 H, C*H*HCOPh), 3.85 (dd, $^2J_{\mathrm{H,H}}$ = 18.3, $^3J_{\mathrm{H,H}}$ = 7.0 Hz, 1 H, CH*H*COPh), 5.34 (t-like, $^3J_{\mathrm{H,H}}$ ≈ 6.6 Hz, 1 H, C*H*COEt), 7.49 (t-like, $^3J_{\mathrm{H,H}}$ ≈ 7.8 Hz, 2 H, *m*-C*H*), 7.55 (t-like, $^3J_{\mathrm{H,H}}$ ≈ 7.7 Hz, 2 H, *m*-C*H*), 7.61 (t-like, $^3J_{\mathrm{H,H}}$ ≈ 7.3 Hz, 1 H, *p*-C*H*), 7.66 (t-like, $^3J_{\mathrm{H,H}}$ ≈ 7.3 Hz, 1 H, *p*-C*H*), 8.01 (d, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 2 H, *o*-C*H*), 8.11 (d, $^3J_{\mathrm{H,H}}$ = 7.6 Hz, 2 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 100 MHz): δ = 8.09 (O=CCH$_2$*C*H$_3$), 36.28 (O=C*C*H$_2$Me), 38.60 (*C*H$_2$COPh), 56.28 (*C*HCOPh), 128.66, 129.11, 129.85, 130.04 (*o*- and *m*-*C*H), 134.01, 134.30 (*p*-*C*H), 136.41, 136.52 (*ipso*-*C*-CO), 196.88 (Et-COCH(Ph)*C*=O), 197.53 (CH$_2$(Ph)*C*=O), 205.45 (Et*C*=O) ppm. ^{1}H and ^{13}C assignments were confirmed by ^{13}C 140 Hz-J-MOD, ^{1}H-^{1}H COSY-DQF-GS, ^{1}H-^{13}C ^{1}J-HMQC, ^{1}H-^{13}C LR-HMQC, and ^{1}H-^{13}C HMBC experiments.

Reaction of 5 with EtMgBr/CeCl$_3$, 3,6-Diphenyl-oct-4-yne-3,6-diol (7c): A solution of EtMgBr in diethyl ether (3.0 M, 0.81 mL, 2.4 mmol) was added by syringe into a solution of $CeCl_3$ (0.60 g, 2.43 mmol) in THF (5 mL) at 0 °C. After stirring for 1.5 h, the mixture was cooled to −78 °C and a solution of diketone **5** (0.285 g, 1.21 mmol) in THF (5 mL) was added. The mixture was warmed to room temp. over 5 h, and the resulting suspension was stirred overnight at room temp. The mixture was then cooled to −40 °C and treated with aqueous acetic acid (10%, 10 mL). The orange solution was extracted with diethyl ether. The ethereal phase was washed sequentially with aqueous NH_4Cl, aqueous $NaHCO_3$, and brine, then dried over $MgSO_4$ and the solvents evaporated to dryness. The residue (0.325 g) was chromatographed over silica gel eluting with pentane/diethyl ether (90:10). Diol **7c** was obtained as a yellow oil (0.087 g, 24%). TLC (pentane/Et_2O, 9:1): R_{f} = 0.42. IR ($CDCl_3$): $\nu_{\mathrm{O-H}}$ = 3591 (s) cm^{-1}; $\nu_{\mathrm{C-H}}$ = 2974 (s), 2938 (m) cm^{-1}; $\nu_{\mathrm{arC=C}}$ = 1601 (m), 1449 (s) cm^{-1}; ν_{COH} = 1326 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 312 ($[M + NH_4]^+$), 294 ($[M + NH_4 - H_2O]^+$), 277 ($[MH - H_2O]^+$), 259 ($[MH - 2H_2O]^+$). ^{1}H NMR ($CDCl_3$, 200 MHz): δ = 0.96 (m, 6 H, CH_3), 1.95 (m ≈ 2q, 4 H, diastereoisotopic C*H*$_2$Me), 3.12 (br, 2 H, O*H*), 7.27−7.39 (m, 6 H, *o*-, *m*-C*H*), 7.58−7.64 (m, 4 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 50 MHz): δ = 9.04 (*C*H$_3$), 38.21 (*C*H$_2$Me), 73.81 (*C*HOH), 88.16 (*C*≡*C*), 125.40, 127.98 (*o*-, *m*-*C*H), 127.49 (*p*-*C*H), 144.12 (*ipso*-*C*) ppm. Further elution gave **7c** as a mixture with the reduced side product **10**, identified by comparison with the ^{1}H NMR spectrum of an authentic sample (see below).

1-Trimethylsilyl-3-methoxy-3-phenylhexa-1,4-diyne (MeC$_2$)(OMe)-PhC(C$_2$SiMe$_3$): This compound was obtained as a byproduct formed during the preparation of **11h** by exhaustive methylation of 1-trimethylsilyl-3-hydroxy-3-phenylpenta-1,4-diyne (HC_2)PhC(OH)-(C_2SiMe_3) with CH_3I.[21]
TLC (hexane/EtOAc, 9:1): R_{f} = 0.67. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.21 [s, 9 H, Si(C*H*$_3$)$_3$], 1.93 (s, 3 H, ≡C-C*H*$_3$), 3.44 (s, 3 H, OC*H*$_3$), 7.33−7.37 (m, 3 H, *m*- and *p*-C*H*), 7.75 (dd, $^2J_{\mathrm{H,H}}$ ≈ 7.8, $^3J_{\mathrm{H,H}}$ ≈ 1.7 Hz, 2 H, *o*-C*H*) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = −0.19 [q, $^1J_{\mathrm{C,H}}$ = 120 Hz, Si(*C*H$_3$)$_3$], 3.90 (q, $^1J_{\mathrm{C,H}}$ = 132 Hz, ≡C−*C*H$_3$), 52.64 (q, $^1J_{\mathrm{C,H}}$ = 143 Hz, O*C*H$_3$), 71.97 (s, *C*OMe), (76.49−77.51, masked signal of ≡*C*−Me ?), 83.22 (s, *C*≡CMe), 91.17 (s, *C*≡C−SiMe$_3$), 102.35 (s, ≡*C*−SiMe$_3$), 126.60 (dt-like, $^1J_{\mathrm{C,H}}$ = 160 Hz, *m*-*C*H), 128.21 (dm, $^1J_{\mathrm{C,H}}$ = 160 Hz, *o*-*C*H), 128.51 (dm, $^1J_{\mathrm{C,H}}$ = 161 Hz, *p*-*C*H), 141 (s, *ipso*-*C*) ppm.

3-Methoxy-3-phenylhexa-1,4-diyne (11g): 1-Trimethylsilyl-3-methoxy-3-phenylhexa-1,4-diyne (2.30 g, 8.97 mmol) was dissolved in methanol (100 mL) at room temp. and K_2CO_3 (18.54 g, 134 mmol) was added. After stirring for 4 h the mixture was filtered and the solution was diluted with diethyl ether, washed with water, and then the solvents were evaporated to dryness. The crude residue (1.71 g) was chromatographed over silica gel (pentane/acetone, 95:5). Diyne **11g** was obtained as an orange oil (1.17 g, 71%).
TLC (pentane/acetone, 95:5): R_{f} = 0.75. MS (DCI/NH_3) *m*/*z* = 202 ($[M + NH_4]^+$), 185 ($[MH]^+$), 170 ($[M + NH_4 - MeOH]^+$), 153 ($[MH - MeOH]^+$). $C_{13}H_{12}O$ (184.2): calcd. C 84.75, H 6.57; found C 84.57, H 6.82. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.95 (s, 3 H, ≡C−C*H*$_3$), 2.74 (s, ≡C−*H*), 3.48 (s, 3 H, OC*H*$_3$), 7.35−7.38 (m, 3 H, *m*- and *p*-C*H*), 7.76 (dd, $^2J_{\mathrm{H,H}}$ ≈ 7.9, $^3J_{\mathrm{H,H}}$ ≈ 1.7 Hz, 2 H, *o*-C*H*) ppm. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 3.98 (q, $^1J_{\mathrm{C,H}}$ = 132 Hz, ≡C−*C*H$_3$), 52.64 (q, $^1J_{\mathrm{C,H}}$ = 143 Hz, O*C*H$_3$), 71.76 (s, *C*OMe), 72.48 (d, $^1J_{\mathrm{C,H}}$ = 254 Hz, ≡*C*H), 76.85 (partly masked m, ≡*C*−Me), 81.90 (d, $^2J_{\mathrm{C,H}}$ ≈ 49 Hz, *C*≡CH), 83.87 (br s, *C*≡CMe), 126.63 (dt-like, $^1J_{\mathrm{C,H}}$ = 159 Hz, *m*-*C*H), 128.51 (dd, $^1J_{\mathrm{C,H}}$ ≈159, $^2J_{\mathrm{C,H}}$ ≈ 7 Hz, *o*-*C*H), 128.88 (dt, $^1J_{\mathrm{C,H}}$ = 161, $^2J_{\mathrm{C,H}}$ ≈ 8 Hz, *p*-*C*H), 140.51 (s, *ipso*-*C*) ppm.

1-Trimethylsilyl-3-(2-tetrahydropyranyl)oxypenta-1,4-diyne (11i): A mixture of racemic 1-trimethylsilylpenta-1,4-diyn-3-ol (1.006 g, 6.62 mmol), dihydropyran (1.8 mL, 20 mmol) and *p*-toluenesulfonic acid (22.9 mg, 0.12 mmol) in toluene (40 mL) was stirred for 6 h at room temp. The reaction was quenched by addition of triethylamine. After removal of the solvent under reduced pressure, dichloromethane (100 mL) and water (100 mL) were added. The organic layer was washed with water, dried over $MgSO_4$, and concentrated to produce a 50:50 mixture of the epimers of **11i** as an orange oil (1.212 g, 77%). IR ($CDCl_3$) $\nu_{\mathrm{O-H}}$ = 3308 (s) cm^{-1}; $\nu_{\mathrm{C-H}}$ = 3018, 2947, 2874, 2854 (s) cm^{-1}; $\nu_{\mathrm{C{\equiv}C}}$ = 2248 (s) cm^{-1}; $\nu_{\mathrm{C-Si}}$ = 1252 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 254 ($[M + NH_4]^+$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.13, 0.14 [2 s, 9 H, Si(C*H*$_3$)$_3$], 1.48−1.81 (m, 6 H, C*H*$_2$C*H*$_2$C*H*$_2$), 2.48, 2.51 (2 d, $^4J_{\mathrm{H,H}}$ = 2.3, 2.4 Hz, 1 H, ≡C-*H*), 3.47−3.54 and 3.80−3.84 (2 m, 2 H, diastereoisotopic C*H*$_2$O), 4.91−4.96 (m, 1 H, C*H*O$_2$), 5.13 and 5.15 (2 d, $^4J_{\mathrm{H,H}}$ = 2.3, 2.4 Hz, 1 H, C*H*OTHP) ppm. ^{13}C{^{1}H} NMR

(CDCl$_3$, 62.9 MHz. Assignment from the ^{13}C{^{1}H} gated spectrum): δ = −0.37 [Si(*C*H$_3$)$_3$], 18.51, 18.70, 25.42, 29.84, 29.90 (*C*H$_2$*C*H$_2$*C*H$_2$), 54.63, 54.78 (*C*HOTHP), 61.72, 61.99 (*C*H$_2$O), 72.35, 73.34 (≡*C*H), 78.76, 79.20 (*C*≡C−H), 89.50, 90.47 (*C*≡C−Si), 95.08, 95.45 (*C*HO$_2$), 99.23, 99.73 (≡*C*−Si) ppm.

1,4-Diphenylbut-2-yne-1,4-diol (10): Bis(trimethylsilyl)acetylene (3.94 mmol, 17.6 mmol) was added to a mixture of KF (30.7 mg, 0.53 mmol, 3 mol%) and [18]crown-6 (0.139 g, 0.53 mmol) at 0 °C. Benzaldehyde (3.6 mL, 35.2 mmol) was then slowly added, and the solution was heated under reflux overnight. Because of the presence of unchanged benzaldehyde, KF (0.012 mg, 0.2 mmol) was added again, and the mixture was heated under reflux for another 1 h. After cooling, the solvent was evaporated and the residue (6.519 g) was analyzed by ^{1}H NMR spectroscopy and found to contain the bis(trimethylsilyl)diether of **10**. Thus, the residue was dissolved in methanol (60 mL), potassium carbonate (9.70 g, 70 mmol) was added, and then the mixture was stirred for 2 h at room temp. The solution was filtered and evaporated, and the residue (7.41 g) was partitioned between saturated aqueous NH$_4$Cl (100 mL) and dichloromethane (100 mL). The organic layer was separated, washed with water until pH 7 was reached, dried over MgSO$_4$, filtered, and then the solvents were evaporated. The orange residue (2.203 g) was chromatographed over silica gel (CH$_2$Cl$_2$/THF, 95:5).

Pure 1-phenylbut-2-yn-1-ol eluted first and was obtained as an orange oil (0.241 g, 10%). TLC (CH$_2$Cl$_2$/THF, 95:5): R_f = 0.72. ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 2.67 (d, $^4J_{H,H}$ = 2.4 Hz, 1 H, ≡C*H*), 3.41 (br s, exchangeable with D$_2$O, 1 H, O*H*), 5.43 (br s, 1 H, C*H*OH), 7.36−7.46 (m, 6 H, *m*- and *p*-C*H*), 7.54−7.59 (m, 4 H, *o*-C*H*) ppm.

Diol **10** was obtained as a white solid (0.280 g, 20%). TLC (CH$_2$Cl$_2$/THF, 95:5): R_f = 0.35. ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 2.22 (d, $^3J_{H,H}$ = 6.0 Hz, exchangeable with D$_2$O, 2 H, O*H*), 5.56 (d, $^3J_{H,H}$ = 5.9 Hz, 2 H, C*H*OH), 7.33−7.41 (m, 6 H, *m*- and *p*-C*H*), 7.52−7.56 (m, 4 H, *o*-C*H*) ppm.

9d from Co$_2$(CO)$_8$ and 10: Solid Co$_2$(CO)$_8$ (0.436 g, 1.26 mmol) was added to a suspension of 1,4-diphenylbut-2-yne-1,4-diol **10** (3.00 g, 1.26 mmol) in dichloromethane (20 mL) at room temp. The medium turned red and CO evolved. After stirring overnight, the solvent was evaporated and the residue dissolved in diethyl ether. The solution was filtered through celite and the solvents were evaporated to dryness. Pure complex **9d** was obtained as a brown foam (0.638 g, 97%).

TLC (pentane/Et$_2$O, 7:3): R_f = 0.73. IR (CDCl$_3$): ν_{O-H} = 3588 (s, free), 3448 (s, hydrogen bonded OH) cm^{-1}; ν_{C-H} = 3032 (w) cm^{-1}; $\nu_{C\equiv O}$ = 2095 (vs), 2059 (vs), 2034 (vs) cm^{-1}; $\nu_{arC=C}$ = 1603 (m), 1494 (m), 1453 (m) cm^{-1}. MS (DCI/NH$_3$): *m/z* = 542 ([M + NH$_4$]$^+$), 507 ([MH − H$_2$O]$^+$), 479 ([MH − H$_2$O − CO]$^+$).

***meso*-9d:** ^{1}H NMR (CDCl$_3$, 200 MHz): δ = 3.44 (br, 2 H, O*H*), 5.96 (s, 2 H, C*H*OH), 7.30−7.47 (m, 10 H, aromatic C*H*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ = 74.52 (*C*HOH), 102.38 (η^2-*C*≡*C*), 125.57 (*o*-*C*H), 128.22 (*p*-*C*H), 128.63 (*m*-*C*H), 143.14 (*ipso*-*C*), 198.49 [Co$_2$(*C*O)$_6$] ppm.

***threo*-9d:** ^{1}H NMR (CDCl$_3$): δ = 3.55 (d, $^3J_{H,H}$ ≈ 2 Hz, 2 H, O*H*), 5.89 (d, $^3J_{H,H}$ ≈ 2 Hz, 2 H, C*H*OH), 7.30−7.47 (m, 10 H, aromatic C*H*) ppm. ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ = 75.10 (*C*HOH), 100.82 (η^2-*C*≡*C*), 125.57 (*o*-*C*H), 125.71 (*p*-*C*H), 128.63 (*m*-*C*H), 143.63 (*ipso*-*C*), 198.49 [br, Co$_2$(*C*O)$_6$] ppm. Integration of the ^{1}H NMR spectra gave *threo*:*meso*, 63:37. The meso and threo configurations were assigned by comparison with the spectrum of **9d**, which was prepared by addition of PhLi or PhMgBr to complex **4** (see below).

9a from 4 and MeLi: A solution of methyllithium in diethyl ether (1.6 M, 0.421 mL, 0.674 mmol) was added by syringe into a solution of acetylene dicarbaldehyde complex **4** (0.124 g, 0.337 mmol) in THF (13 mL) at −78 °C. The mixture was warmed to room temp. and then stirred for 2 h. The mixture was diluted with diethyl ether (50 mL) and then quenched and extracted with saturated aqueous NH$_4$Cl (50 mL). The organic phase was separated, dried over MgSO$_4$, and concentrated. The *de* (12%) was determined by deconvolution of the 400-MHz ^{1}H NMR spectrum of the crude material in CDCl$_3$ at 40 °C. The crude material was chromatographed over silica gel (pentane/EtOAc, 7:3). Complex **9a** was isolated over several fractions with varying values of *de* (0.030 g, 22%). TLC (pentane/EtOAc, 7:3): R_f = 0.66 (single spot). IR (CDCl$_3$): ν_{O-H} = 3305 (s, H-bonded), 3602 (s, free), 2933 (w) cm^{-1}; $\nu_{C\equiv O}$ = 2094 (vs), 2056 (vs), 2030 (vs) cm^{-1}. MS (DCI/NH$_3$): *m/z* = 418 ([M + NH$_4$]$^+$), 383 ([MH − H$_2$O]$^+$), 355 ([MH − H$_2$O − CO]$^+$), 327 ([MH − H$_2$O − 2CO]$^+$), 299 ([MH − H$_2$O − 3CO]$^+$).

***meso*-9a:** ^{1}H NMR (400 MHz, 40 °C, CDCl$_3$): δ = 1.38 (d, $^3J_{H,H}$ = 6.0 Hz, 6 H, C*H*$_3$), 2.38 (s, 2 H, O*H*), 4.75 (large, 2 H, C*H*) ppm. ^{1}H NMR (200 MHz, 21 °C, CDCl$_3$): δ = 1.55 (br, 6 H, C*H*$_3$), 2.89 (s, 2 H, O*H*), 5.03 (br, 2 H, C*H*OH) ppm. ^{13}C{^{1}H} NMR (50 MHz, 21 °C, CDCl$_3$): δ = 24.73 (*C*H$_3$), 68.47 (C*H*OH), 101.68 (η^2-*C*≡*C*),199.36 [Co$_2$(*C*O)$_6$] ppm.

***threo*-9a:** ^{1}H NMR (400 MHz, 40 °C, CDCl$_3$): δ = 1.35 (d, $^3J_{H,H}$ = 6.4 Hz, 6 H, C*H*$_3$), 2.24 (s, 2 H, O*H*), 4.75 (br, 2 H, C*H*OH) ppm. ^{13}C{^{1}H} NMR (50 MHz, 21 °C, CDCl$_3$): δ = 25.18 (*C*H$_3$), 68.91 (*C*HOH), 101.24 (η^2-*C*≡*C*),199.36 [Co$_2$(*C*O)$_6$] ppm.

Monoaddition Product 8a: ^{1}H NMR (200 MHz, 21 °C, CDCl$_3$): δ = 1.55 (br, 6 H, C*H*$_3$), 2.93 (s, 2 H, O*H*), 5.03 (br, 2 H, C*H*OH), 10.31 (s, 1 H, *H*C=O).

9a from 4 and MeMgBr: A solution of methylmagnesium bromide in diethyl ether (3.0 M, 0.362 mL, 1.087 mmol) was added by syringe into a solution of acetylene dicarbaldehyde complex **4** (0.200 g, 0.543 mmol) in THF (26 mL) at −78 °C. The mixture was warmed to room temp. and then stirred for 2 h. The mixture was quenched with saturated aqueous NH$_4$Cl (50 mL) and then extracted with diethyl ether. The organic layer was washed with water until pH 7 was reached, dried over MgSO$_4$, and concentrated. The *de* (22%) was determined by deconvolution of the 400-MHz ^{1}H NMR spectrum of the crude material in C$_6$D$_6$ at 40 °C (***meso*-9a:** δ = 1.41 (d), 2.62 (br), 4.77 (m) ppm. ***threo*-9a:** δ = 1.37 (d), 2.47 (br), 4.78 (m) ppm). The crude material was chromatographed over silica gel eluting with pentane/Et$_2$O mixture of increasing polarity (from 70:30 to 50:50). Complex **9a** was isolated in several fractions of varying *de* (0.176 g, 81%). C$_{12}$H$_{10}$O$_8$Co$_2$ (400.1): calcd. C 36.01, H 2.52, Co 29.47, O 31.0; found 36.05, H 2.71, O 31.68, Co 28.43.

9b from 4 and EtLi: A solution of ethyllithium in diethyl ether (1.3 M, 0.418 mL, 0.544 mmol) was added by syringe into a solution of acetylene dicarbaldehyde complex **4** (0.100 g, 0.272 mmol) in THF (10 mL) at −78 °C. After stirring for 15 min at −78 °C, the mixture was stirred for 1 h at −25 °C, then quenched with saturated aqueous NH$_4$Cl and diluted with diethyl ether. The organic layer was dried over MgSO$_4$, filtered through a small pad of celite, and concentrated. The crude material was chromatographed over silica gel (pentane/EtOAc, 90:10). Complex **9b** was isolated over several fractions with varying *de* (0.027 g, 23%). Elemental analysis for the complex **9b**·0.5 pentane (half an equivalent of pentane measured by NMR spectroscopy). C$_{16.5}$H$_{20}$O$_8$Co$_2$ (463.98):calcd. C 42.67, H 4.34, Co 25.40, O 27.58; ; found C 42.40, H 4.07, Co 23.81, O 27.32. The *de* could not be determined from the ^{1}H NMR spectrum of the crude material. The better resolution of the ^{13}C NMR spec-

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trum allowed for a crude estimation of *de* of ca. 10%. A more precise value (*de* 4%) was obtained as the weighted mean of the values of *de* (measured by integration of ^{1}H NMR spectra) of the three chromatographed fractions containing **9b**.

9b from 4 and EtMgBr: A solution of ethylmagnesium bromide in THF (3.0 M, 0.181 mL, 0.544 mmol) was added by syringe into a solution of acetylene dicarbaldehyde complex **4** (0.100 g, 0.272 mmol) in THF (10 mL) at −78 °C. The mixture was warmed to room temp., stirred for 2 h, quenched with saturated aqueous NH_4Cl, and then extracted with diethyl ether. The organic layer was washed with water until pH 7 was reached, then dried over $MgSO_4$ and concentrated. The crude material was chromatographed over silica gel eluting with pentane/EtOAc mixtures of increasing polarity (from 90:10 to 50:50). The *de* (60%) was determined as the weighted mean of the values of *de* (measured by integration of ^{1}H NMR spectra) of the three fractions containing **9b**. Pure *meso*-**9b** was isolated as an orange-red solid (0.083 g, 71%). IR ($CDCl_3$): ν_{O-H} = 3603 (s, free OH), 3452 (s, hydrogen bonded) cm^{-1}; ν_{C-H} = 2968 (w), 2935 (w), 2878 (w) cm^{-1}; $\nu_{C\equiv O}$ = 2094 (vs), 2056 (vs), 2030 (vs) cm^{-1}. MS (DCI/NH_3): *m/z* = 446 ($[M + NH_4]^+$), 411 ($[MH - H_2O]^+$), 383 ($[MH - H_2O - CO]^+$), 355 ($[MH - H_2O - 2CO]^+$), 327 ($[MH - H_2O - 3CO]^+$).

***meso*-9b:** TLC (pentane/EtOAc, 9:1): R_f = 0.40. ^{1}H NMR ($CDCl_3$): δ = 1.15 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, C*H*$_3$), 1.80 (m, 4 H, C*H*$_2$Me), 2.96 (d, $^3J_{H,H}$ = 3.6 Hz, 2 H, O*H*), 4.71 (m, 2 H, C*H*OH) ppm. ^{13}C NMR: δ = 11.23 (q, $^1J_{C,H}$ = 126.1 Hz, *C*H$_3$), 32.50 (t, $^1J_{C,H}$ = 124.7 Hz, *C*H$_2$Me), 74.06 (d, $^1J_{C,H}$ = 143.9 Hz, *C*HOH), 100.78 (s, η^2-*C*≡*C*), 199.43 [br s, $Co_2(CO)_6$] ppm.

***threo*-9b:** TLC (pentane/EtOAc, 9:1): R_f = 0.49. ^{1}H NMR ($CDCl_3$): δ = 1.15 (t, $^3J_{H,H}$ = 7.3 Hz, 6 H, C*H*$_3$), 1.67 (m, 4 H, C*H*$_2$Me), 2.66 (d, $^3J_{H,H}$ = 4.7 Hz, 2 H, O*H*), 4.71 (m, 2 H, C*H*OH) ppm. ^{13}C{^{1}H} NMR (62.9 MHz, $CDCl_3$): δ = 11.14 (*C*H$_3$), 32.86 (*C*H$_2$), 74.06 (*C*HOH), 100.86 (η^2-*C*≡*C*), 199.57 [$Co_2(CO)_6$] ppm.

9d from 4 and PhLi: A solution of phenyllithium in cyclohexane/diethyl ether (1.6 M, 0.340 mL, 0.544 mmol) was added by syringe into a solution of acetylene dicarbaldehyde complex **4** (0.100 g, 0.272 mmol) in THF (10 mL) at −78 °C. The mixture was warmed to room temp., stirred for 1.5 h, quenched with saturated aqueous NH_4Cl, and then extracted with diethyl ether. The organic layer was washed with water, dried over $MgSO_4$, and concentrated. The *de* (54%) was determined by integration of the resolved ^{1}H NMR spectrum of the crude material in $CDCl_3$. The crude material was chromatographed over silica gel (pentane/EtOAc, 80:20). Complex **9d** was isolated as a red amorphous solid (0.053 g, 37%).

9d from 4 and PhMgBr: A solution of phenylmagnesium bromide in diethyl ether (3.0 M, 0.181 mL, 0.544 mmol) was added by syringe into a solution of acetylene dicarbaldehyde complex **4** (0.100 g, 0.272 mmol) in THF (20 mL) at −78 °C. The mixture was warmed to room temp., stirred at room temp. for 2.5 h, quenched with saturated aqueous NH_4Cl, and then extracted with diethyl ether. The organic layer was washed with water until pH 7 was reached, then dried over $MgSO_4$ and concentrated. The crude material was chromatographed over silica gel eluted with pentane/EtOAc mixtures of increasing polarity (from 90:10 to 80:20). Complex **9d** (mixture of diastereoisomers) was isolated as a brown solid (0.069 g, 48%). Elemental analysis for **9d**·H_2O $C_{22}H_{16}Co_2O_9$: calcd. C 48.71, H 2.98, Co 21.74; found C 48.41, H 2.83.

The stereoselectivity (*de* = 66%) was determined as the weighted mean of the values of *de* (measured by integration of the ^{1}H NMR spectra) of all the three chromatographed fractions containing **9d**. Analyses were consistent with those of the product obtained by reaction of the diol **10** with $Co_2(CO)_8$ (see above).

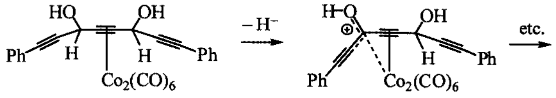
***meso*-9d:** TLC (pentane/EtOAc, 9:1): R_f = 0.40. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.54 (br, 2 H, O*H*), 5.95 (s, 2 H, C*H*OH), 7.34−7.43 (m, 10 H, aromatic C*H*) ppm.

***threo*-9d:** TLC (pentane/EtOAc, 9:1): R_f = 0.53. ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 3.65 (d, $^3J_{H,H}$ = 2.7 Hz, 2 H, O*H*), 5.88 (d, $^3J_{H,H}$ = 2.7 Hz, 2 H, C*H*OH), 7.32−7.48 (m, 10 H, aromatic C*H*) ppm.

Monoaddition Product 8d: ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.80 (d, $^3J_{H,H}$ = 3.1 Hz, 1 H, O*H*), 5.92 (s, 1 H, C*H*OH), 7.32−7.48 (m, 5 H, aromatic C*H*), 10.24 (s, 1 H, C*H*O) ppm.

9e from 4 and PhC≡CLi: A solution of *n*-butyllithium in toluene (2.1 M, 1.04 mL, 2.18 mmol) was added by syringe into a solution of phenylacetylene (0.144 mL, 2.18 mmol) in THF (20 mL) at −78 °C. After stirring for 1 h, during which time the temperature rose to −25 °C, the resulting pink solution was cooled down to −78 °C. A solution of acetylenedicarbaldehyde complex **4** (0.400 g, 1.09 mmol) in THF (36 mL) was added. The mixture was warmed to room temp., stirred for 3.5 h, quenched with saturated aqueous NH_4Cl, and then extracted with diethyl ether. The organic layer was washed with water, dried over $MgSO_4$, filtered through a small pad of celite, and concentrated. The crude material was chromatographed over silica gel with pentane/EtOAc (90:10 then 80:20). Complex **9e** was isolated as an orange oil (0.055 g, 9%) corresponding to a single spot on TLC.

TLC (pentane/EtOAc, 8:2): R_f ≈ 0.25. TLC (pentane/EtOAc, 7:3): R_f ≈ 0.54. IR ($CDCl_3$) ν_{O-H} = 3601 (s, free), 3408 (s, hydrogen-bonded) cm^{-1}; ν_{C-H} = 2927 (w), 2855 (w) cm^{-1}; $\nu_{C\equiv O}$ = 2099 (vs), 2063 (vs), 2039 (vs) cm^{-1}; $\nu_{arC=C}$ = 1600 (m), 1490 (m), 1457 (m) cm^{-1}. MS ($DCI/NH_3/Et_2O$): *m/z* = 586 ($[M - 2H_2 + NH_4]^+$), 569 ($[M - 2H_2 + H]^+$), 553 ($[M - H_2 + H - H_2O]^+$), 499 ($[M + H - H_2O - 2CO)$, 481 ($[M + H - 2H_2O - 2CO]^+$. The invoked oxidation processes are explained by the stabilization of the doubly propargylic carbenium centers:



9e

Scheme 7

If the sample is injected as a CH_2Cl_2 solution, instead of in Et_2O, the isotope pattern analysis allowed for the following assignments: MS ($DCI/NH_3/CH_2Cl_2$): *m/z* = 586 ($[M - 2CO + 2HCl - H_2O + NH_3 - H^{\cdot}]^+$), 569 ($[M - 2CO + 2HCl - H_2O - H^{\cdot}]^+$), 553 ($[M - 2CO + 2HCl - 2H_2O + H]^+$).

^{1}H NMR ($CDCl_3$, 200 MHz): δ = 2.98 (br s, 2 H, O*H*), 5.87 (s, 2 H, C*H*OH), 7.30 (sharp signal, 6 H; *m*- and *p*-C*H)*, 7.39−7.43 (m, 4 H, *o*-C*H*) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz): δ = 64.08 (*C*HOH), 85.96 and 88.08 (*C*≡*C*Ph), 96.39 (η^2-*C*≡*C*), 122.00 (*ipso*-*C*), 128.50 (*m*-*C*H), 128.99 (*p*-*C*H), 131.88 (*o*-*C*H), 198.91 [s, $Co_2(CO)_6$] ppm. Elemental analysis for **9e**·icosane (1 equivalent of C20 alkane in the sample was confirmed by NMR spectroscopy): $C_{46}H_{56}O_8Co_2$ (854.26): calcd. C 64.62, H 6.62; found C 64.50, H 6.44.

NMR spectroscopic data for the minor epimer of **9e** [TLC (pentane/EtOAc, 7:3): R_f = 0.63] were extracted from spectra of the crude material. ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz): δ = 64.08 (*C*HOH), 86.04 and 88.00 (*C*≡*C*Ph), 96.39 (η^2-*C*≡*C*), 122.00 (*ipso*-

C), 128.50 (*m*-*C*H), 128.99 (*p*-*C*H), 131.88 (*o*-*C*H), 198.91 [s, $\mathrm{Co_2}(\mathit{CO})_6$] ppm. Formal integration of the spectrum gave 12 and 28% excesses for the major components of two split *C*≡*CPh* signals; a rough estimation gives *de* of ca. 20 ±10%.

9e from 4 and PhC≡CMgBr: A solution of ethylmagnesium bromide in THF (3.0 M, 0.181 mL, 0.544 mmol) was added to a solution of phenylacetylene (0.037 mL, 0.544 mmol) in THF (10 mL) at −78 °C. After stirring for 0.5 h, during which time the mixtute warmed to room temp., the solution was cooled to −78 °C. A solution of acetylenedicarbaldehyde complex **4** (0.100 g, 0.272 mmol) in THF (13 mL) was added. The mixture was warmed to room temp., stirred for 2.5 h, quenched with saturated aqueous NH_4Cl, and then extracted with diethyl ether. The organic phase was washed with water, dried over Na_2SO_4, and concentrated. The crude material was chromatographed over silica gel (pentane/Et_2O, 80:20). Complex **9e** (0.025 g, 16%) was isolated as an orange oil corresponding to the same (more polar) TLC spot observed for the reaction using Ph_2C_2Li. The less-polar spot corresponds to the minor epimer of **9e**, which was obtained in mixture (0.017 g) with **8e** and the first epimer of **9e** in a ratio **9e**:**8e**, 66:33. Assuming that **9e** here occurs either as a 1:1 mixture of the two epimers (*de* = 0) or, at worst, as a single minor epimer (*de* = −100%), the weighted mean of the values of *de* in the two extreme cases gives the estimated range: 36 < *de* ≈ 68%.
NMR spectroscopic data for **8e**: ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 2.91 (d, $^3J_{H,H}$ = 5.9 Hz, 1 H, O*H*), 5.81 (d, $^3J_{H,H}$ = 5.8 Hz, 1 H, C*H*OH), 7.30−7.41 (m, assumed 5 H, aromatic C*H*), 10.36 (s, 1 H, C*H*O) ppm.

9f from 4 and Me$_3$SiC≡CLi: A solution of *n*-butyllithium in toluene (2.5 M, 0.218 mL, 0.544 mmol) was added by syringe into a solution of trimethylsilylacetylene (0.077 mL, 0.544 mmol) in THF (10 mL) at −78 °C. The mixture was warmed to room temp. and then cooled to −78 °C. A solution of acetylenedicarbaldehyde complex **4** (0.100 g, 0.272 mmol) in THF (13 mL) was added. The mixture was warmed to room temp., stirred for 3.5 h, quenched with saturated aqueous NH_4Cl, and then extracted with diethyl ether. The organic layer was washed with water until pH 7 was reached, dried over $MgSO_4$, and concentrated. The crude material was chromatographed over silica gel with pentane/EtOAc (90:10 then 80:20). Complex **9f** was isolated over several fractions, corresponding to two spots on TLC (each affording the same ^{1}H NMR spectrum), that were combined to give a red amorphous solid (0.082 g, 63%). TLC (pentane/Et_2O, 80:20): R_f = 0.40 and 0.53. IR ($CDCl_3$): ν_{O-H} = 3588 (s) cm^{-1}; ν_{C-H} = 2962 (w) cm^{-1}; $\nu_{C\equiv CSi}$ = 2173 (w) cm^{-1}; $\nu_{C\equiv O}$ = 2099 (vs), 2063 (vs), 2038 (vs) cm^{-1}; ν_{C-Si} = 1252 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 582 ([M + NH_4]$^+$), 547 ([MH − H_2O]$^+$), 491 ([MH − H_2O − 2CO]$^+$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.16 [br s, 18 H, Si(C*H*$_3$)$_3$], 2.95 (br, 2 H, O*H*), 5.57 (br, 2 H, C*H*OH). Because of this broadness, the *de* could not be determined by ^{1}H NMR spectroscopy. ^{13}C{^{1}H} NMR ($CDCl_3$, 62.9 MHz; formal integration of four split signals gave the same 22% excess of the main signals, and allowed for the following assignments): major epimer, δ = −0.45 [Si(*C*H$_3$)$_3$], 63.69 (*C*HOH), 90.82 (η^2-*C*≡*C*), 95.97 (*C*≡C−Si), 103.74 (C≡*C*−Si), 198.64 [s, $\mathrm{Co_2}(\mathit{CO})_6$] ppm; minor epimer, δ = −0.45 [Si(*C*H$_3$)$_3$], 63.61 (*C*HOH), 90.90 (η^2-*C*≡*C*), 95.84 (*C*≡C−Si), 103.82 (C≡*C*−Si), 198.64 [s, $\mathrm{Co_2}(\mathit{CO})_6$] ppm.

9f from 4 and Me$_3$SiC≡CMgBr: A solution of EtMgBr in THF (3 M, 0.362 mL, 1.09 mmol) was added by syringe into a solution of phenylacetylene (0.154 mL, 1.09 mmol) in THF (20 mL) at room temp. and then the solution was heated at 55 °C for 0.5 h. The solution was cooled to 5 °C, and a solution of complex **4** (0.200 g, 0.544 mmol) in THF (20 mL) was added. The resulting dark-brown solution was stirred for 1 h at room temp., then quenched with saturated aqueous NH_4Cl and extracted with diethyl ether. The organic layer was washed with water until pH 7 was reached, dried over $MgSO_4$, and concentrated. The crude brown solid (0.155 g) was analyzed by ^{1}H NMR spectroscopy and integration of the respective signals gave the ratio **4**:**8f**:**9f**, 38:20:42. The crude material was then chromatographed over silica gel with pentane/Et_2O (80:20). A first product [TLC (pentane/Et_2O, 80:20): R_f = 0.56], likely containing complex **8d** (according to its ^{1}H NMR spectrum, δ_{CHO} = 9.97 ppm), was obtained as an impure orange oil (0.007 g, ca. 2%). Subsequently, complex **9f**, as a reddish oil (0.046 g, ca. 15%), and unchanged **4,** as a red powder (0.009 g, 5%), were isolated.

9g from 4 and the Lithium Salt of 11g: A solution of *n*-butyllithium in toluene (2.2 M, 0.197 mL, 0.434 mmol) was added by syringe into a solution of diyne (MeC$_2$)(OMe)PhC-C≡CH **11g** (0.080 g, 0.544 mmol) in THF (6 mL) at −78 °C. The mixture was warmed to 0 °C, and then cooled to −78 °C. A solution of acetylenedicarbaldehyde complex **4** (0.080 g, 0.217 mmol) in THF (10 mL) was added. The mixture was then stirred at room temp. for 1 h, quenched with saturated aqueous NH_4Cl, and extracted with diethyl ether. The organic layer was washed with water, dried over $MgSO_4$, and concentrated. The brown residue was chromatographed over silica gel with pentane/Et_2O mixtures of increasing polarity (from 80:20 to 50:50). Complex **9g** (mixture of diastereoisomers) was isolated as a brown oil (0.024 g, 15%).
IR ($CDCl_3$): ν_{O-H} = 3585 (s) cm^{-1}; ν_{C-H} = 2958 (w), 2935 (w), 2826 (w) cm^{-1}; $\nu_{C\equiv O}$ = 2100 (vs), 2064 (vs), 2038 (vs) cm^{-1}; $\nu_{ar.C=C}$ = 1591 (m), 1489 (m), 1449 (m) cm^{-1}; ν_{C-O} = 1063 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 754 ([M + NH_4]$^+$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 1.91 (s, 6 H, ≡C−C*H*$_3$), 2.97 (br, 2 H, O*H*), 3.44−3.49 (m, 6 H, OC*H*$_3$), 5.54−5.61 (m, 2 H, C*H*OH), 7.33 (m, 6 H, *m*- and *p*-C*H*), 7.71 (m, 4 H, *o*-C*H*) ppm. Surprisingly, the ^{13}C NMR spectrum can be assigned entirely to that of a pseudo-diastereoisomerically pure compound. ^{13}C NMR ($CDCl_3$, 62.9 MHz): δ = 3.64 (q, $^1J_{C,H}$ = 132 Hz, ≡C−*C*H$_3$), 52.83 (q, $^1J_{C,H}$ = 143 Hz, O−*C*H$_3$), 63.28 (d, $^1J_{C,H}$ = 151 Hz, *C*HOH), 71.77 [s, *C*(OMe)Ph), 84.32 (br, *C*≡*C*Me), 95.35 (s, η^2-*C*≡*C*), 126.47 (d, *o*-*C*H), 128.27 (d, *m*-*C*H), 128.64 (d, *p*-*C*H), 140.32 (s, *ipso*-*C*), 198.37 [s, $\mathrm{Co_2}(\mathit{CO})_6$] ppm.

9h from 4 and the Lithium Salt of 11h: A solution of *n*-butyllithium in toluene (2.5 M, 0.217 mL, 0.544 mmol) was added by syringe into a solution of diyne (Me$_3$SiC$_2$)(OMe)PhC−C≡CH **11h** (0.132 g, 0.544 mmol) in THF (10 mL) at −78 °C. The mixture was warmed to room temp. and then the resulting violet solution was cooled to −68 °C. A solution of complex **4** (0.100 g, 0.272 mmol) in THF (13 mL) was added. The mixture was then stirred at room temp. for 2.5 h, quenched with saturated aqueous NH_4Cl, and extracted with diethyl ether. The organic layer was washed with water, dried over $MgSO_4$, and concentrated. The brown residue was chromatographed over silica gel with pentane/EtOAc mixtures of increasing polarity (from 90:10 to 50:50). Complex **9h** (mixture of diastereoisomers) was isolated as a brown oil (0.039 g, 16%).
IR ($CDCl_3$): ν_{O-H} = 3585 (s, free), 3410 (hydrogen bonded) cm^{-1}; ν_{C-H} = 2961 (w), 2936 (w), 2902 (w), 2827 (w) cm^{-1}; $\nu_{C\equiv O}$ = 2100 (vs), 2064 (vs), 2040 (vs) cm^{-1}; $\nu_{ar.C=C}$ = 1587 (w), 1489 (m), 1450 (m) cm^{-1}; ν_{C-O} = 1064 (m) cm^{-1}; ν_{C-Si} = 1252 (m) cm^{-1}. MS (DCI/NH_3): *m*/*z* = 870 ([M + NH_4]$^+$), 835 ([MH − H_2O]$^+$). ^{1}H NMR ($CDCl_3$, 250 MHz): δ = 0.21 [s, 18 H, Si(C*H*$_3$)$_3$], 2.82 (br, 2 H, O*H*), 3.45−3.47 (m, 6 H, OC*H*$_3$), 5.57−5.60 (m, 2 H, C*H*OH), 7.36 (m, 6 H, *m*- and *p*-C*H*), 7.72 (m, 4 H, *o*-C*H*) ppm. Surpris-

ingly, the ^{13}C NMR spectrum can be assigned almost entirely as that of a pseudo-diastereomerically pure compound (except for two C≡C signals). ^{13}C{^{1}H} NMR (CDCl$_3$, 62.9 MHz): δ = −0.37 [Si(*C*H$_3$)$_3$], 53.01 (O-*C*H$_3$), 63.12 (*C*HOH), 71.88 [*C*(OMe)Ph], 83.62, 84.83, 85.00 (diastereoisomeric *C*≡C−Si), 95.18 (η^2-*C*≡*C*), 101.00 (≡*C*−SiMe$_3$), 126.47 (*o*-*C*H), 128.32 (*m*-*C*H), 128.76 (*p*-*C*H), 139.44 (*ipso*-*C*), 198.34 [Co$_2$(*C*O)$_6$] ppm.

9i from 4 and the Lithium Salt of 11i: A solution of *n*-butyllithium in hexane (2.5 M, 0.850 mL, 2.12 mmol) was added by syringe into a solution of 1-trimethylsilyl-3-(tetrahydropyranyloxy)pent-1,4-diyne (**11i**, 0.500 g, 2.12 mmol) in THF (15 mL) at −80 °C. After stirring for 15 min, a solution of complex **4** (0.390 g, 1.06 mmol) in THF (10 mL) was added. The mixture was then stirred at −80 °C for 1 h and at room temp. for 1 h, before being quenched with a saturated aqueous solution of NH$_4$Cl and extracted with diethyl ether. The organic layer was washed with water, dried over MgSO$_4$ and concentrated. The brown residue was purified by flash chromatography through a plug of silica gel eluting with heptane/EtOAc (80:20). Complex **9i** (mixture of diastereoisomers) was isolated as a brown amorphous solid (167 mg, 15%).
IR (CDCl$_3$): ν_{O-H} = 3408 (w) cm^{-1}; ν_{C-H} = 2951, 2854 (m) cm^{-1}; $\nu_{C\equiv C}$ = 2247 (w) cm^{-1}; $\nu_{C\equiv O}$ = 2098, 2063, 2035 (vs) cm^{-1}; ν_{C-Si} = 1251 (m) cm^{-1}; ν_{C-O} = 1117 (m) cm^{-1}. MS (DCI/NH$_3$): *m*/*z* = 839 ([M − H]$^+$). ^{1}H NMR (CDCl$_3$, 250 MHz): δ = 0.13 [m, 18 H, Si(C*H*$_3$)$_3$], 1.22 and 1.51 (2 m, 12 H, C*H*$_2$C*H*$_2$C*H*$_2$), 3.49 and 3.83 (2 m, 4 H, C*H*$_2$O), 4.91 (m, 2 H, C*H*O$_2$), 5.20 (m, 2 H, C*H*−OTHP), 5.63 (m, 2 H, C*H*OH) ppm. ^{13}C NMR (CDCl$_3$, 62.9 MHz): δ: −0.43 [Si(*C*H$_3$)$_3$], 18.35, 18.58, 19.66, 25.23, 25.39, 29.63, 29.86, 30.26, 30.62 (*C*H$_2$*C*H$_2$*C*H$_2$), 54.92−55.26 (*C*HOTHP), 61.61−62.01 (*C*HOTHP), 62.83 (*C*HOH), 94.57−95.67 (*C*HO$_2$, *C*≡*C*), 98.76−99.00 (≡*C*−Si), 198.53 [Co$_2$(*C*O)$_6$] ppm.

X-ray Analysis of 4, 9b, and 9d: Data were collected at low temperature on a Stoe Imaging Plate Diffraction System (IPDS), equipped with an Oxford Cryosystems Cryostream Cooler Device and by using graphite-monochromated Mo-*K* radiation (λ = 0.71073 Å). The final unit cell parameters were obtained by means of a least-squares refinement of a set of 5000 well-measured reflections. Crystal decay was monitored in the course of data collection by measuring 200 reflections by image; no significant fluctuations of intensities have been observed during all measurements. All structures have been solved by Direct Methods using SIR92,[29] and refined by least-squares procedures on F^2 with the aid of SHELXL.[30] The Atomic Scattering Factors were taken from International Tables for X-ray Crystallography.[31] All hydrogen atoms were located on difference Fourier maps, and refined by using a riding model with an isotropic thermal parameter fixed at 20% higher to carbons atoms to which they are connected. Exceptions are the hydrogens atoms H(3) and H(4) of the CHO function of **4**, and the hydrogens atoms H(1) and H(2) of the -OH groups of **9b** and **9d**, which were isotropically refined. A semi-empirical correction absorption was applied for all models (DIFABS-N),[32] all non-hydrogens atoms were anisotropically refined, and in the last cycles of refinement a weighting scheme was used,[33] where weights are calculated from the following formula: $w = 1/[2(F_o^2) + (aP)^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$. Molecules were drawn using the program ZORTEP with 50% probability displacement ellipsoids for non-hydrogen atoms.[34]

MM Modeling of Intermediates B[Li(THF)$_2$] and B[MgBr(THF)]: Optimization of the geometry of lithium and magnesium bromide salts of **8b** have been carried out with ESSF (Extensive Systematic Force Field) implemented in the Discover software.[35] The input geometries were designed starting from the X-ray crystal structure of **8b**, appending a frozen Co$_2$(CO)$_6$ core at the triple bond, and replacing one of the *sp*^{3} carbinol groups for a *sp*^{2} formyl group. The remaining OH proton of **8b** was then replaced by a metal unit [M = Li(THF)$_2$ or MgBr(THF)], placed at nonbonding distances from the formyl function and diversely oriented. Finally, ESSF optimization led to the closure of a seven-membered metallacycle by a new O→[M] bond in a pseudo-boat conformation **B[M]**.

Supporting Information: (see footnote on the first page of this article) Cartesian coordinates for the ESFF-optimized structures **B[Li(THF)$_2$]** and **B[MgBr(THF)]**.

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