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Stereoselective Pinacol Coupling of (Propargyl aldehyde)$Co_2(CO)_6$ Complexes

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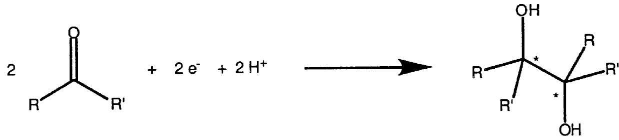
Propargyl aldehyde complexes, (RC≡CCHO)$Co_2(CO)_6$ (**1a**−**c**; R = Ph, Me, H), undergo pinacol coupling with a variety of reductants, exclusively giving *syn* (*dl*)-diacetylenic diol complexes **2a**−**c**. The X-ray structures of **2a** and **2c** have been determined. The free diol *syn*-PhC≡C−CH(OH)CH(OH)−C≡CPh (**4a**) is obtained efficiently from its cobalt complex **2a** upon treatment with $(NH_4)_2Ce(NO_3)_6$.

Introduction

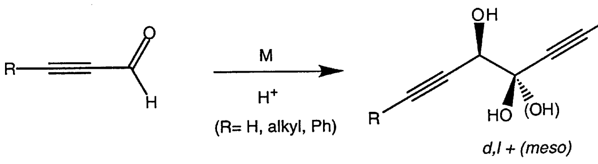
The reductive (pinacol) coupling of carbonyl compounds is a useful method for the creation of C−C bonds with 1,2-difunctionality (eq 1).[1] Although detailed mechanistic studies of pinacol coupling are lacking, the reactions are generally considered to involve the generation and reaction of the substrate ketyl (radical anion) with either the neutral substrate or another ketyl species. Unfortunately, traditional metal reductants for pinacolization rarely afford useful stereoselectivity and are intolerant of many functional groups. Recently, more efficient and stereoselective pinacol couplings of aromatic aldehydes (including enantioselective variants) have been developed using milder stoichiometric reductants (e.g., Zn, Mn, etc.) in combination with transition metal catalysts (e.g., Cp_2TiCl_2, Cp_2VCl_2, etc.).[2] The more difficult-to-reduce and less sterically biased aliphatic aldehydes and ketones typically react more sluggishly and exhibit poorer stereoselectivities.[1,3,4]



(1)

When α,β-unsaturated carbonyl compounds are reductively coupled, regioselectivity also becomes an important issue since pinacols (head/head coupling), 1,6-dicarbonyl (tail/tail coupling), and γ-hydroxycarbonyls (head/tail coupling) are possible. Regioisomers are frequently obtained in such reactions, although the Lewis acidity and complexing power of the low-valent metal can enable 1,2-coupling in some cases. Reductive coupling of α,β-unsaturated carbonyl compounds is usually not highly stereoselective. Exceptions are provided by the ill-defined reductants Cp_2TiCl_2/*sec*-BuMgCl[5] and TiI_4,[6] which are reported to give excellent *syn (d,l)*-selectivity in the coupling of acrolein derivatives.

The pinacolization of propargyl aldehydes/ketones has received rather little attention (eq 2). Conventional reductants (e.g., Zn/HOAc; Zn-Cu/HOAc) effect these reactions with only low to moderate yields and variable *meso*-stereoselectivity,[7] probably a result of competing regiochemical coupling pathways and the modest steric demand of the linear acetylenic unit. The aforementioned reagent, TiI_4, has been found to induce *syn* selective pinacolization of phenylpropynal.[6] The diacetylenic diol products are attractive intermediates for the preparation of densely functionalized natural (and unnatural) products via established regio- and stereocontrolled transformations of the alkyne units.



(2)

Our group and others have begun to investigate the potential stabilizing and reactivity-altering effects of coordinating transition metal fragments to organic radicals. In this context (propargyl)$Co_2(CO)_6$ radicals have been found to undergo novel and highly stereoselective 1,1-dimerizations[8,9] and regioselective atom-

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transfer cyclizations,[10] suggesting the operation of significant stabilizing and stereodirecting effects on the radical by the $-Co_2(CO)_6$ unit. Stereoselective reactions presumed to involve intermediate α-(aryl)Cr(CO)$_3$ radicals have also been reported recently[11] and evaluated computationally;[12] these include SmI$_2$-induced, *syn*-selective pinacol coupling of (aryl aldehyde)Cr(CO)$_3$ complexes.[13]

The potential for achieving regio- and stereoselective reactions of $(R-C{\equiv}C-CHO)Co_2(CO)_6$ complexes has been demonstrated, including the addition enol derivatives and chiral allyl boranes as nucleophiles.[14] In view of the synthetic potential of 3,4-difunctionalized-1,5-diynes and the growing interest in the chemistry of radicals derived from transition metal complexes, we report herein an investigation of the pinacol coupling of (propargyl aldehyde)Co$_2$(CO)$_6$ complexes.

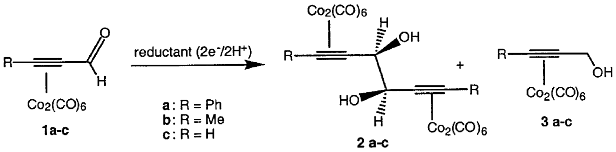
Results and Discussion

The representative acetylenic aldehyde complexes **1a**−**c** were prepared in good yield either by hydrolysis of the corresponding acetal derivatives (for **1a**,**b**) or by direct complexation of the aldehyde (**1c**) with $Co_2(CO)_8$. The aldehyde complexes were then subjected to reaction with several pinacolization reagents, including Zn/HOAc, Cp_2TiCl_2/*sec*-BuMgCl,[5] $TiCl_3$[15] Cp_2TiCl_2/Mn/Me_3SiCl,[16] SmI_2,[17] and Cp_2TiCl_2/SmI_2 (eq 3). In general, the reactions proceeded at or below room temperature. Following workup the products were separated by chromatography and were identified spectroscopically and (in two cases) by X-ray diffraction. A summary of the results is provided in Table 1.

Table 1. Pinacolization of (Propargyl aldehyde)Co$_2$(CO)$_6$ Complexes

aldehyde	reductant (equiv)	solvent	pinacol (**2**)	% yield[a,b]
1a	Cp_2TiCl_2 (2), *sec*-BuMgCl (2)	THF	*syn*-**2a**	54
1a	$TiCl_3$	CH_2Cl_2	*syn*-**2a**	51 (69)
1a	Zn	HOAc	*syn*-**2a**	8[c]
1a	Cp_2TiCl_2 (0.1), Mn (0.55), Me_3SiCl (1.1)	THF	*syn*-**2a**	43[d]
1a	Cp_2TiCl_2 (0.1), SmI_2 (2.0)	THF	*syn*-**2a**	45 (72)
1a	SmI_2	THF	*syn*-**2a**	32 (71)[e]
1b	Cp_2TiCl_2 (1), *sec*-BuMgCl (1)	THF	*syn*-**2b**	50 (67)
1b	Cp_2TiCl_2 (0.1), Mn (0.55), Me_3SiCl (1.1)	THF	*syn*-**2b**	49 (74)
1c	SmI_2 (2.5)	THF	*syn*-**2c**	45

[a] Isolated yield. [b] Number in parentheses is the yield based on recovered aldehyde **1**. [c] 30% of alcohol **3a** also formed. [d] 18% of **3a** formed. [e] 41% of **3a** formed.



(3)

Key features of these reactions include (1) pinacols (**2a**−**c**) are the exclusive product complexes in most systems, with the exception of the reactions of **1a** with Zn/HOAc, SmI_2, and Mn/Cp_2TiCl_2/Me_3SiCl, which produced significant amounts of the alcohol **3a** resulting from simple reduction; (2) a single pinacol diastereomer was isolated in all instances, established as the *syn* isomer (vide infra); (3) the yields of **2** are moderate and largely independent of the substrate complex or the reductant. The mass balance in the reactions was only fair (60−70%), the result of significant demetalation. In contrast to the selectivity observed in the pinacolization-complexed aldehydes **1a**−**c**, free PhC≡CCHO afforded a complex mixture of products upon treatment with Cp_2TiCl_2/*sec*-BuMgCl.

Although it was apparent from the ^1H NMR spectra of the products **2a**−**c** that single isomers were formed, their relative stereochemistry was uncertain. To address this issue, crystals of **2a** and **2c** were produced and subjected to X-ray structure determination. As can be seen from Figures 1 and 2, the relative stereochemistry of these compounds is *syn* (*d*,*l*). In the solid state **2a** adopts a conformation in which the two bulky $-(C_2Ph)$-$Co_2(CO)_6$ units are *anti* and the two hydroxyl groups are *gauche*. Interestingly, although **2c** is also the *syn* diastereomer, both the OH groups and the organocobalt units are *gauche* to each other. The reason for the different conformations of **2a** and **2c** is not certain but could reflect the differing steric demand of the Co_2C_2 clusters when capped by −Ph versus −H. As is typical of (alkyne)Co$_2$(CO)$_6$ complexes,[18] the coordinated alkyne units in **2a** and **2c** are severely bent, with angles of 143−145° defined by the coordinated alkyne carbon atoms and the α-carbons. This feature, and the attendant lengthening of the C−C bond of the coordinated alkyne (1.33 vs 1.21 Å), reflects substantial rehybridization of and strong back-bonding to the alkyne from the cobalt carbonyl moiety. The methanol molecule of crystallization with **2c** is involved in hydrogen bonding with the diol's two hydroxyl groups.

Importantly, the free pinacols can be recovered from their cobalt complexes efficiently and without loss of

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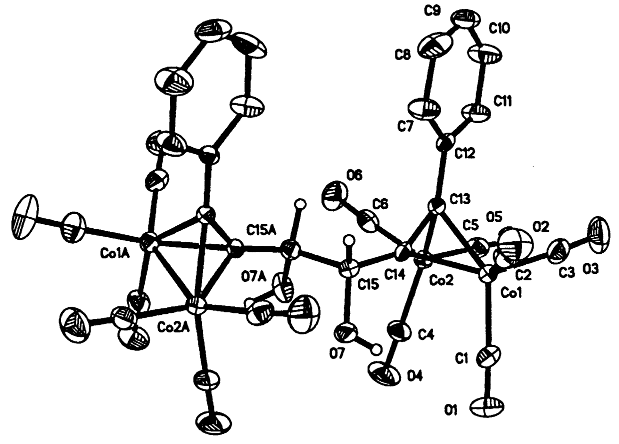


Figure 1. ORTEP diagram of **2a**. Selected bond lengths (Å) and angles (deg): Co(1)–C(13) 1.967(4), Co(1)–C(14) 1.958(4), Co(1)–Co(2) 2.4647(9), Co(2)–C(13) 1.954(4), Co(2)–C(14) 1.956(4), O(1)–C(1) 1.129(6), C(13)–C(14) 1.336(5), C(14)–C(15) 1.503(5), C(2)–Co(1)–C(1) 101.0(2), O(1)–C(1)–Co(1) 177.9(5), C(13)–C(14)–C(15) 142.8(4).

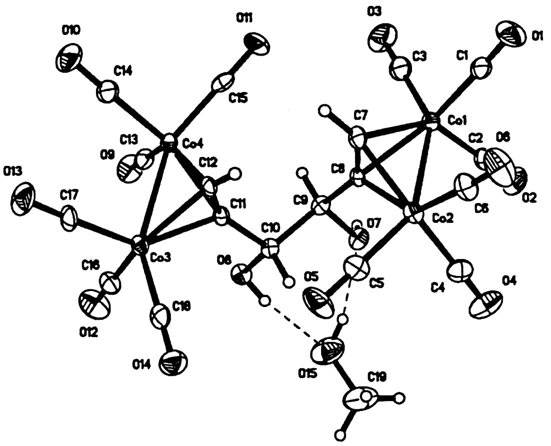


Figure 2. ORTEP diagram of **2c**. Selected bond lengths (Å) and angles (deg): Co(1)–C(7) 1.942(3), Co(1)–C(8) 1.950(3), Co(1)–Co(2) 2.4648(9), Co(2)–C(7) 1.950(4), Co(2)–C(8) 1.953(3), O(1)–C(1) 1.118(5), C(7)–C(8) 1.325(5), C(8)–C(9) 1.490(4), C(3)–Co(1)–C(2) 97.54(18), O(1)–C(1)–Co(1) 175.9(4), C(7)–C(8)–C(9) 145.6(3).

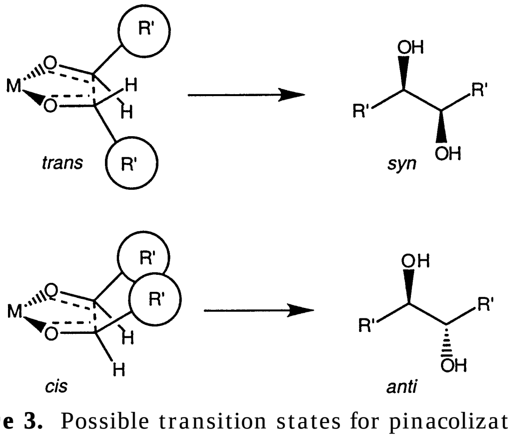
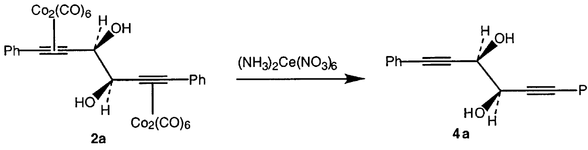


Figure 3. Possible transition states for pinacolization.

stereochemical integrity upon treatment with mild oxidants. For example, complex **2a** reacted with $(NH_4)_2Ce(NO_3)_6$/acetone at −78 °C to give *syn*-1,6-diphenyl-1,5-hexadiyne-3,4-diol (**4a**) in 89% yield (eq 4).



(4)

The high (complete) *syn (d,l)* stereoselectivity observed in the pinacol coupling of the acetylenic aldehyde-cobalt complexes stands in contrast to the limited or *meso* preference for the pinacolization of free acetylenic aldehydes.[7] This probably is a result of the greatly increased steric demand of the (alkynyl)$Co_2(CO)_6$ unit *vis à vis* the free alkynyl group. Although the exact transition state for these reactions is uncertain, a cyclic arrangement involving the metal (or organometallic) reductant and the coupling aldehydes (ketyls) is likely (Figure 3). The *trans* orientation of the bulky (alkynyl)-$Co_2(CO)_6$ (= R′) groups would minimize their steric interaction in the transition state and lead to the formation of the observed *syn*-diol. The insensitivity of the stereoselectivity to the nature of the reductant is noteworthy in light of the pinacolizations of aromatic aldehydes, which show significant variation of the stereoselectivity with the particular reducing system.[19] Even the low pinacolization stereoselectivity often found with SmI_2[16] is overridden in its reaction with complex **1c**. The extraordinary *syn* selectivity for all three complexes **1a**–**c** is synthetically appealing but not completely anticipated since the bent coordinated alkyne unit could place the sterically variable acetylenic substituent R in proximity of the reacting carbonyl group.[20]

The partial decomposition suffered by the cobalt complexes under the reaction conditions indicates the intervention of competing reactions during the formation of and/or subsequent coupling of the complexed aldehyde ketyl. (Alkyne)$Co_2(CO)_6$ complexes are known to undergo electrochemical reduction,[21] which is chemically reversible with electron-deficient alkynes but irreversible (with decomposition to $Co(CO)_4^-$) with more electron-rich alkynes. These observations raise the question of the unpaired electron (and charge) density in the (presumed) intermediate ketyl complexes. EPR studies of the (alkyne)$Co_2(CO)_6$ radical anions and supporting extended Hückel MO calculations indicate substantially delocalized unpaired electron density, including at the cobalt atoms and the associated carbonyl ligands.[21] Additionally, we have calculated the LUMO of aldehyde complex **1c** and the HOMO of its radical anion **1c**$^{\bullet}$ using the semiempirical PM3 method.[22] Both calculations suggest that addition of an electron to **1** will result in a delocalized species with only a small fraction of radical character at the aldehydic carbon,

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possibly accounting for the incomplete C−C coupling chemoselectivity found in the reactions. It is possible that electronic variations of R or of auxiliary ligands could enhance the coupling chemoselectivity by concentrating radical character at the carbonyl group.

In summary, (propargyl aldehyde)$Co_2(CO)_6$ complexes have been found to undergo completely regio- and *syn*-stereoselective pinacol coupling reactions with several reducing agents, providing new illustrations of the extraordinary stereoselectivities associated with propargyl-cobalt radical species. The derived 1,5-diyne-*syn*-3,4-diols hold considerable promise as intermediates in the synthesis of densely functionalized products bearing multiple adjacent stereocenters.

Experimental Section

All reactions of the cobalt complexes were conducted under a nitrogen atmosphere. ^1H NMR spectra were obtained at 300 MHz with $CDCl_3$ or C_6D_6 as solvent. (Phenylpropynal diethylacetal)$Co_2(CO)_6$ and (2-butynal)$Co_2(CO)_6$ were prepared from the reaction of the commercial diethyl acetals and $Co_2(CO)_8$ as reported.[23] Compounds **1a** and **1b** were prepared by hydrolysis of the corresponding diethyl acetal complexes;[24] **1c** was prepared by the reaction of propynal with dicobalt octacarbonyl.[23] PM3 MO calculations[22] were carried out using the MacSpartan Plus program (Wavefunction).

Pinacolization of (Phenylpropynal)dicobalt Hexacarbonyl (1a). Cp_2TiCl_2/*sec*-BuMgCl. Cp_2TiCl_2 (0.25 g, 1.0 mmol) was placed in a sidearm flask with a stirring bar under nitrogen atmosphere, and THF (10 mL) was added. The flask was cooled to −78 °C, and then *sec*-BuMgCl in ether (0.48 mL, 1.0 mmol) was transferred to the flask. The solution was stirred for 30 min, allowed to warm slowly to room temperature, and then recooled to −78 °C. A solution of the **1a** (0.20 g, 0.50 mmol) dissolved in THF (15 mL) was then added. The mixture was stirred for 30 min and allowed to warm to room temperature, and then NaOH (5M, 0.5 mL) was added; this mixture was stirred for 45 min. The solution was filtered through a short column of potassium carbonate topped with a layer of Celite, eluting with THF (250 mL). Column chromatography on silica gel (95:5 petroleum ether/ether) afforded the diol **2a** (0.11 g).

$TiCl_3$. Aldehyde **1a** (1.35 g, 3.25 mmol) was dissolved in CH_2Cl_2 (10 mL) in a sidearm flask containing a stirring bar and fitted with a septum under nitrogen. A solution of $TiCl_3$ in HCl/water (10 wt %, 10 mmol) was added by syringe, and the mixture was stirred at room temperature for 5 h. The reaction was quenched by the addition of water (10 mL) and stirred for 18 h. The mixture was transferred to a separatory funnel, and the phases were separated. The aqueous layer was washed twice with ethyl acetate, and the combined organic phases were dried over $MgSO_4$. Silica gel flash chromatography of the concentrated organic residue (98:2 petroleum ether/ether) provided unreacted aldehyde **1a** (0.25 g) and diol **2a** (0.56 g).

Zn/HOAc. Aldehyde **1a** (0.090 g, 0.22 mmol) was placed in a sidearm flask containing HOAc (10 mL) and a stirring bar. The mixture was stirred while Zn (0.10 g, 1.5 mmol) was added to the solution; stirring was continued for 20 h. The residual zinc was removed by filtration, and the solution was washed with water, followed by 10% $NaHCO_3$. The organic phase was rotary evaporated and the residue purified by preparative TLC (95:5 petroleum ether/ether): recovered **1a** (0.010 g), diol **2a** (0.007 g), and alcohol **3a** (0.030 g) were isolated.

Table 2. Crystal Data and Structure Refinement for 2a and 2c

	2a	**2c**
empirical formula	$C_{30}H_{14}Co_4O_{14}$	$C_{19}H_{10}Co_4O_{15}$
fw	834.13	713.99
temperature	188(2) K	173(2) K
wavelength	0.71073 Å	0.71073 Å
cryst syst	monoclinic	triclinic
space group	$C2/c$	$P\bar{1}$
unit cell dimens	$a = 12.203(3)$ Å, $b = 12.011(2)$ Å, $c = 21.905(5)$ Å $\alpha = 90°$ $\beta = 95.795(16)°$ $\gamma = 90°$	$a = 9.262(3)$ Å $b = 10.983(3)$ Å c = 13.797(3) Å $\alpha = 89.613(18)°$ $\beta = 72.026(18)°$ $\gamma = 69.918(19)°$
volume	3194.0(12) Å^3	1246.0(6) Å^3
Z	4	2
density (calcd)	1.735 Mg/m^3	1.903 Mg/m^3
abs coeff	2.110 mm^{-1}	2.689 mm^{-1}
F(000)	1656	704
cryst size	0.24 × 0.32 × 0.34 mm^3	0.42 × 0.36 × 0.32 mm^3
θ range for data collection	1.87 to 26.00°	2.39 to 25.00°
index ranges	$0 < h < 15$, $0 < k < 14$, $-27 < l < 26$	$-10 < h < 0$, $-12 < k < 12$, $-16 < l < 15$
no. of reflns collected	3298	4638
no. of ind reflns	3149 [R(int) = 0.0467]	4350 [R(int) = 0.0613]
completeness to $\theta = 25.00°$	99.9%	99.5%
abs corr	none	empirical
refinement method	full-matrix least-squares on F^2	full-matrix least-squares on F^2
no. of data/restraints/params	3149/0/221	4350/3/353
goodness-of-fit on F^2	1.096	1.036
final R indices [$I>2\sigma(I)$]	R1 = 0.0465, wR2 = 0.1154	R1 = 0.0415, wR2 = 0.1005
R indices (all data)	R1 = 0.0661, wR2 = 0.1342	R1 = 0.0549, wR2 = 0.1085
largest diff peak and hole	0.673 and −1.015 e·Å^{-3}	0.803 and −0.744 e·Å^{-3}

SmI_2. **1a** (0.078 g, 0.19 mmol) was placed in a sidearm flask under N_2 with a magnetic stir bar. A 0.10 M solution of SmI_2 in THF (5.6 mL, 0.56 mmol) was added to the solid **1a**, and the mixture was stirred for 3 h at room temperature. The reaction was terminated by addition of 5 M NaOH (5 mL). Diethyl ether (50 mL) was added to the reaction mixture, and the organic phase was washed with saturated NaCl solution (3 × 50 mL) and then dried over $MgSO_4$. Volatiles were removed by rotary evaporation, and the products were isolated by preparative TLC on silica gel, affording aldehyde **1a** (0.0023 g), diol **2a** (0.025 g), and alcohol **3a** (0.0032 g).

SmI_2/Cp_2TiCl_2. Cp_2TiCl_2 (0.12 g, 0.50 mmol) was placed in a sidearm flask with a stirring bar under nitrogen. The flask was cooled to −78 °C, and then a 0.1 M solution of SmI_2 in THF (4.9 mL, 0.5 mmol) was transferred to the flask. The mixture was stirred for 30 min at −78 °C, slowly warmed to room temperature, and then recooled to −78 °C. The cooled mixture was then transferred via cannula to a chilled flask (−78 °C) containing **1a** (0.10 g, 0.25 mmol), and the mixture was stirred for 30 min. After warming to room temperature, 0.1 M HCl (5 mL) was added and stirring was continued for 15 min. Diethyl ether (50 mL) was added, and the organic phase was washed three times with saturated NaCl solution and then dried over $MgSO_4$. Rotary evaporation of the solution volatiles and silica gel preparative TLC gave **1a** (0.027 g) and diol complex **2a** (0.046 g).

Mn/Cp_2TiCl_2/TMSCl. Into a sidearm flask 4 Å molecular sieves (2.0 g), Mn (0.0060 g, 0.10 mmol), Cp_2TiCl_2 (0.0050 g, 0.018 mmol), and a stirring bar were added under nitrogen followed by 10 mL of THF. This mixture was allowed to stir for 20 min, followed by the addition of TMSCl (0.026 mL, 0.20 mmol). A solution of aldehyde **1a** (0.076 g, 0.18 mmol) in 10

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[23] Stuart, J. G.; Nicholas, K. M. *Synthesis* **1989**, *6*, 454. Tester, R.; Varghese, V.; Montana, A. M.; Khan, M.; Nicholas, K. M. *J. Org. Chem.* **1990**, *55*, 186.

[24] Ganesh, P.; Nicholas, K. M. *J. Org. Chem.* **1997**, *43*, 1737.

mL of THF was added, and the mixture was stirred for 4 h. The mixture was filtered through a short column of silica gel, rinsing with a 3:1 petroleum ether/ether solution. The eluant was concentrated by rotary evaporation and the residue subjected to preparative TLC (97:3 petroleum ether/ether). The diol **2a** (0.033 g) and alcohol **3a** (0.014 g) were isolated.

2a. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 7.40 (m, 10H), 5.35 (d, $J = 6.6$ Hz, 2H), 2.85 (d, $J = 6.6$ Hz, 2H). IR ($CHCl_3$): 2091, 2056, 2027 cm^{-1} (M − CO).

Decomplexation of Bis(dicobalt hexacarbonyl)-1,6-diphenyl-1,5-di-yne-3,4-diol. The diol complex **2a** (0.063 g, 0.075 mmol) dissolved in 1 mL of acetone was cooled to −78 °C and stirred while $(NH_4)_2Ce(NO_3)_6$ (0.215 g, 0.48 mmol) was added with stirring. After approximately 3 h the mixture was warmed to room temperature. Saturated NaCl solution (2 mL) was added, and the mixture was extracted three times with 2 mL portions of ethyl acetate. The combined organic phase was dried over $MgSO_4$, and the solvent was removed by rotary evaporation. The diol **7** (0.017 g, 89% yield) was obtained as a white solid after preparative silica gel TLC (1:1 petroleum ether/diethyl ether). The ^{1}H NMR spectrum of 1,6-diphenyl-5,6-hexadiyn-3,4-diol [($CDCl_3$) 7.2 (m, 4H), 6.9 (m, 6H), 4.6 (bs, 2H), 2.2 (bs, 2H)] was identical to that reported.[6] MS (EI, 70eV) 262 (M, 1), 261 (M-1, 3), 131 (1/2M, 100), 103 (50), 77(47).

Pinacolization of (2-Butynal)dicobalt Hexacarbonyl (1b). Cp_2TiCl_2/*sec*-BuMgCl. Aldehyde **1b** (0.12 g, 0.34 mmol) was treated with Cp_2TiCl_2/*sec*-BuMgCl according to the procedure described for **1a**. Column chromatography (97:3 petroleum ether/ether) was used to separate the two cobalt complexes: aldehyde **1b** (0.020 g) and diol **2b** (0.050 g).

Mn/Cp_2TiCl_2/Me_3SiCl. Aldehyde **1b** (0.17 g, 0.48 mmol) was treated with Mn (0.015 g, 0.25 mmol), Cp_2TiCl_2 (0.014 g, 0.051 mmol), Me_3SiCl (1.0 mmol), and 4 Å molecular sieves (2.0 g) as described above. Preparative TLC (97:3 petroleum ether/ether) separated the two components, aldehyde **1b** (0.043 g) and diol **2b** (0.061 g).

2b. ^{1}H NMR ($CDCl_3$): δ 4.94 (d, $J = 7.2$ Hz, 2H), 2.72 (s, 6H), 2.55 (d, $J = 7.2$ Hz, 3H). IR (CH_2Cl_2): 2090, 2055, 2042 cm^{-1}. MS (EI, 12 eV): 626 (M − 4CO), 570 (M − 5CO), 542 (M − 6CO), 514 (M − 7CO).

Pinacolization of (Propynal)dicobalt Hexacarbonyl (1c). SmI_2. Aldehyde **1c** (0.117 g, 0.343 mmol) in a sidearm flask under nitrogen was cooled to 0 °C and then treated with 8.6 mL of 0.1 M SmI_2 in THF with stirring. The reaction was allowed to warm to room temperature and stirred overnight. The mixture was then treated with 5 mL of 0.1 M HCl and 5 mL of saturated NaCl and extracted three times with 10 mL portions of ethyl acetate, and the combined organic phase was dried over $MgSO_4$. The solution was concentrated and the residue subjected to preparative TLC, developing with 4:1 petroleum ether/ether. In addition to recovered **1c**, diol **2c** was obtained (R_f 0.5) as a dark red solid in 40−50% yield.

2c. ^{1}H NMR (d_6-benzene): 5.25 (s, 2H), 3.9 (s, 2 H), 2.3 (s, 2H). MS (FAB): 654 (M − CO), 598 (M − 3CO), 570 (−4CO), 542 (M − 5CO), 514 (M − 6CO), 486 (M − 7CO), 458 (M − 8CO).

X-ray Structure Determination of 2a and 2c. X-ray quality crystals of **2a** were obtained by cooling a saturated solution in toluene for 2 days at −10 °C. Crystals of **2c** were obtained by cooling a saturated methanol solution at −10 °C over a few days.

The data for **2a** and **2c** were obtained on a Siemens/Brucker P4 diffractometer using Mo Kα ($\lambda = 0.71073$ Å) radiation. The data were corrected for Lorentz and polarization effects; an absorption correction based on ψ-scans was applied. The structures were solved by the direct method using the SHELXTL system[25] and refined by full-matrix least-squares on F^2 using all reflections. All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms were included with idealized parameters except for **2c**, for which the hydrogen atoms at O7 and O8 were located and refined isotropically. For **2a** the final R1 = 0.047 is based on 2509 “observed reflections” [$I > 2\sigma(I)$], and wR2 = 0.134 is based on all reflections (3149 unique data). Details of the crystal data are given in Table 2. Thermal ellipsoids are drawn at the 50% level for Figure 1.

The asymmetric unit for **2c** contains one molecule of $C_{18}H_6Co_4O_1$ and one CH_3OH solvent molecule. The hydroxyl groups from **2c** and the solvent molecule form H-bonds as listed in Table 2. For **2c** the final R1 = 0.047 is based on 3575 “observed reflections” [$I > 2\sigma(I)$], and wR2 = 0.109 is based on all reflections (4350 unique data). Details of the crystal data are given in Table 1. Thermal ellipsoids are drawn at the 40% level in Figure 2.

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Supporting Information Available: Details of crystal data and structure refinement for **2a** and **2c** including atom coordinates, isotropic displacement factors, bond lengths and angles, and hydrogen coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

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(25) Bruker. *SHELXTL*, Version 5.1; Bruker AXS: Madison, WI, 1997.