greatest preference. However, the presence of significant steric interactions can also lead to additional variations in preferences, notably for cyclic dienyl species, and further studies will be required to better understand the extent of these contributions.

Acknowledgment. R.D.E. is grateful to the National Science Foundation for support of this work and to Prof. John Gladysz for helpful discussions.

Supplementary Material Available: Tables of thermal and hydrogen atom parameters, least-squares plane data, and atomic parameters for the atoms in $Os(C_5H_5)(2,4\text{-}C_7H_{11})$, $Ru(2,4\text{-}C_7H_{11})(2,4\text{-}C_7H_{12})(CO)^+BF_4^-$, $Ru(2,4\text{-}C_7H_{11})(CO)_2(PEt_3)^+BF_4^-$, $Ru(2,4\text{-}C_7H_{11})(CO)(PEt_3)_2^+BF_4^-$, and "$HRu(2,4\text{-}C_7H_{11})_2^+BF_4^-$" (12 pages); tables of structure factors (53 pages). Ordering information is given on any current masthead page.

Diastereoselective Ligand and Vertex Substitutions in Bimetallic Bridged Alkyne Clusters: X-ray Crystal Structure of (μ_2-*endo*-2-Propynylborneol)hexacarbonyldicobalt

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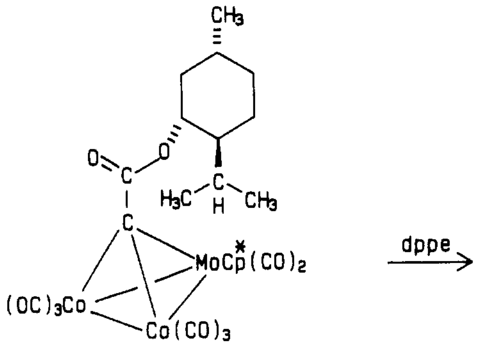
Enantiomerically pure dicobalt μ-alkyne clusters that possess diastereotopic $Co(CO)_3$ vertices can be synthesized by the treatment of (propargyl alcohol)$Co_2(CO)_6$ with menthol or borneol or by the reaction of $Co_2(CO)_8$ with *endo*-2-propynylborneol. Ligand substitution reactions with phosphines occur with some degree of diastereoselectivity to give mixtures of monosubstituted complexes. Moreover, diastereoselective replacement of a metal vertex by isolobal groups, $(C_5H_4R)M(CO)_2$, where M = Mo, W, has been observed. The hexacarbonyldicobalt complex, 6, of *endo*-2-propynylborneol has been synthesized and characterized by X-ray crystallography. The crystals are orthorhombic of space group $P2_12_12_1$ with a = 12.136 (3) Å, b = 12.682 (2) Å, c = 13.652 (3) Å, V = 2101 (1) Å^3, D_c = 1.51 g cm^{-3}, and D_m = 1.49 g cm^{-3} for Z = 4 and R_1 = 0.0546 and R_2 = 0.0567 for 3713 unique reflections (R_1 = 0.0437 and R_2 = 0.0463 for 2953 reflections with $I > 2.5\sigma(I)$).

Introduction

It has been recently reported that mixed metal clusters, such as 1, that bear a chiral substituent derived from a natural product are readily synthesizable on the multigram scale.[1,2] In these molecules, the two tricarbonylcobalt vertices are rendered diastereotopic and so, in principle, should be differently susceptible to attack by incoming ligands. Indeed, we have shown that use of bulky phosphines can lead to a small degree of chiral discrimination. The diastereotopic character of these vertices was readily demonstrated by the incorporation of a bidentate ligand, e.g., $Ph_2PCH_2CH_2PPh_2$, yielding 2, which exhibited two distinct phosphorus resonances in the ^{31}P NMR spectrum.[1] Moreover, a recent note from Nicholas' laboratory[3] describes elegant work whereby reaction of triphenylphosphine with a racemic mixture of chiral (propargyl alcohol)$Co_2(CO)_6$ clusters leads to preferential diastereomer formation; this prompts us to report the results of our own studies, which demonstrate the generality of this phenomenon for $(R^*C{\equiv}CR)Co_2(CO)_6$ complexes in which R* is a chiral substituent derived from a natural product.[4]

It is clear that there exists some tendency for preferential attack by an incoming ligand because of the intrinsic diastereotopic nature of the metal vertices. However, one might also envisage an extension of this concept to include the direct replacement of only one $Co(CO)_3$ vertex by an isolobal metal fragment, thus generating enantiomerically pure, chiral heterobimetallic clusters without the need to resort to time-consuming diastereomer separations. To this end, we have prepared several enantiomerically pure dicobalt μ-alkyne clusters and examined not only ligand substitutions but also complete vertex replacement processes on these compounds.



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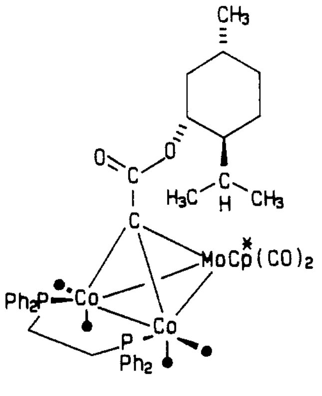

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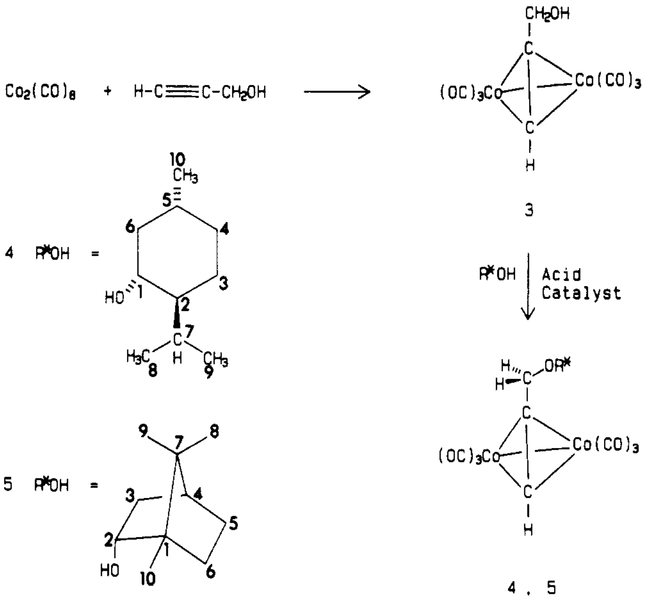
Scheme I



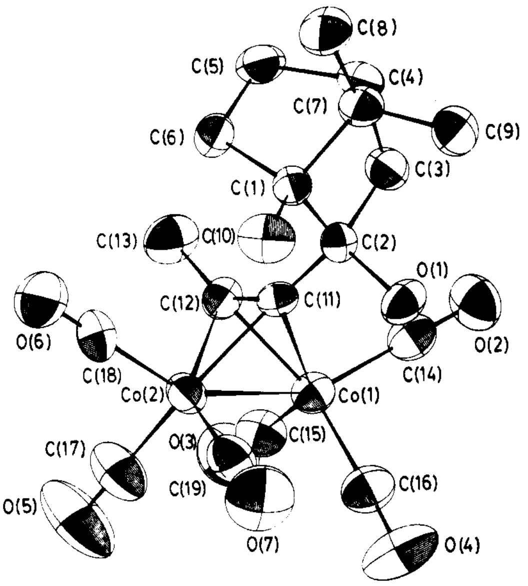


Figure 1. View of 6 showing the atom numbering scheme.

Results and Discussion

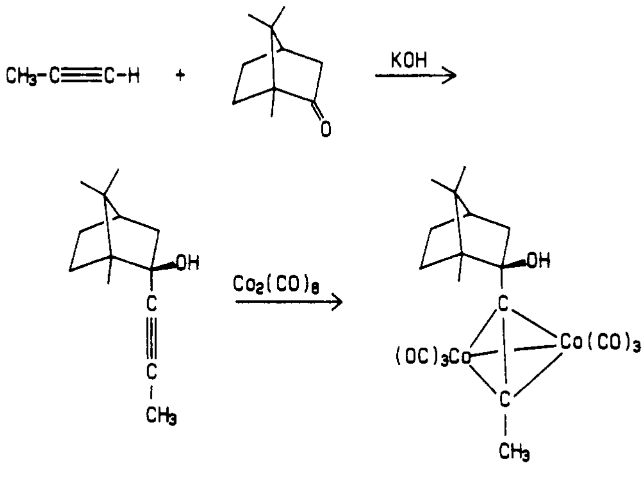
(a) Cluster Syntheses. During the course of this project, three different enantiomerically pure dicobalt μ-alkyne clusters were used as chiral starting materials upon which ligand or vertex substitutions were attempted. Two of these dicobalt species were synthesized by following the same general route as was used by Schreiber[5] and involves the incorporation of a natural product into an existing bimetallic cluster. As shown in Scheme I, the reaction of $Co_2(CO)_8$ with propargyl alcohol generates in good yield the μ-alkyne species 3 bearing a hydroxymethyl substituent; subsequent treatment with a CH_2Cl_2 solution of either (1*R*,2*S*,5*R*)-(−)-menthol or (1*S*)-*endo*-(−)-borneol in the presence of an acid catalyst ($HBF_4{\cdot}Et_2O$) over a 4-Å molecular sieve gives the enantiomerically pure ether clusters 4 and 5, respectively.

The second route to chiral clusters involved the reaction of dicobalt octacarbonyl with an alkyne derivative of a natural product. In this instance, we elected to position the chiral entity closer to the cobalt vertices when forming the resulting bimetallic μ-alkyne cluster. This was accomplished by allowing the propynyl anion to react with (1*R*)-(+)-camphor.[6] The presence of the bulky dimethyl bridge causes the alkyne anion to approach from the lower face of the molecule, thus generating *endo*-2-propynylborneol. Subsequent addition of $Co_2(CO)_8$ led to the desired molecule 6.

Table I. Crystal Data for $[(Co(CO)_3)_2(C_{13}H_{19}OH)]$

formula	$C_{19}H_{20}O_7Co_2$
fw	478.23
system	orthorhombic
systematic absences	$h00$, $h \neq 2n$; $0k0$, $k \neq 2n$; $00l$, $l \neq 2n$
space group	$P2_12_12_1$ (No. 19)
a, Å	12.136 (3)
b, Å	12.682 (2)
c, Å	13.652 (3)
V, Å^3	2101 (1)
Z	4
D_c, g cm^{-3}	1.51
D_m, g cm^{-3}	1.49
$F(000)$	978.80 (976)
μ(Mo Kα), cm^{-1}	16.75 (15.37)
final R_1, R_2[a,d]	0.0546, 0.0567
weighting scheme	$w = (\sigma^2F + 0.001833F^2)^{-1}$
error in observn of unit wt[b]	1.0713
highest peak, e Å^{-3}; location	0.67; 0.2029, 0.0016, 0.9815[c]
lowest peak, e Å^{-3}	−0.50

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$; $R_2 = (\sum w(|F_o| - |F_c|)^2/\sum wF_o^2)^{1/2}$. [b] $S = (\sum w(|F_o| - |F_c|)^2/(m - n))^{1/2}$. m = number of reflections, n = number of variables. [c] 1.15 Å from Co(2). [d] R_1, R_2 for 2953 reflections with $I > 2.5{*}(I)$ 0.0437, 0.0463, respectively.



6

These clusters, along with all of the others reported herein, were fully characterized by using a variety of techniques including ^{13}C, ^{1}H, and ^{31}P NMR spectroscopies as well as IR spectroscopy, mass spectrometry, and elemental analyses. Furthermore, in an attempt to gain an understanding of the steric factors involved in these substitution reactions, the structure of the chiral dicobalt cluster 6 was determined X-ray crystallographically.

(b) X-ray Crystal Structure of 6. Reddish-black prismatic crystals of 6 were grown from dichloromethane/hexane. Figure 1 shows a view of the molecule showing the atom numbering scheme, while a stereoview of the unit cell contents viewed down b appears as Figure 2. The crystallographic data for molecule 6 are collected

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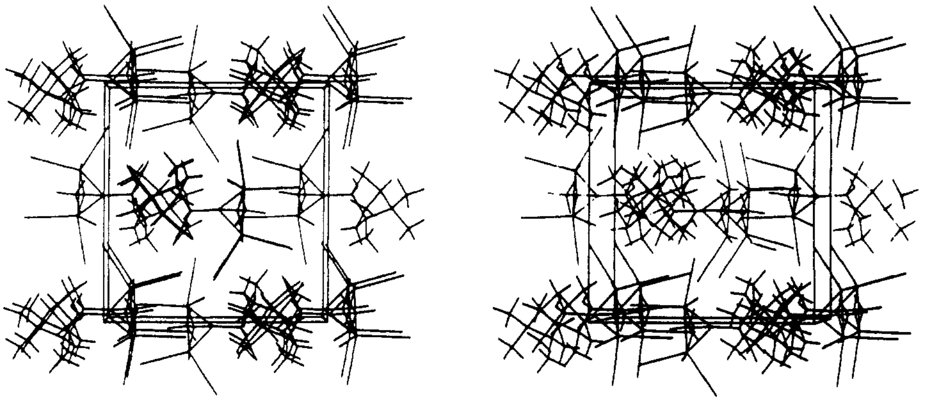

Figure 2. Stereoview of the unit cell contents of **6**; the view is down the *b* axis.

Table II. Positional Parameters ($\times 10^4$) and U_{eq} (Å$^2 \times 10^4$) for [$(Co(CO)_3)_2(C_{13}H_{19}OH)$] with Standard Errors in Parentheses

atom	*x*	*y*	*z*	$U_{eq}{}^a$
Co(1)	1184.9 (5)	1375.9 (5)	9602.8 (4)	398
Co(2)	1291.6 (5)	-564.2 (5)	9692.2 (5)	419
C(1)	-1790 (4)	-674 (3)	8905 (3)	355
O(1)	-1448 (3)	662 (3)	10163 (2)	490
C(2)	-1153 (3)	352 (3)	9183 (3)	326
C(3)	-1609 (4)	1161 (4)	8417 (4)	450
C(4)	-2415 (4)	500 (4)	7796 (4)	481
C(5)	-1717 (4)	-246 (5)	7168 (4)	531
C(6)	-1311 (4)	-1064 (4)	7930 (3)	457
C(7)	-2939 (4)	-233 (4)	8554 (4)	475
C(8)	-3688 (5)	-1081 (5)	8096 (4)	634
C(9)	-3638 (4)	343 (5)	9314 (4)	613
C(10)	-1828 (5)	-1505 (4)	9715 (4)	569
C(11)	90 (3)	297 (3)	9134 (3)	338
C(12)	959 (4)	339 (4)	8545 (3)	402
C(13)	1330 (5)	329 (5)	7491 (4)	618
C(14)	406 (4)	2528 (4)	9272 (4)	492
C(15)	2570 (5)	1733 (4)	9211 (4)	527
C(16)	1169 (5)	1560 (4)	10914 (4)	570
C(17)	2781 (5)	-616 (5)	9780 (6)	767
C(18)	1065 (5)	-1843 (4)	9156 (4)	639
C(19)	802 (5)	-822 (4)	10934 (74)	578
O(2)	-102 (3)	3248 (3)	9080 (3)	660
O(3)	3421 (3)	1952 (4)	8926 (4)	803
O(4)	1211 (5)	1678 (4)	11737 (3)	947
O(5)	3701 (4)	-634 (5)	9826 (6)	1259
O(6)	914 (5)	-2638 (3)	8821 (4)	1072
O(7)	479 (5)	-986 (4)	11693 (4)	985

[a] $U_{eq} = {}^1/_3(U_{11} + U_{22} + U_{33})$.

in Tables I–III and reveal that the alkynedicobalt moiety adopts the characteristic pseudotetrahedral core typical of such clusters. As shown in Figure 1, the Co_2C_2 cluster is indeed attached to the borneol at the *endo*-2 position, thus confirming that the attack by the propynyl anion at the ketonic carbon in camphor had occurred on the less hindered face. The bonding within the cluster fragment is rather reminiscent of that previously reported[7] for (t-BuC≡CBu-t) $Co_2(CO)_6$, **7**, in which the alkyne substituents are sterically demanding. Thus, for **6** and **7**, the Co–Co distances are 2.467 (1) and 2.463 (1) Å, respectively. The average Co–CO and CoC–O distances (1.811 and 1.129 Å for **6**; 1.805 and 1.133 Å for **7**) are also similar. The cobalt–alkyne-carbon bonds average to 1.985 and 1.996 Å for **6** and **7**, respectively, but the alkyne carbon–carbon bonds are rather short at 1.327 Å for **6** and 1.335 Å for **7**. These values may be compared to those for clusters bearing less bulky substituents in which alkyne carbon–carbon distances normally range from 1.35 to 1.38 Å.[8-12] In alkyne–dimetal cluster complexes, the RC≡CR moiety is no longer linear, and in **6** the substituents are bent back by ≈35°. Furthermore, in **6** the bulk of the substituents leads to a twisting of the C(12)–C(13) bond relative to the C(11)–C(2) vector; this dihedral angle is 11.7°. Figure 3 depicts a view along the C(2)–C(11) bond and shows the "staggered ethane type" conformation adopted by this fragment. The dihedral angle C(1)–C(2)–C(11)–C(12) would be 60° for perfect staggering and is 80.4° in **6**. An interesting point is the orientation of the α-hydroxy substituent, which is directed between the two cobalt atoms. We are aware of only two other crystallographically characterized systems of this type.[3,13] In both cases, the hydroxy group is oriented in a similar fashion to that found in **6**, and one might speculate that there is an interaction between the hydroxyl moiety and the cobalt atoms.

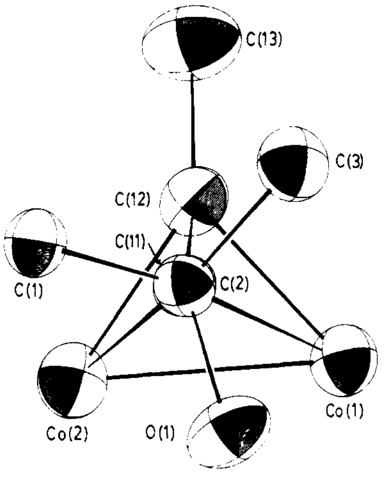

Figure 3. View along the C(2)–C(11) bond in **6** showing the approximately staggered orientation of this "ethane-type" fragment.

(c) Substitutions with Phosphines. As a continuation of our previous work on reactions of phosphines with carbyne-capped trimetallic tetrahedral clusters,[1] each of the bimetallic clusters, viz., **4**–**6**, was subjected to ligand substitution reactions involving a variety of phosphines. It is possible to replace a carbonyl ligand in the cobalt cluster with a phosphine by using any one of a number of

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Table III. Selected Bond Lengths (Å) and Bond Angles (deg) for [$(Co(CO)_3)_2(C_{13}H_{19}OH)$], with Estimated Standard Deviations in Parentheses

(i) Cobalt Coordination			
Co(1)–Co(2)	2.467 (1)		
Co(1)–C(11)	2.011 (4)	Co(2)–C(11)	1.976 (4)
Co(1)–C(12)	1.973 (4)	Co(2)–C(12)	1.982 (5)
Co(1)–C(14)	1.798 (6)	Co(2)–C(17)	1.814 (6)
Co(1)–C(15)	1.821 (6)	Co(2)–C(18)	1.801 (6)
Co(1)–C(16)	1.806 (6)	Co(2)–C(19)	1.825 (4)
C(11)–Co(1)–C(12)	38.9 (2)	C(11)–Co(2)–C(12)	39.2 (2)
C(11)–Co(1)–C(14)	97.2 (2)	C(11)–Co(2)–C(17)	141.5 (2)
C(11)–Co(1)–C(15)	133.3 (2)	C(11)–Co(2)–C(18)	103.3 (2)
C(11)–Co(1)–C(16)	113.3 (2)	C(11)–Co(2)–C(19)	102.6 (2)
C(12)–Co(1)–C(14)	106.5 (2)	C(12)–Co(2)–C(17)	106.1 (3)
C(12)–Co(1)–C(15)	94.6 (2)	C(12)–Co(2)–C(18)	99.7 (2)
C(12)–Co(1)–C(16)	144.2 (2)	C(12)–Co(2)–C(19)	140.5 (2)
C(14)–Co(1)–C(15)	102.1 (2)	C(17)–Co(2)–C(18)	98.3 (3)
C(14)–Co(1)–C(16)	98.0 (2)	C(17)–Co(2)–C(19)	104.8 (3)
C(15)–Co(1)–C(16)	105.6 (3)	C(18)–Co(2)–C(19)	99.6 (3)
Co(2)–Co(1)–C(11)	51.1 (1)	Co(1)–Co(2)–C(11)	52.4 (1)
Co(2)–Co(1)–C(12)	51.6 (1)	Co(1)–Co(2)–C(12)	51.2 (1)
Co(2)–Co(1)–C(14)	148.3 (2)	Co(1)–Co(2)–C(17)	95.3 (2)
Co(2)–Co(1)–C(15)	102.4 (2)	Co(1)–Co(2)–C(18)	150.5 (2)
Co(2)–Co(1)–C(16)	94.6 (2)	Co(1)–Co(2)–C(19)	102.0 (2)
Co(1)–C(11)–Co(2)	76.4 (1)	Co(1)–C(12)–Co(2)	77.2 (2)
Co(1)–C(11)–C(2)	127.9 (3)	Co(2)–C(11)–C(2)	138.1 (3)
Co(1)–C(11)–C(12)	69.0 (3)	Co(2)–C(11)–C(12)	70.7 (3)
Co(1)–C(12)–C(11)	72.1 (3)	Co(2)–C(12)–C(11)	70.2 (3)
Co(1)–C(12)–C(13)	131.4 (4)	Co(2)–C(12)–C(13)	133.5 (4)
(ii) 1,7,7-Trimethyl-2-propynyl-2-hydroxynorbornyl			
C(2)–C(3)	1.567 (6)	C(6)–C(1)	1.534 (6)
C(2)–O(1)	1.439 (5)	C(1)–C(10)	1.527 (6)
C(2)–C(1)	1.562 (6)	C(1)–C(7)	1.578 (6)
C(2)–C(11)	1.512 (6)	C(7)–C(9)	1.528 (7)
C(3)–C(4)	1.543 (7)	C(7)–C(8)	1.540 (7)
C(4)–C(5)	1.533 (7)	C(11)–C(12)	1.327 (6)
C(4)–C(7)	1.529 (7)	C(12)–C(13)	1.508 (7)
C(5)–C(6)	1.548 (7)		
O(1)–C(2)–C(3)	110.7 (3)	C(2)–C(1)–C(10)	114.5 (4)
O(1)–C(2)–C(1)	109.3 (3)	C(6)–C(1)–C(10)	114.7 (4)
C(3)–C(2)–C(1)	102.1 (3)	C(2)–C(1)–C(7)	102.4 (3)
O(1)–C(2)–C(11)	107.6 (3)	C(6)–C(1)–C(7)	100.6 (4)
C(3)–C(2)–C(11)	110.6 (3)	C(10)–C(1)–C(7)	116.0 (4)
C(1)–C(2)–C(11)	116.4 (3)	C(4)–C(7)–C(1)	93.1 (3)
C(2)–C(3)–C(4)	103.5 (4)	C(4)–C(7)–C(9)	113.5 (4)
C(3)–C(4)–C(5)	107.0 (4)	C(1)–C(7)–C(9)	117.0 (4)
C(3)–C(4)–C(7)	102.9 (4)	C(4)–C(7)–C(8)	113.3 (4)
C(5)–C(4)–C(7)	103.4 (4)	C(1)–C(7)–C(8)	113.4 (4)
C(4)–C(5)–C(6)	102.3 (4)	C(9)–C(7)–C(8)	106.4 (4)
C(5)–C(6)–C(1)	104.3 (4)	C(2)–C(11)–C(12)	144.9 (4)
C(2)–C(1)–C(6)	107.0 (3)	C(11)–C(12)–C(13)	144.7 (5)
(iii) Carbonyls			
C(14)–O(2)	1.134 (6)	C(17)–O(5)	1.118 (7)
C(15)–O(3)	1.141 (6)	C(18)–O(6)	1.122 (7)
C(16)–O(4)	1.134 (6)	C(19)–O(7)	1.127 (7)
Co(1)–C(14)–O(2)	178.4 (5)	Co(2)–C(17)–O(5)	178.8 (6)
Co(1)–C(15)–O(3)	177.1 (5)	Co(2)–C(18)–O(6)	179.2 (6)
Co(1)–C(16)–O(4)	176.8 (6)	Co(2)–C(19)–O(7)	178.5 (6)

techniques, including both thermal and catalytic routes. The method employed in this work for the generation of the monophosphine-substituted clusters was modeled on that of Robinson et al.[14] in which a THF solution of the cluster and the phosphine was stirred together at room temperature with benzophenone ketyl (BPK). This synthetic technique is advantageous in that it generates the monosubstituted clusters in good yields under mild conditions. The latter point is very significant when one wishes to carry out the substitution reactions under kinetic control. The syntheses of the bridging phosphine–dicobalt clusters were achieved by using a thermal route because the catalytic approach gives phosphine-linked clusters as the major products.[15]

The tricarbonylcobalt vertices in the two ether-containing clusters **4** and **5** are diastereotopic and hence should not be equally susceptible to the replacement of a carbonyl group by a phosphine ligand. In the trimetallic clusters described previously,[1] the extent of phosphine attack at the two cobalt vertices was monitored via ^{31}P NMR spectroscopy. Phosphorus nuclei attached to different cobalt sites would be expected to give rise to different ^{31}P NMR resonances. Using two phosphine ligands of comparable basicity but different steric demand (as measured by their cone angles), we had hoped to be able to establish a simple reactivity pattern and then correlate the observed diastereoselectivity to the bulk of the phosphine ligand. Accordingly, triphenylphosphine (cone angle 145°) and tricyclohexylphosphine (cone angle 170°) were allowed to react with the ether clusters **4** and **5** to give the complexes **8–11**, as in Scheme II.

The two pairs of monophosphine-substituted dicobalt clusters were synthesized, characterized, and examined for diastereoselectivity by using ^{31}P NMR spectroscopy. However, in each of the four cases, the ^{31}P NMR spectrum consisted of a single line. One could interpret this observation in two ways: either (i) the substitution was completely selective for one cobalt vertex over the other in all cases, or (ii) it was not possible in these molecules to resolve the different resonances for the two diasterotopic sites because the chemical shift differences were small. We preferred to adopt the more conservative position and chose to try to establish the existence of two overlapping resonances. To this end, molecules **12** and **13**, each of which contained the bridging diphenylphosphinomethane ligand, were prepared from the two starting hexacarbonyl clusters by heating them under reflux in hexane with dppm. In both cases, mass spectral analysis confirmed the successful replacement of two carbonyl groups by dppm while the ^{13}C NMR spectroscopic results demonstrated that dppm was bridging the two cobalts rather than forming a chelate at a single cobalt center. It follows that two different resonances should have been observed in the ^{31}P NMR spectra of **12** and **13** (as is the case for **2**), corresponding to the two different phosphorus environments, provided the chemical shifts of the nuclei were sufficiently well separated. The ^{31}P NMR spectra obtained for both **12** and **13** were single lines, clearly indicating that the phosphorus nuclei in these clusters did not possess distinct chemical shifts and in fact were overlapping, even at high magnetic field. The same explanation, i.e., overlapping ^{31}P resonances, can therefore be invoked for the monophosphine-substituted clusters **8–11**.

4 R = H, R^* = $-CH_2-O-$menthyl
5 R = H, R^* = $-CH_2-O-$bornyl
6 R = CH_3, R^* = borneol

12 R = H, R^* = $-CH_2-O-$menthyl
13 R = H, R^* = $-CH_2-O-$bornyl
14 R = CH_3, R^* = borneol

Nevertheless, this does not answer the question of whether any diastereoselectivity was occurring during the ligand substitution reactions. Although it was not possible

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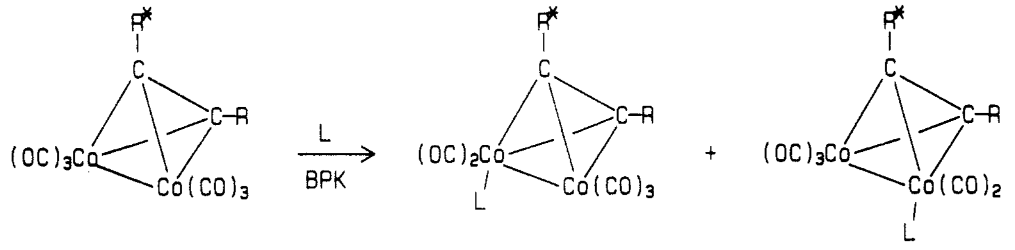
Scheme II



4 R = H, R* = -CH_2-O-menthyl
5 R = H, R* = -CH_2-O-bornyl
6 R = CH_3, R* = borneol

8 R = H, R* = -CH_2-O-menthyl, L = PPh_3
9 R = H, R* = -CH_2-O-menthyl, L = PCy_3
10 R = H, R* = -CH_2-O-bornyl, L = PPh_3
11 R = H, R* = -CH_2-O-bornyl, L = PCy_3
15 R = CH_3, R* = borneol, L = PPh_3

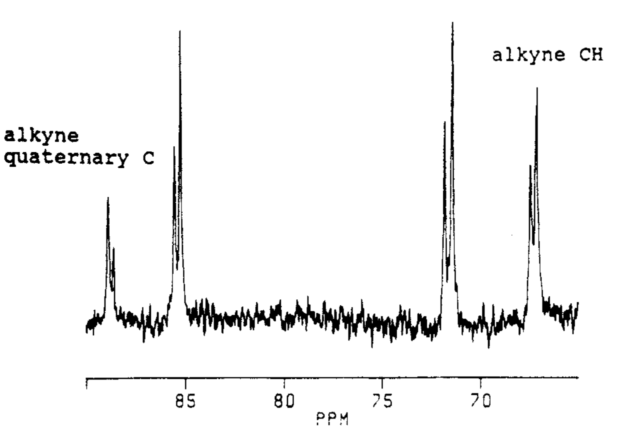


Figure 4. Section of the 62.5-MHz ^{13}C NMR spectrum of **11** showing the presence of major and minor diastereomers derived from the reaction of tricyclohexylphosphine with **5**.

to observe two resonances in the ^{31}P NMR spectra, pairs of corresponding carbons in the two diastereomers were detectable in the ^{13}C NMR spectra, and it was apparent that some degree of selectivity by the incoming phosphine had taken place. By comparing the intensities of the corresponding carbons, it was possible to draw conclusions regarding the extent of selective ligand substitution. When triphenylphosphine is used as the attacking ligand on either of the starting clusters, the two possible diastereomers are formed in equivalent amounts; the ratio of the corresponding pairs of carbon resonances in the diastereomers is 1:1. In contrast, use of tricyclohexylphosphine as the incoming ligand toward either **4** or **5** reveals (see Figure 4) that one diastereomer is being preferentially formed over the other isomer in a ratio of approximately 3:2 in both cases. Since tricyclohexylphosphine possesses a larger cone angle than does triphenylphosphine, the small discrimination in selectivity is presumably governed largely by steric factors.

In the cluster **6**, which is derived from *endo*-2-propynylborneol, the chiral substituent is substantially closer to the cobalt vertices than is the case for the ether clusters **4** and **5** discussed above. One might thus anticipate greater discrimination between the two vertices in **6**. Indeed, the corresponding dppm derivative, **14**, which was synthesized by the thermal reaction of dppm with **6**, exhibited two well-separated ^{31}P NMR resonances. However, treatment of **6** with Ph_3P under catalytic conditions yielded only a 1:1 mixture of the diastereomeric monophosphine-substituted clusters **15**. Attempts to carry out the analogous substitution reaction with tricyclohexylphosphine were unsuccessful, so at this point we chose to focus on complete vertex substitution.

(d) Heterobimetallic Clusters. Heterobimetallic μ-alkyne transition-metal clusters have been the subject of numerous investigations over the past few years.[16-21] These compounds are normally generated either through the interaction of an alkyne with a heterobimetallic complex or by the isolated substitution of a different organometallic vertex into an appropriate alkyne–homobimetallic cluster. The presence of the bulky chiral substituent in the enantiomerically pure dicobalt–alkyne clusters suggested that it might be feasible to generate mixed metal bimetallic clusters with some degree of control over the ratio of the diastereomeric products. Through the use of high-field ^{13}C NMR spectroscopy, it is possible to estimate the degree of chiral discrimination that occurs in the substitution of a (cyclopentadienyl)dicarbonylmolybdenum or -tungsten fragment for a $Co(CO)_3$ moiety. This is accomplished by comparing the intensities of the peaks assigned to corresponding pairs of carbons in the two diastereomers.

In order to ensure that the ^{13}C NMR results obtained would not be prejudiced as a consequence of different relaxation times for corresponding carbons in the resultant diastereomeric mixed metal clusters, two different routes to the chiral mixed metal ether clusters were devised. As shown in Scheme III, the diastereomers **19–24** are necessarily formed in a 50:50 ratio by the first route. Substitution of $Co(CO)_3$ by the new vertex, i.e., $(C_5H_5)Mo(CO)_2$, $(C_5H_4Me)W(CO)_2$, or $(C_5H_4Me)Mo(CO)_2$, in the hydroxymethyl cluster **3** obviously involves no chiral discrimination and must lead to racemic **16**, **17**, or **18**. These racemic complexes were then treated with either (1*R*,2*S*,5*R*)-(−)-menthol or (1*S*)-*endo*-(−)-borneol and an acid catalyst over 4-Å molecular sieves to give the resultant 50:50 diaste-

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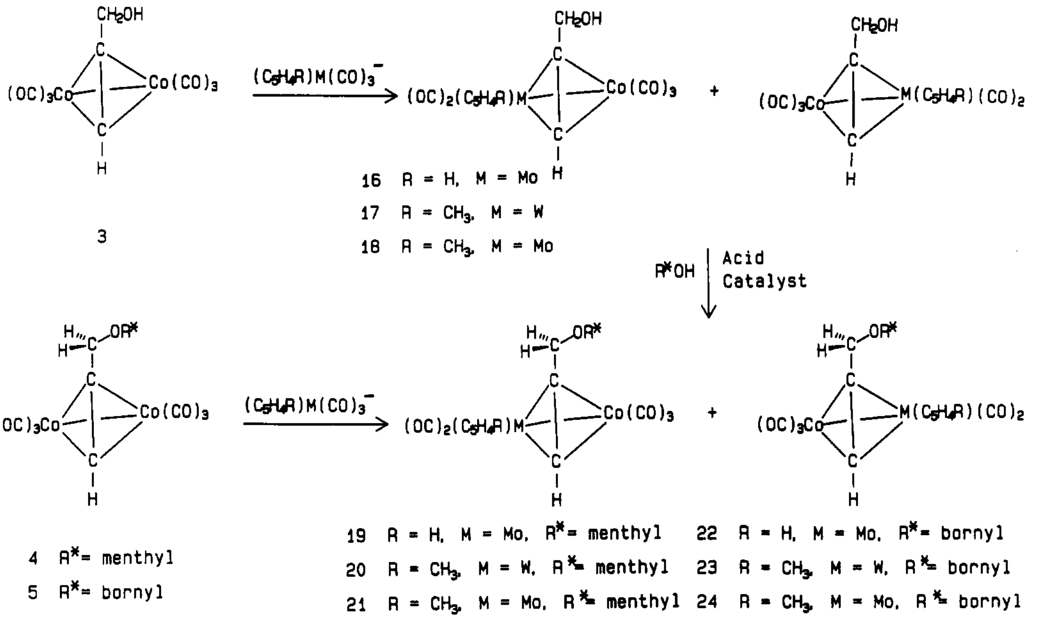
Scheme III



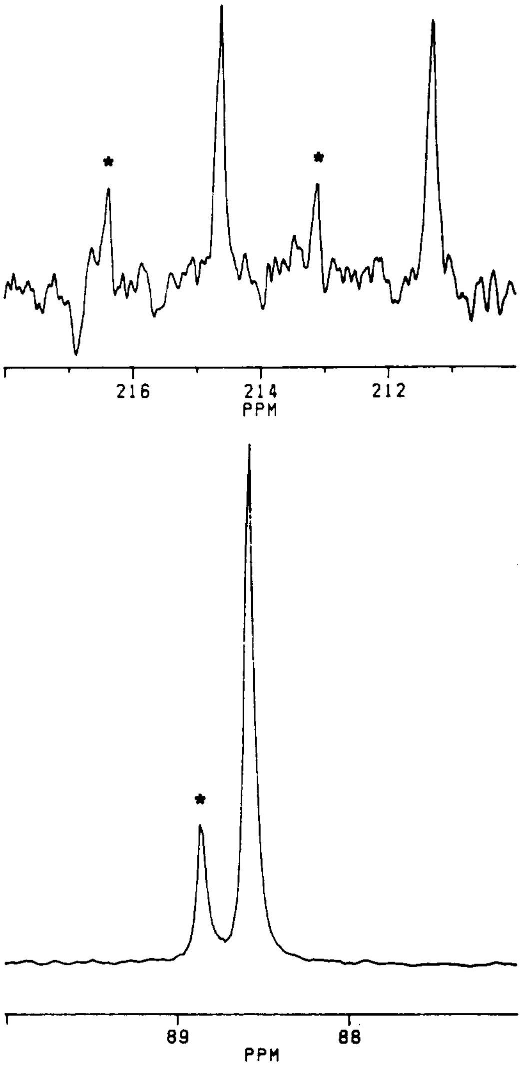


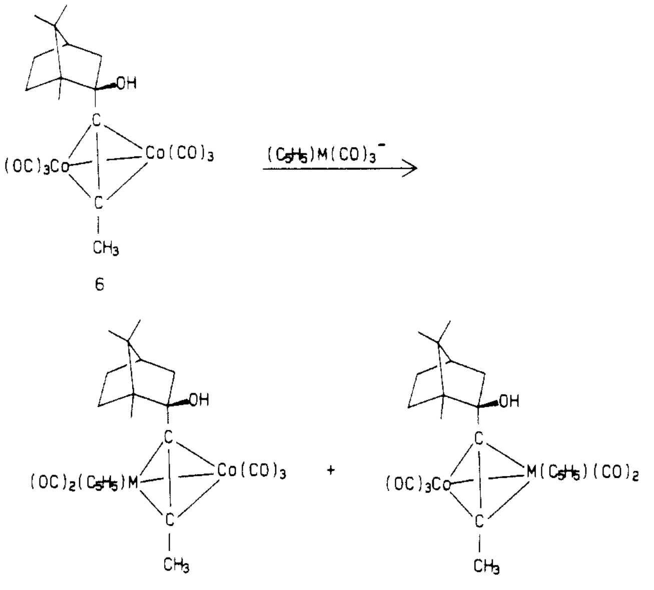
Figure 5. Section of the 62.5-MHz ^{13}C NMR spectrum of **26** showing the cyclopentadienyl and tungsten carbonyl resonances for the major and minor(*) diastereomers.

reomeric mixtures of the heterobimetallic species possessing a chiral natural product substituent. Now in the second approach a simple reversal of these steps results in conditions in which there is the potential for selective vertex replacement. Reaction of the (cyclopentadienyl)-$M(CO)_3^-$ anions with the already enantiomerically pure cluster **4** or **5** produces diastereomeric mixtures of the clusters **19**–**24**, which are not necessarily in a 50:50 ratio.

By following this procedure, the ^{13}C NMR spectra of the 50:50 mixtures obtained via the first synthetic procedure could be used as standards against which to normalize the spectra obtained for the substitution products derived from the latter route. The rationale behind our approach is actually quite simple and takes into account the fact that the corresponding pairs of carbon nuclei in the two diastereomers would not necessarily have identical relaxation times. The latter point is significant because it means that even if the two diastereomers formed via the second "potentially selective" route were actually present in a 50:50 ratio, the peaks assigned to the corresponding pairs of carbons might not have the same intensities. However, if the relative ^{13}C NMR peak intensities are established for the pairs of corresponding carbons in a mixture known to be 50:50, (from the first route), then any variations resulting from chiral discrimination (in route 2) will be evident. A careful scrutiny of the normalized ^{13}C NMR spectra revealed a small degree of diastereoselectivity during the course of the vertex substitution reactions such that the heterometallic diastereomers were present in a ratio of approximately 55:45 in all cases.

In an attempt to improve upon the chiral discrimination observed with the ether clusters **4** and **5**, a similar set of isolobal replacement reactions was carried out with the *endo*-2-propynylborneol cluster **6** in which the chiral fragment is sited much closer to the $Co(CO)_3$ vertices. Gratifyingly, the ^{13}C NMR spectra of the reaction products revealed that replacement of a tricarbonylcobalt vertex by $C_5H_5Mo(CO)_2$ yielded a 65:35 mixture of the diastereomeric heterobimetallic clusters **25**. Furthermore, the analogous reaction with $C_5H_5W(CO)_3^-$ gave a 75:25 diastereomeric mixture **26**. This diastereoselectivity is quite evident in Figure 5, which depicts the resonances associated with the carbonyl and cyclopentadienyl carbons derived from the tungsten reaction.

At this point, we are focusing our efforts on determining the solution structures of the two diastereomers to identify that which is formed preferentially. By synthesizing the dimolybdenum and ditungsten complexes of *endo*-2-



6

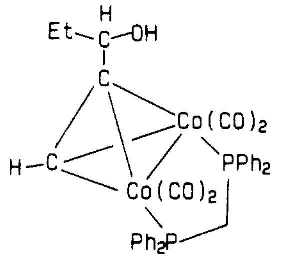
25 M = Mo

26 M = W

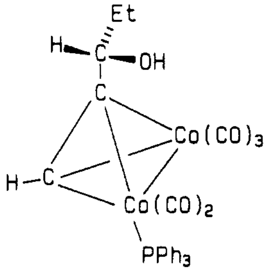
propynylborneol, it is anticipated that NMR studies (in particular, NOE measurements) will allow a determination of the orientations of the cyclopentadienyl rings with respect to the bridgehead methyl of the borneol. A comparison of the ^{1}H and ^{13}C NMR shifts of the diastereomeric heterobimetallic mixture and of the homobimetallic cluster would then allow conclusions to be drawn regarding which vertex in the dicobalt–μ-alkyne starting cluster was the preferred site for substitution.

As we were completing the final synthetic aspects of this work, a paper appeared that described reactions of triphenylphosphine with $(HC{\equiv}CCH(R)OH)Co_2(CO)_6$ clusters.[3] In these systems, the chiral nature of the α-carbon rendered the $Co(CO)_3$ vertices diastereotopic, and selective substitution of triphenylphosphine for CO at one cobalt vertex was observed. Furthermore, it was established crystallographically that the carbonyl ligand that had been replaced was trans to the cobalt–cobalt bond. In the light of these interesting observations, we chose to extend our study to include propargyl alcohol complexes of the type described by Nicholas. We selected $(HC{\equiv}CCH(Et)OH)Co_2(CO)_6$, **27**, as being a representative cluster which had not been previously examined.

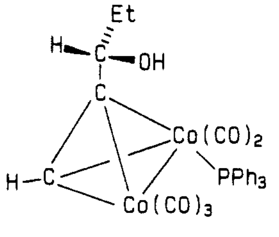
Treatment of **27** with $Ph_2PCH_2PPh_2$ yielded the complex **28**, which exhibited only a single ^{31}P signal despite the diastereotopic character of the phosphorus nuclei. The ^{13}CO peaks appeared as two broadened resonances at 207.9 and 203.9 ppm. As anticipated from the work of Nicholas, the reaction of **27** with triphenylphosphine gave major (67%) and minor (33%) diastereomers, **29a** and **29b**, respectively, which were separable by column chromatography; the disubstituted cluster **30** was also obtained.



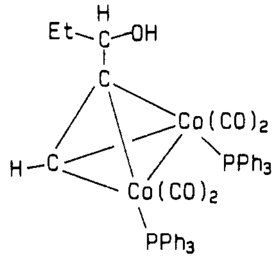
28



29a



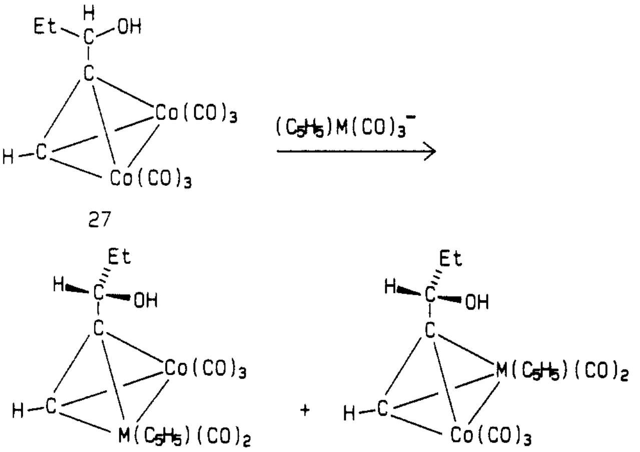
29b



30

One must rationalize why the diastereoselectivity of Ph_3P attack on **27** (and the related clusters described by Nicholas) is noticeably better than that found with the borneol cluster **6**. Molecular modeling studies based on our X-ray data for **6** reveal that incorporation of a bulky triphenylphosphine into the position trans to the cobalt–cobalt vector leads to major steric problems. We must therefore conclude that the phosphine replaces a pseudoaxial carbonyl ligand in **6** rather than a pseudoequatorial one. Thus, the diastereoselectivity is much less influenced by the chiral substituent than would otherwise be the case.

Treatment of the dicobalt cluster **27** with the (cyclopentadienyl)tricarbonylmolybdenum anion led to a 70:30 diastereomeric mixture **31**; the diastereomer ratio was readily determined from the relative intensities of the signals in the ^{13}C NMR spectrum. Although these molybdenum clusters were not readily separable chromatographically, the analogous tungsten complexes, **32**, were synthesized in a 60:40 ratio and the major isomer (the first to elute from the column) was cleanly isolable. We reiterate, however, that phosphine-substituted or metal-substituted clusters obtained by attack on systems such as **4**, **5**, or **6** are diastereomers and are optically active whereas the products **29a** and **29b** (which were obtained via the Nicholas procedure) and also the mixed metal clusters **31** and **32** are still racemic mixtures since the starting cluster **27** is a racemate. [For simplicity, only a single enantiomer of each cluster is shown.] These mixed metal clusters



27

31 M = Mo

32 M = W

bearing an α-hydroxy substituent are convenient sources of mixed metal vinylidene cations, CpM(CO)$_2$Co(CO)$_3$-[HC=C=CHR]$^+$, where M = Mo or W, and an NMR spectroscopic study of their molecular dynamics will be the topic of a future report.[22]

To conclude, we report that in chiral dicobalt–μ-alkyne clusters the sites of carbonyl ligand substitutions or of tricarbonylcobalt vertex substitutions by a variety of isolobal organometallic fragments can be influenced by the nature and proximity of the alkyne substituents. The observed preferential formation of one diastereomer over another suggests that careful control of vertex substitution reactions may provide a simple and direct route to enantiomerically pure heterobimetallic clusters without the need for tedious separations.

Experimental Section

All reactions were carried out under an atmosphere of dry nitrogen by employing conventional benchtop and glovebag techniques. All solvents were dried according to standard procedures before use.[23] ^{13}C NMR spectra were recorded with Bruker AM 500, WM 250, and AC 200 spectrometers. ^{1}H NMR spectra were recorded with Bruker AM 500 and Varian EM390 spectrometers. ^{31}P NMR spectra were recorded with a Bruker WM 250 spectrometer. ^{13}C and ^{1}H chemical shifts reported were referenced to tetramethylsilane while ^{31}P chemical shifts were referenced to 85% H$_3$PO$_4$. [When diastereomers are present in other than a 50:50 ratio, the resonances attributed to the minor isomer are marked with an asterisk.] Infrared spectra were recorded on a Perkin-Elmer 283 instrument using KBr solution cells. Mass spectra were obtained with a double-focusing VG ZAB-E mass spectrometer under positive ion fast atom bombardment (FAB+) and negative ion fast atom bombardment (FAB−) conditions. 3-Nitrobenzyl alcohol was used as the matrix, and xenon was the bombarding species (8 keV). Microanalytical data are from Guelph Chemical Laboratories, Guelph, Ontario.

[(OC)$_3$CoCo(CO)$_3$][HC≡CCH$_2$OH], 3. A solution of Co$_2$(CO)$_8$ (13.812 g, 40.39 mmol) and propargyl alcohol (2.4 cm^3, 41.23 mmol) in THF (100 cm^3) was stirred for 1 h at room temperature under an atmosphere of N$_2$. After the solvent was removed, the cluster **3** was obtained in approximately 83% yield by recrystallization from hexane.

[(OC)$_3$CoCo(CO)$_3$][HC≡CCH$_2$O-menthyl], 4. A solution of [Co$_2$(CO)$_6$][HC≡CCH$_2$OH] (**3**, 0.568 g, 1.66 mmol), (1*R*,2*S*,5*R*)-(−)-menthol (0.478 g, 3.06 mmol), and HBF$_4$·Et$_2$O (4 drops) in CH$_2$Cl$_2$ (30 cm^3) was stirred under N$_2$ in the presence of an activated 4-Å molecular sieve for 0.5 h. The solution was filtered to separate off the molecular sieve. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, hexane) yield **4** (R_f 0.22) as a red–orange oil (0.606 g, 1.26 mmol, 75.9%). ^{1}H NMR (C$_6$D$_6$): δ 5.50 (s, 1 H); 4.44 (d, 1 H); 4.14 (d, 1 H); 3.01 (m, 1 H); 2.42 (m, 1 H); 1.92 (d, 1 H); 1.50 (d, 1 H); 1.30 (m, 1 H); 1.14 (m, 1 H); 0.96 (d, 3 H); 0.92 (m, 1 H); 0.84 (overlapping peaks, 8 H), 0.75 (m, 1 H). ^{13}C NMR (C$_6$D$_6$): δ 199.9 (carbonyls); 93.5 (alkyne quaternary *C*); 79.2 (*C*-1); 71.1 (alkyne *C*H); 68.0 (*C*H$_2$O); 48.3 (*C*-2); 40.2 (*C*-6); 34.5 (*C*-4); 31.5 (*C*-5); 25.6 (*C*-7); 23.3 (*C*-3); 22.2 (*C*-8); 20.9 (*C*-10), 16.2 (*C*-9). IR (CH$_2$Cl$_2$): ν_{CO} 2090 (m), 2050 (s), 2020 (vs) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 480 (10) ((M)$^+$, C$_{19}$H$_{22}$O$_7$Co$_2$); 452 (20) (M − CO)$^+$; 424 (38) (M − 2CO)$^+$; 396 (100) (M − 3CO)$^+$; 368 (90) (M − 4CO)$^+$; 340 (16) (M − 5CO)$^+$; 312 (12) (M − 6CO)$^+$; 325 (52) (M − (O–menthyl))$^+$; 297 (67) (M − (O–menthyl) − CO)$^+$; 269 (33) (M − (O–menthyl) − 2CO)$^+$; 241 (25) (M − (O–menthyl) − 3CO)$^+$; 213 (12) (M − (O–menthyl) − 4CO)$^+$. Anal. Calcd for C$_{19}$H$_{22}$O$_7$Co$_2$: C, 47.52; H, 4.62. Found: C, 47.32; H, 4.65.

[(OC)$_3$CoCo(CO)$_3$][HC≡CCH$_2$O-bornyl], 5. A solution of [Co$_2$(CO)$_6$][HC≡CCH$_2$OH] (**3**, 0.685 g, 2.00 mmol), (1*S*)-*endo*-(−)-borneol (0.591 g, 3.83 mmol), and HBF$_4$·Et$_2$O (4 drops) in CH$_2$Cl$_2$ (35 cm^3) was stirred under an atmosphere of N$_2$ in the presence of excess activated 4-Å molecular sieve for 2 h. After filtration to remove the molecular sieve and evaporation of the resultant solution, the crude material was purified by flash chromatography on silica gel (eluent, hexane) to give **5** (R_f 0.30) as a red–orange oil (0.728 g, 1.52 mmol, 76.0%). ^{1}H NMR (C$_6$D$_6$): δ 5.50 (s, 1 H); 4.33 (d, 1 H); 4.22 (d, 1 H); 3.60 (d, 1 H); 2.33 (br, 1 H); 2.03 (br, 1 H); 1.74 (br, 1 H); 1.60 (br, 1 H); 1.34 (m, 2 H); 1.08 (d, 1 H); 0.98 (s, 3 H); 0.83 (s, 3 H), 0.82 (s, 3 H). ^{13}C NMR (C$_6$D$_6$): δ 200.2 (carbonyls); 93.6 (alkyne quaternary *C*); 85.3 (*C*-2); 71.0 (alkyne *C*H); 69.8 (CH$_2$O); 49.7 (*C*-1 or C-7); 48.1 (C-1 or *C*-7); 45.5 (*C*-4); 36.3 (*C*-3); 28.6 (*C*-5); 26.9 (*C*-6); 19.9 (*C*-9); 19.0 (*C*-8); 14.1 (*C*-10). IR (CH$_2$Cl$_2$): ν_{CO} 2085 (m), 2045 (s), 2020 (vs) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 450 (14) ((M − CO)$^+$, C$_{18}$H$_{20}$O$_6$Co$_2$); 422 (15), (M − 2CO)$^+$; 394 (100) (M − 3CO)$^+$; 366 (95) (M − 4CO)$^+$; 338 (36) (M − 5CO)$^+$; 325 (33) (M − (O–bornyl))$^+$; 310 (10) (M − 6CO)$^+$; 297 (56) (M − (O–bornyl) − CO)$^+$; 269 (45) (M − (O–bornyl) − 2CO)$^+$; 241 (48) (M − (O–bornyl) − 3CO)$^+$; 213 (20) (M − (O–bornyl) − 4CO)$^+$. Mass spectra (FAB−): *m/z* (%) 450 (100) (M − CO)$^-$; 421 (32) (M − H − 2CO)–; 394 (20) (M − 3CO)$^-$; 338 (11) (M − 5CO)$^-$. Anal. Calcd for C$_{19}$H$_{20}$O$_7$Co$_2$: C, 47.72; H, 4.22. Found: C, 47.50; H, 4.17.

[(OC)$_3$CoCo(CO)$_3$][CH$_3$C≡C-borneol], 6. A solution of Co$_2$(CO)$_8$ (1.694 g, 4.95 mmol) and *endo*-2-propynylborneol (0.768 g, 4.00 mmol) in THF (40 cm^3) was stirred under a nitrogen atmosphere for 0.5 h. After removal of the solvent, the crude mixture was purified by flash chromatography on silica gel (eluent, hexane) to give **6** (R_f 0.18) as a red solid (1.290 g, 2.70 mmol, 67.5%). ^{1}H NMR (C$_6$D$_6$): δ 2.32 (3 H, alkyne C$_{H3}$); 2.25, 1.41 (2 H, $H_{3\alpha,3\beta}$); 1.71 (1 H, O*H*); 1.62 (1 H, H_4); 1.61, 0.95 (2 H, $H_{6\alpha,6\beta}$); 1.31, 1.23 (2 H, $H_{5\alpha,5\beta}$); 1.19 (3 H, Me_8); 0.91 (3 H, Me_{10}); 0.79 (3 H, Me_9). ^{13}C NMR (C$_6$D$_6$): δ 200.5 (carbonyls); 108.3, 94.2 (alkyne quaternary *C*'s); 82.9 (*C*-2); 55.1 (*C*-1 or *C*-7); 53.0 (*C*-3); 51.2 (*C*-1 or *C*-7); 45.7 (*C*-4); 30.8 (*C*-5); 27.8 (*C*-6); 21.7 (*C*-9); 21.6 (*C*-8); 21.2 (alkyne *C*H$_3$); 10.9 (*C*-10). IR (CH$_2$Cl$_2$): ν_{CO} 2080 (m), 2040 (s), 2020 (s) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 461 (14) ((M − OH)$^+$ C$_{19}$H$_{19}$O$_6$Co$_2$); 450 (45) (M − CO)$^+$; 433 (15) (M − OH − CO)$^+$; 422 (90) (M − 2CO)$^+$; 405 (18) (M − OH − 2CO)$^+$; 394 (100) (M − 3CO)$^+$; 377 (14) (M − OH − 3CO)$^+$; 366 (13) (M − 4CO)$^+$; 338 (55) (M − 5CO)$^+$; 310 (52) (M − 6CO)$^+$; 293 (10) (M − OH − 6CO)$^+$. Mass spectra (FAB−): *m/z* (%) 477 (16) (M − H)$^-$; 450 (100) (M − CO)$^-$; 422 (24) (M − 2CO)$^-$; 393 (9) (M − H 3CO)$^-$; 366 (6) (M − 4CO)$^-$. Anal. Calcd for C$_{19}$H$_{20}$O$_7$Co$_2$: C, 47.72; H, 4.22. Found: C, 47.73; H, 4.12.

Benzophenone Ketyl (BPK). As described by Arewgoda et al.,[14] a solution of benzophenone ketyl can be prepared by refluxing benzophenone in deoxygenated tetrahydrofuran with a slight molar excess of sodium. However, as suggested by the authors,[14] for most of the reactions described herein the BPK solution was simply syringed from a still used to purify THF.

[Ph$_3$P(OC)$_2$CoCo(CO)$_3$][HC≡CCH$_2$O-menthyl], 8. A solution of [(OC$_3$CoCo(CO)$_3$][HC≡CCH$_2$O-menthyl] (4, 0.385 g, 0.80 mmol), triphenylphosphine (0.262 g, 1.00 mmol), and BPK (1.5 cm^3) in THF (35 cm^3) was stirred overnight under an atmosphere of N$_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as a reddish band (R_f 0.32). After the solvent was removed, the crude material was purified by flash chromatography on silica gel (eluent, hexane) to give 8 as an orange–red solid (0.475 g, 0.66 mmol, 82.5%) containing an approximately 50:50 mixture of the diastereomers. ^{31}P NMR (CD$_2$Cl$_2$): δ 54.2 (single peak). ^{13}C NMR (CD$_2$Cl$_2$): δ 205.9 (2 carbonyls); 202.5 (3 carbonyls); 135.4 (d, ipso *C*'s of phenyl rings, $^{1}J(^{13}C{-}^{31}P)$ = 41.0 Hz); 133.6 (d, ortho *C*'s of phenyl rings, $^{2}J(^{13}C{-}^{31}P)$ = 10.5 Hz); 130.7 (para *C*'s of phenyl rings); 129.0 (d, meta *C*'s of phenyl rings, $^{3}J(^{13}C{-}^{31}P)$ = 9.5 Hz); 90.5 (alkyne quaternary *C*); 79.7 (*C*-1); 72.0 (alkyne *C*H); 68.9, 68.5 (CH$_2$O); 49.1, 48.9 (*C*-2); 41.4, 41.1 (*C*-6); 35.1 (*C*-4); 32.1 (*C*-5); 25.7 (*C*-7); 23.8 (*C*-3); 22.6 (*C*-8); 21.4 (*C*-10); 16.5 (*C*-9). IR (CH$_2$Cl$_2$): ν_{CO} 2050 (m), 2000 (s), 1970 (sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 630 (6) ((M − 3CO)$^+$, C$_{33}$H$_{37}$O$_3$PCo$_2$); 602 (12) (M − 4CO)$^+$; 574 (100) (M − 5CO)$^+$. Mass spectra (FAB−): *m/z* (%) 452 (100) (M − PPh$_3$)$^-$; 423 (30) (M − H − PPh$_3$ CO)$^-$; 396 (12) (M − PPh$_3$ − 2CO)$^-$. Anal. Calcd for C$_{36}$H$_{37}$O$_6$PCo$_2$: C, 60.52; H, 5.22; P, 4.33. Found: C, 60.22; H, 5.41; P, 4.48.

[Cy$_3$P(OC)$_2$CoCo(CO)$_3$][HC≡CCH$_2$O-menthyl], 9. A solution of [(OC)$_3$CoCo(CO)$_3$][HC≡CCH$_2$O-menthyl] (4, 0.358 g, 0.75 mmol), tricyclohexylphosphine (0.266 g, 0.95 mmol), and BPK

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(1.5 cm^3) was stirred in THF (35 cm^3) overnight under an atmosphere of N$_2$. The reaction was monitored by TLC on Kieselgel (eluent, hexane), which showed the formation of the product as an orange–red band (R_f 0.20). The solvent was removed and the crude material purified by flash chromatography on silica gel (eluent, hexane) to give **9** as an orange-red solid (0.228 g, 0.31 mmol, 41.3%) containing an approximately 60:40 mixture of the diastereomers. ^{31}P NMR (C$_6$D$_6$): δ 65.3 (single peak). ^{13}C NMR (C$_6$D$_6$): δ 208.4, 207.21, 202.9 (carbonyls, 1:1:3 ratio); 88.7 (alkyne quaternary *C*); 79.8, *79.5 (*C*-1); 70.3, *69.9 (*C*H$_2$O); 67.9, *68.5 (alkyne *C*H); 49.0 (*C*-2); 41.3 (*C*-6); 37.3 (d, ipso *C*'s of cyclohexyl rings, $^1J(^{13}C-^{31}P)$ = 15.9 Hz); 34.9 (*C*-4); 31.9 (*C*-5); 30.0 (d, α-*C*'s of cyclohexyl rings, $^2J(^{13}C-^{31}P)$ = 14.7 Hz); 27.9 (β-*C*'s of cyclohexyl ring); 26.6 (γ-*C*'s of cyclohexyl rings); 25.8 (*C*-7); 23.7 (*C*-3); 22.6 (*C*-8); 21.3 (*C*-10); 16.6 (*C*-9). IR (CH$_2$Cl$_2$): ν_{CO} 2040 (m), 1995 (s), 1950 (sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 648 (100) ((M – 3CO)$^+$, C$_{33}$H$_{55}$O$_3$PCo$_2$); 538 (22) (Co$_2$(CO)$_5$PCy$_3$)$^+$. (FAB–): *m/z* (%) 537 (5) ((Co$_2$(CO)$_5$PCy$_3$) – H)$^-$; 452 (100) (M – PCy$_3$)$^-$; 423 (65) (M – H – PCy$_3$ – CO)$^-$; 396 (23) (M –PCy$_3$ – 2CO)$^-$. Anal. Calcd for C$_{36}$H$_{55}$O$_6$PCo$_2$: C, 59.02; H, 7.57; P, 4.23. Found: C, 58.69; H, 7.72; P, 4.12.

[Ph$_3$P(CO)$_2$CoCo(CO)$_3$][HC$\equiv$CCH$_2$O-bornyl], 10. A solution of [(OC)$_3$CoCo(CO)$_3$][HC$\equiv$CCH$_2$O-bornyl] (**5**, 0.499 g, 1.04 mmol), triphenylphosphine (0.273 g, 1.04 mmol), and BPK (1.5 cm^3) was stirred in THF (30 cm^3) under an atmosphere of N$_2$. The reaction was monitored by TLC on Kieselgel (eluent, hexane), and the formation of the product as an orange–red band (R_f 0.17) was detected. After the mixture was stirred overnight, the solvent was removed and the residue purified by flash chromatography on silica gel (eluent, hexane) to yield **10** as an orange–red solid (0.409 g, 0.57 mmol, 54.8%) containing an approximately 50:50 mixture of the diastereomers. ^{31}P NMR (CD$_2$Cl$_2$): δ 54.4 (single peak). ^{13}C NMR (CDCl$_3$): δ 205.7, 205.5, 201.8 (carbonyls, 1:1:3 ratio); 135.0 (d, ipso *C*'s of phenyl rings, $^1J(^{13}C-^{31}P)$ = 40.9 Hz); 133.0 (d, ortho *C*'s of phenyl rings, $^2J(^{13}C-^{31}P)$ = 10.9 Hz); 130.1 (para *C*'s of phenyl rings); 128.2 (d, meta *C*'s of phenyl rings, $^3J(^{13}C-^{31}P)$ = 9.5 Hz); 90.3, 89.9 (alkyne quaternary *C*); 84.9, 84.5 (*C*-2); 70.8, 70.3 (*C*H$_2$); 69.8, 69.4 (alkyne *C*H); 49.4 (*C*-1 or *C*-7); 47.9, 47.4 (*C*-1 or *C*-7); 45.2 (*C*-4); 36.2, 35.9 (*C*-3); 28.2 (*C*-5); 26.9 (*C*-6); 19.8 (*C*-9); 18.9 (*C*-8); 14.0 (*C*-10). IR (CH$_2$Cl$_2$): ν_{CO} 2050 (m), 2000 (s), 1970 (sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 656 (4) ((M – 2CO)$^+$, C$_{34}$H$_{35}$O$_4$PCo$_2$); 628 (13) (M – 3CO)$^+$; 600 (24) (M – 4CO)$^+$; 572 (100) (M – 5CO)$^+$. Mass spectra (FAB–): 450 (100) (M – PPh$_3$)$^-$; 421 (29) (M – H – PPh$_3$ – CO); 394 (13) (M – PPh$_3$ – 2CO)$^-$. Anal. Calcd for C$_{36}$H$_{35}$O$_6$PCo$_2$: C, 60.69; H, 4.95; P, 4.35. Found: C, 60.98; H, 5.27; P, 4.13.

[Cy$_3$P(OC)$_2$CoCo(CO)$_3$][HC$\equiv$CCH$_2$O-bornyl], 11. A solution of [(OC)$_3$CoCo(CO)$_3$][HC$\equiv$CCH$_2$O-bornyl] (**5**, 0.377 g, 0.79 mmol), tricyclohexylphosphine (0.331 g, 1.18 mmol), and BPK (1.5 cm^3) in THF (35 cm^3) was stirred under an atmosphere of N$_2$. The reaction was monitored by TLC on Kieselgel (eluent, hexane), which showed the formation of the product as an orange–red band (R_f 0.20). After further stirring of the mixture overnight, the solvent was removed and the residue purified by flash chromatography on silica gel (eluent, hexane) to yield **11** as an orange–red solid (0.287 g, 0.39 mmol, 49.4%) containing an approximately 60:40 mixture of the diastereomers. ^{31}P NMR (C$_6$D$_6$): δ 65.6 (single peak). ^{13}C NMR (C$_6$D$_6$): δ 208.3, 207.1, 203.0 (carbonyls, 1:1:3 ratio); 88.9, *88.6 (alkyne quaternary *C*); 85.2, *85.5 (*C*-2); 71.4, *71.8 (*C*H$_2$); 67.1, *67.4 (alkyne *C*H); 49.9 (*C*-1 or *C*-7); 48.0 (*C*-1 or *C*-7); 45.7 (*C*-4); 37.2 (d, ipso *C*'s of cyclohexyl rings, $^1J(^{13}C-^{31}P)$ = 16.4 Hz); 36.5, *36.7 (*C*-3); 29.9 (d, α-*C*'s of cyclohexyl rings, $^2J(^{13}C-^{31}P)$ = 17.0 Hz); 28.7 (*C*-5); 27.8 (d, β-*C*'s of cyclohexyl rings, $^3J(^{13}C-^{31}P)$ = 9.3 Hz); 27.1 (*C*-6); 26.5 (γ-*C*'s of cyclohexyl rings); 19.9 (*C*-9); 19.1 (*C*-8); 14.3 (*C*-10). IR (CH$_2$Cl$_2$): ν_{CO} 2045 (m), 2000 (s), 1950 (sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 730 (7) ((M)$^+$, C$_{36}$H$_{53}$O$_6$PCo$_2$); 702 (25) (M – CO)$^+$: 675 (5) (M + H – 2CO)$^+$; 646 (100) (M – 3CO)$^+$; 577 (14) (M – (O-bornyl))$^+$: 549 (11) (M – (O-bornyl) – CO)$^+$; 493 (11) (M – (O-bornyl) – 3CO)$^+$. Mass spectra (FAB–): *m/z* (%) 450 (100) (M – PCy$_3$)$^-$; 421 (44) (M – H – PCy$_3$ – CO)$^-$. Anal. Calcd for C$_{36}$H$_{53}$O$_6$PCo$_2$: C, 59.18; H, 7.31; P, 4.24. Found: C, 59.71; H, 7.43, P, 4.15.

[(dppm)((OC)$_2$CoCo(CO)$_2$)][HC$\equiv$CCH$_2$O-menthyl], 12. A solution of [(OC)$_3$CoCo(CO)$_3$][HC$\equiv$CCH$_2$O-menthyl] (**4**, 0.408 g, 0.85 mmol) and dppm (0.461 g, 1.20 mmol) in hexane (30 cm^3) was stirred at reflux under an atmosphere of N$_2$ for 2.5 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 10/90), which showed the formation of the product as an orange–red band (R_f 0.31). After cooling to room temperature and removal of the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/hexane, 3/97) to give **12** as an orange oily material (0.596 g, 0.74 mmol, 87.0%). ^{31}P NMR (CD$_2$Cl$_2$): δ 42.0 (single peak). ^{13}C NMR (CD$_2$Cl$_2$): δ 207.4, 204.6 (carbonyls, 2:2 ratio); 137.5 (d, ipso *C*'s of phenyl rings, $^1J(^{13}C-^{31}P)$ = 20.4 Hz); 132.3 (d, ortho *C*'s of phenyl rings, $^2J(^{13}C-^{31}P)$ = 5.7 Hz); 129.9 (para *C*'s of phenyl rings); 128.7 (d, meta *C*'s of phenyl rings, $^3J(^{13}C-^{31}P)$ = 4.1 Hz); 98.6 (alkyne quaternary *C*); 79.8 (*C*-1); 74.4 (alkyne *C*H); 72.0 (*C*H$_2$); 49.1 (*C*-2); 41.6 (t, *C*H$_2$ of dppm, $^1J(^{13}C-^{31}P)$ = 20.8 Hz); 41.3 (*C*-6); 35.3 (*C*-4); 32.2 (*C*-5); 25.9 (*C*-7); 23.9 (*C*-3); 22.7 (*C*-8); 21.4 (*C*-10); 16.6 (*C*-9). IR (CH$_2$Cl$_2$): ν_{CO} 2010 (m), 1995 (s), 1970 (m), 1950 (sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 780 (12) ((M – CO)$^+$, C$_{41}$H$_{44}$O$_4$P$_2$Co$_2$); 724 (35) (M – 3CO)$^+$; 696 (100) (M – 4CO)$^+$; 625 (5) (M – (O-menthyl) – CO)$^+$: 542 (20) (M + H – (O-menthyl) – 4CO)$^+$; 425 (62) (M + H – dppm)$^+$. Mass spectra (FAB–): 807 (100) (M – H)$^-$; 780 (97) (M – CO)$^-$; 752 (10) (M – 2CO)$^-$; 586 (20) (Co$_2$(CO)$_3$dppm)$^-$. Anal. Calcd for C$_{42}$H$_{42}$O$_5$P$_2$Co$_2$: C, 62.39; H, 5.48; P, 7.66. Found: C, 61.34; H, 5.58; P, 7.58.

[(dppm)((OC)$_2$CoCo(CO)$_2$)][HC$\equiv$CCH$_2$O-bornyl], 13. A solution of [(OC)$_3$CoCo(CO)$_3$][HC$\equiv$CCH$_2$O-bornyl] (**5**, 0.589 g, 1.23 mmol) and dppm (0.614 g, 1.60 mmol) in hexane (35 cm^3) was stirred at reflux under an atmosphere of N$_2$ for 6.0 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as an orange–red band (R_f 0.17). After cooling to room temperature and removing the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/hexane, 5/95) to give **13** as an orange–red solid (0.766 g, 0.95 mmol, 77.2%). ^{31}P NMR (CDCl$_3$): δ 42.3 (single peak). ^{13}C NMR (CDCl$_3$): ν 206.8, 203.8 (carbonyls, 2:2 ratio); 137.0 (d, ipso *C*'s of phenyl rings, $^1J(^{13}C-^{31}P)$ = 18.8 Hz); 131.8 (ortho *C*'s of phenyl rings); 129.4 (para *C*'s of phenyl rings); 128.2 (meta *C*'s of phenyl rings); 97.9 (alkyne quaternary *C*); 84.2 (*C*-2); 73.5 (alkyne *C*H); 72.6 (*C*H$_2$); 49.4 (*C*-1 or *C*-7); 47.9 (*C*-1 or *C*-7); 45.2 (*C*-4); 41.4 (t, *C*H$_2$ of dppm, $^1J(^{13}C-^{31}P)$ = 20.3 Hz); 36.2 (*C*-3); 28.3 (*C*-5); 26.7 (*C*-6); 19.9 (*C*-9); 18.9 (*C*-8); 14.1 (*C*-10). IR (CH$_2$Cl$_2$): ν_{CO} 2010 (m), 1995 (s), 1975 (m), 1950 (sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 778 (15) ((M – CO)$^+$, C$_{41}$H$_{42}$O$_4$P$_2$Co$_2$); 722 (40) (M – 3CO)$^+$; 694 (100) (M – 4CO)$^+$; 542 (100) (M + H – (O-bornyl) – 4CO)$^+$; 502 (45) (Co$_2$(dppm))$^+$; 443 (65) (Co(dppm))$^+$; 425 (59) (Co$_2$(dppm) – C$_6$H$_5$)$^+$; 348 (40) (Co$_2$(dppm) – 2C$_6$H$_5$)$^+$. Mass spectra (FAB–): *m/z* % 805 (95) (M – H)$^-$; 778 (100) (M – CO)$^-$; 750 (18) (M – 2CO)$^-$; 721 (7) (M – H – 3CO)$^-$. Anal. Calcd for C$_{42}$H$_{42}$O$_5$P$_2$Co$_2$: C, 62.54; H, 5.25; P, 7.68. Found: C, 62.87; H, 5.42; P, 7.68.

[(dppm)((OC)$_2$CoCo(CO)$_2$)][CH$_3$C$\equiv$C-borneol], 14. A solution of [(OC)$_3$CoCo(CO)$_3$][CH$_3$C$\equiv$C-borneol] (**6**, 0.623 g, 1.30 mmol) and dppm (0.650 g, 1.69 mmol) in hexane (50 cm^3) was stirred at reflux under an atmosphere of N$_2$ for 1.5 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as a red band (R_f 0.15). After cooling the mixture to room temperature and removing the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/hexane, 5/95) to yield **14** as an orange–red solid (0.577 g, 0.72 mmol, 55.4%). ^{31}P NMR (CDCl$_3$): δ 42.1 (d, $^2J(^{31}P-^{31}P)$ = 125 Hz); 40.9 (d, $^2J(^{31}P-^{31}P)$ = 125 Hz). ^{13}C NMR (carbonyls) (CDCl$_3$): δ 207.3, 206.7, 204.3, 203.7 (1:1:1:1 ratio). IR (CH$_2$Cl$_2$): ν_{CO} 2005 (m), 1990 (s), 1965 (m), 1940 (sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 789 (3) ((M – OH)$^+$, C$_{42}$H$_{41}$O$_4$P$_2$Co$_2$); 778 (11) (M – CO)$^+$; 761 (5) (M – OH – CO)$^+$; 732 (3) (M – H$_2$O – 2CO)$^+$; 722 (16) (M – 3CO)$^+$; 704 (9) (M – H$_2$O – 3CO)$^+$; 694 (11) (M – 4CO)$^+$; 676 (100) (M – H$_2$O – 4CO)$^+$; 502 (33) (Co$_2$(dppm)$^+$; 425 (30) (Co$_2$(dppm)$^+$; 348 (27) (Co$_2$(dppm) – 2C$_6$H$_5$)$^+$. Mass spectra (FAB–): *m/z* (%) 805 (100) (M – H)$^-$; 778 (74) (M – CO)$^-$; 586 (30) (Co$_2$(CO)$_3$dppm)$^-$; 393 (26) (M – CO – dppm – H)$^-$. Anal. Calcd for C$_{42}$H$_{42}$O$_5$P$_2$Co$_2$: C, 62.54; H, 5.25; P, 7.68. Found: C, 62.54; H, 6.17; P, 7.53.

[Ph$_3$P(OC)$_2$CoCo(CO)$_3$][CH$_3$C$\equiv$C-borneol], 15. A solution of [(OC)$_3$CoCo(CO)$_3$][CH$_3$C$\equiv$C-borneol] (**6**, 0.453 g, 0.95 mmol), triphenylphosphine (0.248 g, 0.95 mmol), and BPK (1.5 cm^3) in THF (35 cm^3) was stirred overnight under an atmosphere of N$_2$. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as a red band (R_f 0.27). The solvent was removed and the residue purified by flash chromatography on silia gel (eluent, ether/hexane, 1/99) to yield **15** as a red oily material (0.132 g, 0.19 mmol, 20.0%) containing an approximately 50:50 mixture of the diastereomers. ^{31}P NMR ($CDCl_3$): δ 48.8, 44.2 (1:1 ratio). ^{13}C NMR (carbonyls) ($CDCl_3$): 205.4, 201.5 (2:3 ratio). IR (CH_2Cl_2): ν_{CO} 2040 (m), 2000 (s), 1995 (s), 1960 (sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 695 (2) ((M − OH)$^+$, $C_{36}H_{34}O_5PCo_2$); 684 (2) (M − CO)$^+$; 667 (2) (M − OH − CO)$^+$; 656 (19) (M − 2CO)$^+$; 639 (6) (M − OH − 2CO)$^+$; 628 (2) (M − 3CO)$^+$; 600 (100) (M − 4CO)$^+$; 572 (78) (M − 5CO)$^+$; 554 (13) (M − H_2O − 5CO)$^+$. Mass spectra (FAB−): *m/z* (%) 711 (5) (M − H)$^-$; 450 (100) (M − PPh_3)$^-$; 422 (30) (M − PPh_3 − CO)$^-$; 393 (11) (M − PPh_3 − 2CO − H)$^-$; 258 (44) ($Co_2(CO)_5$)$^-$. Anal. Calcd for $C_{36}H_{35}O_6PCo_2$: C, 60.69; H, 4.95; P, 4.34. Found: C, 58.03; H, 5.12; P, 4.64.

$(C_5H_4R)M(CO)_3^-Na^+$ (R = H, CH_3; M = Mo, W). To a solution of $[(C_5H_4R)M(CO)_3]_2$ (1.0 mmol) in THF (25 cm^3) was added an excess of finely divided Na metal. The mixture was stirred at room temperature under an atmosphere of N_2 until the solution lost the red color associated with the presence of the dimer and took on the yellow color of the anion. Filtration under N_2 to remove any solid present gave a clear solution of the anion, which was then used in subsequent reactions.

$[(C_5H_5)Mo(CO)_2Co(CO)_3][HC{\equiv}CCH_2OH]$, 16. A solution of $(C_5H_5)Mo(CO)_3^-Na^+$ (prepared as described above) and $[Co_2(CO)_6][HC{\equiv}CCH_2OH]$ (**3**, 0.342 g, 1.0 mmol) in THF (25 cm^3) was stirred at reflux for 30 min under an atmosphere of N_2. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 35/65), which showed the formation of the product as an orange band (R_f 0.14). Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 35/65) yielded the product **16** as an orange-red solid (0.326 g, 0.78 mmol, 78.4%). ^1H NMR (C_6D_6): δ 5.58 (s, 1 H, alkyne CH), 5.35 (s, 5 H, Cp ring H's), 4.71 (m, 2 H, CH_2), 1.46 (br, 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 225.1 (molybdenum carbonyls), 203.0 (cobalt carbonyls), 90.4 (Cp ring *C*H's), 74.5 (alkyne CH), 66.5 (CH_2) (Note: Despite running the sample in a variety of solvents, the alkyne quaternary carbonyl was not found). IR (CH_2Cl_2): ν_{CO} 2050 (m), 1990 (s), 1950 (br, sh), 1890 (br, sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 418 (27) ((M)$^+$, $C_{13}H_9O_6MoCo$; 401 (16) (M − OH)$^+$; 390 (73) (M − CO)$^+$; 373 (35) (M − OH − CO)$^+$; 362 (100) (M − 2CO)$^+$; 334 (40) (M − 3CO)$^+$; 317 (13) (M − OH − 3CO)$^+$; 306 (31) (M − 4CO)$^+$; 278 (40) (M − 5CO)$^+$. Anal. Calcd for $C_{13}H_9O_6MoCo$: C, 37.53; H, 2.18. Found: C, 37.85; H, 2.39.

$[(CH_3C_5H_4)W(CO)_2Co(CO)_3][HC{\equiv}CCH_2OH]$, 17. A solution of $(CH_3C_5H_4)W(CO)_3^-Na^+$ and $[Co_2(CO)_6][HC{\equiv}CCH_2OH]$ (**3**, 0.513 g, 1.50 mmol) in THF (35 cm^3) was stirred at reflux for 30 min under N_2. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 50/50), which showed the formation of the product as an orange spot (R_f 0.22). Removal of the solvent and purification of the residue by flash chromatography on silica gel (eluent, ether/hexane, 30/70) yielded the product **17** as a burnt-orange solid (0.451 g, 0.87 mmol, 58.0%). ^1H NMR ($CDCl_3$): δ 5.35 (s, 1 H, alkyne CH), 5.27 (br, 4 H, Cp ring H's), 4.90 (m, 2 H, CH_2), 2.16 (s, 3 H, Cp ring CH_3), 1.43 (m, 1 H, OH). ^{13}C NMR ($CDCl_3$): δ 212.6, 212.3 (tungsten carbonyls, 1:1 ratio); 202.0 (cobalt carbonyls); 106.0 (Cp ring quaternary C), 89.7, 88.4, 88.0, 87.7 (Cp ring *C*H's); 84.6 (alkyne quaternary *C*); 67.8 (alkyne CH); 66.4 (CH_2); 14.0 (Cp ring CH_3). IR (CH_2Cl_2): ν_{CO} 2040 (m), 2000 (s), 1980 (s), 1940 (br, sh), 1880 (br, sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 518 (23) ((M)$^+$, $C_{14}H_{11}O_6CoW$; 501 (18) (M − OH)$^+$; 490 (45) (M − CO)$^+$; 477 (28) (M − OH − CO)$^+$; 462 (100) (M − 2CO)$^+$; 445 (13) (M − OH − 2CO)$^+$; 434 (42) (M − 3CO)$^+$; 417 (9) (M − OH − 3CO)$^+$; 406 (33) (M − 4CO)$^+$; 389 (12) (M − OH − 4CO)$^+$; 378 (31) (M − 5CO)$^+$; 361 (12) (M − OH − 5CO)$^+$. Anal. Calcd for $C_{14}H_{11}O_6WCo$: C, 32.46; H, 2.14. Found: C, 32.78; H, 2.24.

$[(C_5H_4CH_3)Mo(CO)_2Co(CO)_3][HC{\equiv}CCH_2OH]$, 18. A solution of $(CH_3C_5H_4)Mo(CO)_3^-Na^+$ and $[Co_2(CO)_6][HC{\equiv}CCH_2OH]$ (**3**, 0.622 g, 1.82 mmol) in THF (30 cm^3) was stirred at reflux for 30 min under an atmosphere of N_2. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 30/70), and the formation of the product as an orange band (R_f 0.16) was observed. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 25/75) yielded the product **18** as a red oily solid (0.384 g, 0.89 mmol, 48.9%). ^{13}C NMR (C_6D_6): δ 226.5, 226.4 (molybdenum carbonyls, 1:1 ratio); 204.3 (cobalt carbonyls); 108.4 (Cp ring quaternary *C*); 91.3, 90.3, 90.2, 89.8 (Cp ring *C*H's); 75.6 (alkyne *C*H); 66.1 (CH_2); 13.7 (Cp ring CH_3) (Note: alkyne quaternary C not located). IR (CH_2Cl_2): ν_{CO} 2040 (m), 1990 (s), 1945 (br, sh), 1890 (br, sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 432 (12) ((M)$^+$, $C_{14}H_{11}O_6CoMo$; 415 (16) (M − OH)$^+$; 404 (38) (M − CO)$^+$; 387 (48) (M − OH − CO)$^+$; 376 (100) (M − 2CO)$^+$; 359 (40) (M − OH − 2CO)$^+$; 348 (66) (M − 3CO)$^+$; 331 (24) (M − OH − 3CO)$^+$; 320 (40) (M − 4CO)$^+$; 303 (25) (M − OH − 4CO)$^+$; 292 (49) (M − 5CO)$^+$; 275 (30) (M − OH − 5CO)$^+$. Mass spectra (FAB−): *m/z* (%) 431 (78) (M − H)$^-$; 387 (45) (M − OH − CO)$^-$; 401 (100) (M − CH_2OH)$^-$; 359 (28) (M − OH − 2CO)$^-$; 373 (60) (M − CH_2OH − CO)$^-$; 331 (34) (M − OH − 3CO)$^-$. Anal. Calcd for $C_{14}H_{11}O_6MoCo$: C, 39.10; H, 2.58. Found: C, 38.47; H, 2.60.

$[(C_5H_5)Mo(CO)_2Co(CO)_3][HC{\equiv}CCH_2O\text{-menthyl}]$, 19. Method 1. A solution of $[(C_5H_5)Mo(CO)_2Co(CO)_3][HC{\equiv}CCH_2OH]$ (**16**, 0.262 g, 0.63 mmol), (1*R*,2*S*,5*R*)-(−)-menthol (0.196 g, 1.26 mmol), and a small amount of pTsOH (50 mg) in CH_2Cl_2 (25 cm^3) was stirred under N_2 in the presence of excess activated 4-Å molecular sieve for 18 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 15/85), which showed the formation of the product as a red band (R_f 0.50). After the solution was filtered to remove the molecular sieve and the solvent was evaporated, flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 15/85) yielded **19** as a red-orange oil (0.240 g, 0.43 mmol, 63.0%) containing a 50:50 mixture of the diastereomers. Method 2. A solution of $(C_5H_5)Mo(CO)_3^-Na^+$ and $[(OC)_3CoCo(CO)_3][HC{\equiv}CCH_2O\text{-menthyl}]$ (**4**, 0.20 g, 0.42 mmol) in THF (25 cm^3) was stirred at reflux for 1.0 h under an N_2 atmosphere. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded the product **19** as a red-orange oil (0.187 g, 0.34 mmol, 81.0%) containing an approximately 55:45 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 90.5 (Cp ring *C*H's); 89.4 (alkyne quanternary *C*); 79.2 (*C*-1); 74.2, *74.7 (alkyne *C*H); 71.9, *71.6 (CH_2); 48.8 (*C*-2); 40.7 (*C*-6); 34.8 (*C*-4); 31.8 (*C*-5); 25.9 (*C*-7); 23.6 (*C*-3); 22.6 (*C*-8); 21.3 (*C*-10), 16.5 (*C*-9). IR (CH_2Cl_2): ν_{CO} 2040 (m), 1990 (s), 1940 (br, sh), 1880 (br, sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 500 (34) ((M − 2CO)$^+$, $C_{21}H_{27}O_4CoMo$); 472 (100) (M − 3CO)$^+$; 444 (5) (M − 4CO)$^+$; 416 (12) (M − 5CO)$^+$; 401 (8) (M − (O-menthyl))$^+$. Anal. Calcd for $C_{23}H_{27}O_6CoMo$: C, 49.83; H, 4.91. Found: C, 49.59; H, 4.68.

$[(CH_3C_5H_4)W(CO)_2Co(CO)_3][HC{\equiv}CCH_2O\text{-menthyl}]$, 20. Method 1. A solution of $[(CH_3C_5H_4)W(CO)_2Co(CO)_3][HC{\equiv}CCH_2OH]$ (**17**, 0.473 g 0.91 mmol), (1*R*,2*S*,5*R*)-(−)-menthol (0.354 g, 2.27 mmol) and a small amount of $HBF_4{\cdot}Et_2O$ (6 drops) in CH_2Cl_2 (30 cm^3) was stirred in the presence of activated 4-Å molecular sieve under an atmosphere of N_2 for 18 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as an orange-red band (R_f 0.30). The solution was filtered to remove the molecular sieve, and the solvent was evaporated. Flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 2/98) yielded **20** as an orange-red oil (0.112 g, 0.17 mmol, 18.7%) containing a 50:50 mixture of the diastereomers. Method 2. A solution of $(C_5H_4CH_3)W(CO)_3^-Na^+$ and $[(OC)_3CoCo(CO)_3][HC{\equiv}CCH_2O\text{-menthyl}]$ (**4**, 0.600 g, 1.25 mmol) in THF (30 cm^3) under an atmosphere of N_2 was stirred at reflux for 1.0 h. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded the product **20** as an orange-red oil (0.473 g, 0.72 mmol, 57.6%) containing an approximately 55:45 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 213.6, 213.4 (tungsten carbonyls, 1:1 ratio); 202.9 (cobalt carbonyls); 105.6 (Cp ring quaternary *C*); 89.8, 89.3, 88.7, 88.2, 87.7, 87.4 (Cp ring *C*H's); 83.6 (alkyne quaternary *C*); 79.2, *79.1 (*C*-1); 72.0, *71.5 (CH_2); 67.8 (alkyne *C*H); 48.9, *48.7 (*C*-2); 40.8 (*C*-6); 34.8 (*C*-4); 31.8 (*C*-5); 25.8 (*C*-7); 23.6 (*C*-3); 22.6 (*C*-8); 21.3 (*C*-10); 16.5 (*C*-9); 13.5 (Cp ring CH_3). IR (CH_2Cl_2): ν_{CO} 2035 (m) 1995 (s), 1980 (s), 1940 (br, sh), 1870 (br, sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 600 (29) ((M − 2CO)$^+$, $C_{22}H_{29}O_4CoW$; 572 (100) (M − 3CO)$^+$; 544 (9) (M − 4CO)$^+$; 516 (20) (M − 5CO)$^+$; 501 (4) (M − (O-menthyl))$^+$; 473 (15) (M − (O-menthyl) − CO)$^+$; 445 (12) (M − (O-menthyl) − 2CO)$^+$. Mass spectra (FAB−): 655 (8) (M − H)$^-$; 627 (100) (M − H − CO)$^-$; 600 (28) (M

$-$ 2CO)$^-$. Anal. Calcd for $C_{24}H_{29}O_6CoW$: C, 43.92, H, 4.45. Found: C, 44.01; H, 4.05.

$[(C_5H_4CH_3)Mo(CO)_2Co(CO)_3][HC\equiv CCH_2O$-menthyl], 21. Method 1. A solution of $[(C_5H_4CH_3)Mo(CO)_2Co(CO)_3][HC\equiv C$-$CH_2OH]$ (**18**, 0.262 g, 0.61 mmol), (1*R*,2*S*,5*R*)-(−)-menthol (0.302 g, 1.93 mmol) and $HBF_4{\cdot}Et_2O$ (6 drops) in CH_2Cl_2 (35 cm^3) was stirred overnight under N_2 in the presence of an excess of activated 4-Å molecular sieve. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as a red band (R_f 0.42). The solution was filtered to remove the molecular sieve. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 3/97) yielded **21** as a red oil (0.126 g, 0.22 mmol, 36.1%) containing a 50:50 mixture of the diastereomers. Method 2. A solution of $(C_5H_4CH_3)Mo(CO)_3{}^-Na^+$ and $[(OC)_3CoCo(CO)_3][HC\equiv CCH_2O$-menthyl] (**4**, 0.417 g, 0.87 mmol) in THF (30 cm^3) was stirred at reflux for 1.0 h under N_2. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, hexane) yielded the product **21** as a red oil (0.436 g, 0.77 mmol, 88.5%) containing an approximately 55:45 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 226.9, 226.5 (molybdenum carbonyls, 1:1 ratio); 204.3 (cobalt carbonyls); 108.3 (Cp ring quaternary *C*); 91.6, 91.3, 90.8, 90.5, 90.4, 89.9, 89.6 (Cp ring *C*H's); 89.4 (alkyne quaternary *C*); 79.2, *79.1 (*C*-1); 75.4, *75.2 (alkyne *C*H); 71.8, *71.3 (*C*H$_2$); 48.8, *48.6 (*C*-2); 40.7 (*C*-6); 34.8 (*C*-4); 31.8 (*C*-5); 25.7 (*C*-7); 23.5 (*C*-3); 21.5 (*C*-8); 21.3 (*C*-10); 16.5 (*C*-9); 13.8 (Cp ring *C*H$_3$). IR (CH_2Cl_2): ν_{CO} 2040 (m), 1990 (s), 1940 (br, sh), 1885 (br, sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 542 (10) ((M − CO)$^+$, $C_{23}H_{29}O_5CoMo$); 514 (30) (M − 2CO)$^+$; 486 (100) (M − 3CO)$^+$; 458 (8) (M − 4CO)$^+$; 430 (18) (M − 5CO)$^+$. Anal. Calcd for $C_{24}H_{29}O_6CoMo$: C, 50.72, H, 5.14. Found: C, 50.62; H, 5.38.

$[(C_5H_5)Mo(CO)_2Co(CO)_3][HC\equiv CCH_2O$-bornyl], 22. Method 1. A solution of $[(C_5H_5)Mo(CO)_2Co(CO)_3][HC\equiv CCH_2OH]$ (**16**, 0.365 g, 0.88 mmol), (1*S*)-*endo*-(−)-borneol (0.403 g, 2.61 mmol), and pTsOH (50 mg) in CH_2Cl_2 (25 cm^3) was stirred under an atmosphere of N_2 in the presence of excess activated 4-Å molecular sieve for 18 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as a red spot (R_f 0.41). The solution was filtered to remove the molecular sieve. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded **22** as a red oil (0.334 g, 0.61 mmol, 69.3%) containing a 50:50 mixture of the diastereomers. Method 2. A solution of $(C_5H_5)Mo(CO)_3{}^-Na^+$ and $[(OC)_3CoCo(CO)_3][HC\equiv CCH_2O$-bornyl] (**5**, 0.300 g, 0.63 mmol) in THF (25 cm^3) was stirred at reflux for 1.0 h under N_2. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded the product **22** as a red oil (0.224 g, 0.41 mmol, 64.4%) containing an approximately 55:45 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 225.9, 225.8, 225.7, 225.6 (molybdenum carbonyls, 1:1:1:1 ratio); 204.4 (cobalt carbonyls); 90.4 (Cp ring *C*H's); 88.9 (alkyne quaternary *C*); 85.0, *85.1 (*C*-2); 74.5, *74.3 (alkyne *C*H); 73.5 (*C*H$_2$); 49.6 (*C*-1 or *C*-7); 48.0 (*C*-1 or *C*-7); 45.5 (*C*-4); 36.4 *36.3 (*C*-3); 28.6, *28.5 (*C*-5); 27.0 (*C*-6); 19.9 (*C*-9); 19.0 (*C*-8); 14.3, *14.1 (*C*-10). IR (CH_2Cl_2): ν_{CO} 2050 (m), 1985 (s), 1945 (br, sh), 1885 (br, sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 554 (6) ((M)$^+$, $C_{23}H_{25}O_6MoCo$); 498 (56) (M − 2CO)$^+$; 470 (100) (M − 3CO)$^+$; 442 (18) (M − 4CO)$^+$; 414 (12) (M − 5CO)$^+$; 401 (10) (M − (O–bornyl))$^+$; 373 (22) (M − (O–bornyl) − CO)$^+$; 345 (20) (M − (O–bornyl) − 2CO)$^+$. Mass spectra (FAB−): *m/z* (%) 553 (10) (M − H)$^-$; 525 (100) (M − H − CO)$^-$; 497 (35) (M − H − 2CO)$^-$. Anal. Calcd for $C_{23}H_{25}O_6CoMo$: C, 50.02; H, 4.56. Found: C, 49.59; H, 4.73.

$[(C_5H_4CH_3)W(CO)_2Co(CO)_3][HC\equiv CCH_2O$-bornyl], 23. Method 1. A solution of $[(C_5H_4CH_3)W(CO)_2Co(CO)_3][HC\equiv CCH_2OH]$ (**17**, 0.451 g, 0.87 mmol), (1*S*)-*endo*-(−)-borneol (0.402 g, 2.61 mmol), and $HBF_4{\cdot}Et_2O$ (4 drops) in CH_2Cl_2 (30 cm^3) was stirred under an atmosphere of N_2 in the presence of activated 4-Å molecular sieve overnight. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 6/94), which showed the formation of the product as a red spot (R_f 0.47). The solution was filtered to remove the molecular sieve, and then the solvent was evaporated. Flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 1/99) yielded **23** as an orange–red oil (0.089 g, 0.14 mmol, 16.1%) containing a 50:50 mixture of the diastereomers. Method 2. A solution of $(C_5H_4CH_3)W(CO)_3{}^-Na^+$ and $[(OC)_3CoCo(CO)_3][HC\equiv CCH_2O$-bornyl] (**5**, 0.609 g, 1.27 mmol) in THF (35 cm^3) under N_2 was stirred at reflux for 1.0 h. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, hexane) yielded the product **23** as an orange–red oil (0.552 g, 0.84 mmol, 66.9%) containing an approximately 55:45 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 213.4, 212.9 (tungsten carbonyls, 1:1 ratio); 203.0 (cobalt carbonyls); 105.6 (Cp ring quaternary *C*); 89.6, 88.4, 88.3, 87.8 (Cp ring *C*H's); 85.1, *85.2 (*C*-2); 83.1 (alkyne quaternary *C*); 73.6 (*C*H$_2$); 68.1, *68.3 (alkyne *C*H); 49.7 (*C*-1 or *C*-7); 48.0 (*C*-1 or *C*-7); 45.6 (*C*-4); 36.4, *36.5 (*C*-3); 28.6 (*C*-5); 27.1 (*C*-6); 19.9 (*C*-9); 19.0 (*C*-8); 14.3 (*C*-10); 13.5 (Cp ring *C*H$_3$). IR (CH_2Cl_2): ν_{CO} 2040 (m), 1995 (s), 1980 (s), 1940 (br, sh), 1880 (br, sh) cm^{-1}. Mass spectral (FAB+): *m/z* (%) 626 (8) ((M − CO)$^+$, $C_{23}H_{27}O_5CoW$); 598 (40) (M − 2CO)$^+$; 570 (100) (M − 3CO)$^+$; 542 (20) (M − 4CO)$^+$; 514 (24) (M − 5CO)$^+$; 473 (19) (M − (O–bornyl) − CO)$^+$; 445 (15) (M − (O–bornyl) − 2CO)$^+$. Mass spectra (FAB−): *m/z* (%) 653 (15) (M − H)$^-$; 625 (100) (M − H − CO)$^-$; 597 (51) (M − H − 2CO)$^-$; 570 (27) (M − 3CO)$^-$; 542 (15) (M − 4CO)$^-$. Anal. Calcd for $C_{24}H_{27}O_6CoW$: C, 44.06; H, 4.16. Found: C, 44.21; H, 4.38.

$[(C_5H_4CH_3)Mo(CO)_2Co(CO)_3][HC\equiv CCH_2O$-bornyl], 24. Method 1. A solution of $[(C_5H_4CH_3)Mo(CO)_2Co(CO)_3][HC\equiv C$-$CH_2OH]$ (**18**, 0.341 g, 0.79 mmol), (1*S*)-*endo*-(−)-borneol (0.359 g, 2.32 mmol), and a small amount of $HBF_4{\cdot}Et_2O$ (2 drops) in CH_2Cl_2 (30 cm^3) was stirred under N_2 over an excess of activated 4-Å molecular sieve for 1.0 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 3/97) which showed the formation of the product as a red band (R_f 0.30). After the molecular sieve was filtered off and the solvent removed, flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 3/97) yielded **24** as a red oil (0.202 g, 0.36 mmol, 45.6%) containing a 50:50 mixture of the diastereomers. Method 2. A solution of $(C_5H_4CH_3)Mo(CO)_3{}^-Na^+$ and $[(OC)_3CoCo(CO)_3][HC\equiv CCH_2O$-bornyl] (**5**, 0.532 g, 1.11 mmol) in THF (30 cm^3) was stirred at reflux for 1.0 h under an atmosphere of N_2. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, hexane) yielded the product **24** as a red oil (0.342 g, 0.60 mmol, 54.1%) containing an approximately 55:45 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 226.5, 226.4 (molybdenum carbonyls, 1:1 ratio); 204.5 (cobalt carbonyls); 108.2 (Cp ring quaternary *C*); 91.3, 90.4, 89.8 (Cp ring *C*H's); 88.9 (alkyne quaternary *C*); 85.0, *85.2 (*C*-2); 75.2 (alkyne *C*H); 73.4, *73.3 (*C*H$_2$); 49.7 (*C*-1 or *C*-7); 48.0 (*C*-1 or *C*-7); 45.5 (*C*-4); 36.4 (*C*-3); 28.6 (*C*-5); 27.0 (*C*-6); 19.9 (*C*-8); 14.3 (*C*-10); 13.8 (Cp ring *C*H$_3$). IR (CH_2Cl_2): ν_{CO} 2040 (m), 1985 (s), 1940 (br, sh), 1890 (br, sh) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 540 (9) ((M − CO)$^+$, $C_{23}H_{27}O_5CoMo$); 512 (56) (M − 2CO)$^+$; 484 (100) (M − 3CO)$^+$; 456 (18) (M − 4CO)$^+$; 428 (14) (M − 5CO)$^+$; 387 (19) (M − (O–bornyl) − CO)$^+$; 359 (12) (M − (O–bornyl) − CO)$^+$. Anal. Calcd for $C_{24}H_{27}O_6CoMo$: C, 50.90; H, 4.81. Found: C, 50.71; H, 5.05.

$[(C_5H_5)Mo(CO)_2Co(CO)_3][CH_3C\equiv C$-borneol], 25. A solution of $(C_5H_5)Mo(CO)_3{}^-Na^+$ and $[(OC)_3CoCo(CO)_3][CH_3C\equiv C$-borneol] (**6**, 0.629 g, 1.32 mmol) in THF (55 cm^3) was stirred at reflux for 2.0 h under N_2. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as a red band (R_f 0.25). After cooling to room temperature, the reaction mixture was allowed to stir overnight. Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 2/98) yielded the product **25** as a red solid (0.319 g, 0.58 mmol, 43.9%) containing an approximately 65:35 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 227.1, *228.8 (1 molybdenum carbonyl); 225.3, *226.9 (1 molybdenum carbonyl); 204.5 (cobalt carbonyls); 102.2, *102.6 (quaternary *C*); 90.5, *90.7 (Cp ring *C*H's); 85.2, *85.4 (quaternary *C*); 55.3, *56.1 (quaternary *C*); 53.5, *50.9 (*C*-3); 51.5, *51.3 (quaternary *C*); 49.9 (quaternary *C*); 45.9, *45.4 (*C*-4); 33.0 *27.4 (*C*-5 or *C*-6); 30.4, *28.0 (*C*-5 or *C*-6); 22.5, 22.1, 21.6, 21.3 (alkyne *C*H$_3$, *C*-8 and *C*-9); 12.0, *11.4 (*C*-10). IR (CH_2Cl_2): ν_{CO} 2025 (m), 1995 (s), 1980 (br), 1935 (br) cm^{-1}. Mass spectra (FAB+): *m/z* (%) 526 (30) ((M − CO)$^+$, $C_{22}H_{25}O_5CoMo$); 498 (100) (M − 2CO)$^+$; 480 (44) (M − H_2O − 2CO)$^+$; 470 (24) (M − 3CO)$^+$; 452 (95) (M − H_2O − 3CO)$^+$. Mass spectra (FAB−): *m/z* (%) 553 (19) (M − H)$^-$; 526 (12) (M − CO)$^-$; 373 (13) (M − borneol − CO)$^-$; 334 (18)

$(CpMoCo(CO)_4)^-$; 306 (100) $(CpMoCo(CO)_3)^-$. Anal. Calcd for $C_{23}H_{25}O_6CoMo$: C, 50.02; H, 4.56. Found: C, 49.57; H, 4.41.

$[(C_5H_5)W(CO)_2Co(CO)_3][CH_3C{\equiv}C\text{-borneol}]$, 26. A solution of $(C_5H_5)W(CO)_3^-Na^+$ and $[(OC)_3CoCo(CO)_3][CH_3C{\equiv}C\text{-borneol}]$ (**6**, 1.371 g, 2.86 mmol) in THF (65 cm^3) under N_2 was stirred at reflux for 3.0 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 5/95), which showed the formation of the product as a red–orange band (R_f 0.07). Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/hexane, 5/95) yielded the product **26** as a red–orange solid (0.280 g, 0.44 mmol, 15.4%) containing an approximately 75:25 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 214.7, *216.4 (1 tungsten carbonyl); 211.4, *213.2 (1 tungsten carbonyl); 204.0 (cobalt carbonyls); 95.7, *96.3 (quaternary *C*); 88.6, *88.9 (Cp ring *C*H's); 84.9, *86.3 (quaternary *C*); 55.3, *55.9 (quaternary *C*); 53.5, *50.7 (*C*-3); 51.5, *51.2 (quaternary *C*); 49.0 (quaternary *C*); 46.0, *45.2 (*C*-4); 30.2, *33.0 (*C*-5); 27.9, *27.4 (*C*-6); 22.2, 22.1, 21.6, 21.3 (alkyne CH_3, *C*-8 and *C*-9); 12.2, *11.4 (*C*-10). IR (CH_2Cl_2): ν_{CO} 2020 (m), 1995 (s), 1975 (br), 1925 (br) cm^{-1}. Mass spectra (FAB+): m/z (%) 640 (3) ($(M)^+$, $C_{23}H_{25}O_6CoW$); 623 (3) $(M - OH)^+$; 612 (12) $(M - CO)^+$; 595 (5) $(M - OH - CO)^+$; 584 (95) $(M - 2CO)^+$; 566 (30) $(M - H_2O - 2CO)^+$; 556 (11) $(M - 3CO)^+$; 538 (95) $(M - H_2O - 3CO)^+$; 528 (38) $(M - 4CO)^+$; 510 (100) $(M - H_2O - 4CO)^+$; 500 (22) $(M - 5CO)^+$; 482 (25) $(M - H_2O - 5CO)^+$. Mass spectra (FAB−): m/z (%) 639 (88) $(M - H)^-$; 612 (78) $(M - CO)^-$; 583 (34) $(M - H - 2CO)^-$; 459 (100) $(M - \text{borneol} - CO)^-$; 431 (26) $(M - \text{borneol} - 2CO)^-$; 420 (83) $(CpWCo(CO)_4)^-$. Anal. Calcd for $C_{23}H_{25}O_6CoW$: C, 43.15, H, 3.94. Found: C, 42.58; H, 4.31.

$[(OC)_3CoCo(CO)_3][HC{\equiv}CCH(OH)Et]$, 27. A solution of $Co_2(CO)_8$ (3.964 g, 11.59 mmol) and 1-pentyn-3-ol (1.0 cm^3, 11.59 mmol) in THF (40 cm^3) was stirred under N_2 for 2 h. After the solvent was removed and the residue extracted with hexane, the cluster **27** was obtained as a reddish oil (3.809 g, 10.29 mmol, 88.8%). ^{1}H NMR ($CDCl_3$): δ 6.06 (s, 1 H); 4.60 (t, 1 H); 1.80 (overlapping multiplets, 3 H); 1.14 (t, 3 H). IR (CH_2Cl_2): ν_{CO} 2090 (m), 2050 (s), 2030 (s) cm^{-1}. Mass spectra (FAB+): m/z (%) 370 (8) ($(M)^+$, $C_{11}H_8O_7Co_2$); 353 (20) $(M - OH)^+$; 342 (65) $(M - CO)^+$; 325 (38) $(M - OH - CO)^+$; 314 (97) $(M - 2CO)^+$; 297 (21) $(M - OH - 2CO)^+$; 286 (100) $(M - 3CO)^+$; 269 (12) $(M - OH - 3CO)^+$; 258 (38) $(M - 4CO)^+$; 241 (23) $(M - OH - 4CO)^+$; 230 (11) $(M - 5CO)^+$; 213 (12) $(M - OH - 5CO)^+$; 202 (14) $(M - 6CO)^+$. Mass spectra (FAB−): m/z (%) 369 (35) $(M - H)^-$; 342 (100) $(M - CO)^-$; 314 (30) $(M - 2CO)^-$; 286 (16) $(M - 3CO)^-$; 258 (20) $(M - 4CO)^-$; 230 (9) $(M - 5CO)^-$.

$[(dppm)((OC)_2CoCo(CO)_2)][HC{\equiv}CCH(OH)Et]$, 28. A solution of $[(OC)_3CoCo(CO)_3][HC{\equiv}CCH(OH)Et]$ (**27**, 0.570 g, 1.54 mmol) and dppm (0.576 g, 1.50 mmol) in hexane (50 cm^3) was stirred at reflux under an atmosphere of N_2 for 1.0 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 15/85), which showed the formation of the product as a blood red band (R_f 0.11). After removing the solvent, the residue was purified by flash chromatography on silica gel (eluent, ether/hexane, 15/85) to give **28** as a red solid (0.369 g, 0.53 mmol, 35.3%). ^{31}P NMR (CH_2Cl_2): δ 43.0 (single peak). ^{13}C NMR (CH_2Cl_2): δ 207.9, 203.9 (carbonyls, 2:2); 136.6 (d, ipso *C*'s of phenyl rings, $^1J(^{13}C{-}^{31}P)$ = 19.9 Hz); 132.0 (d, ortho *C*'s of phenyl rings, $^2J(^{13}C{-}^{31}P)$ = 14.6 Hz); 129.8 (para *C*'s of phenyl rings); 128.4 (meta *C*'s of phenyl rings); 107.2 (alkyne quaternary *C*); 75.6 (*C*H); 73.1 (alkyne *C*H); 41.3 (t, CH_2 of dppm, $^1J(^{13}C{-}^{31}P)$ = 21.5 Hz); 32.7 (CH_2); 10.7 (CH_3). IR (CH_2Cl_2): ν_{CO} 2010 (m), 1995 (s), 1970 (m) cm^{-1}. Mass spectra (FAB+): m/z (%) 681 (2) ($(M - OH)^+$, $C_{34}H_{29}O_4P_2Co_2$); 670 (14) $(M - CO)^+$; 642 (4) $(M - 2CO)^+$; 614 (43) $(M - 3CO)^+$; 586 (65) $(M - 4CO)^+$; 568 (10) $(M - H_2O - 4CO)^+$; 519 (35) $(M - H_2O - 3CO - C_6H_5)^+$; 502 (28) $(Co_2(dppm))^+$; 443 (100) $(M - OH - 3CO - 2C_6H_5)^+$; 425 (30) $(Co_2(dppm) - C_6H_5)^+$; 348 (26) $(Co_2(dppm) - 2C_6H_5)^+$. Mass spectra (FAB−): m/z (%) 697 (95) $(M - H)^-$; 670 (100) $(M - CO)^-$; 641 (20) $(M - H - 2CO)^-$; 586 (14) $(M - 4CO)^-$.

Thermal Reaction of Ph_3P with $[(OC)_3CoCo(CO)_3][HC{\equiv}CCH(OH)Et]$. A THF/$Et_2O$ (40 cm^3/15 cm^3) solution of $[(OC)_3CoCo(CO)_3][HC{\equiv}CCH(OH)Et]$ (**27**, 0.617 g, 1.67 mmol) and triphenylphosphine (0.350 g, 1.34 mmol) was stirred at 50 °C under an atmosphere of N_2 for 5 h. The reaction was monitored by TLC on Kieselgel (eluent, ether/pentane, 20/80), which showed the formation of three products as reddish-orange bands (R_f 0.28, 0.18, 0.10). After cooling to room temperature and allowing the mixture to stir overnight, the solvent was removed and the crude material was purified by flash chromatography on silica gel (eluent, Et_2O/pentane, 20/80). The three bands were collected and subsequently identified as the major monosubstituted diastereomeric product **29a** (0.411 g, 0.68 mmol, 50.8%), the bis(triphenylphosphine)-substituted cluster **30** (0.111 g, 0.13 mmol, 19.9%), and the minor monosubstituted diastereomeric product **29b** (0.201 g, 0.33 mmol, 24.6%). Major diastereomer **29a**. ^{31}P NMR (CH_2Cl_2): δ 54.1 (single peak). ^{13}C NMR (CH_2Cl_2): δ 205.9, 205.3, 201.8 (carbonyls, 1:1:3); 134.3 (d, ipso *C*'s of phenyl rings, $^1J(^{13}C{-}^{31}P)$ = 41.8 Hz); 132.9 (d, ortho *C*'s of phenyl rings, $^2J(^{13}C{-}^{31}P)$ = 11.1 Hz); 130.4 (para *C*'s of phenyl rings); 128.5 (d, meta *C*'s of phenyl rings, $^3J(^{13}C{-}^{31}P)$ = 9.8 Hz); 96.4 (alkyne quaternary *C*); 72.6 (*C*H); 71.7 (alkyne *C*H); 33.3 (CH_2); 10.3 (CH_3). IR (CH_2Cl_2): ν_{CO} 2060 (m), 2005 (s), 1970 (sh) cm^{-1}. Mass spectra (FAB+): m/z (%) 604 (3) ($(M)^+$, $C_{28}H_{23}O_6PCO_2$); 587 (4) $(M - OH)^+$; 576 (2) $(M - CO)^+$; 559 (4) $(M - OH - CO)^+$; 548 (18) $(M - 2CO)^+$; 531 (4) $(M - OH - 2CO)^+$; 520 (35) $(M - 3CO)^+$; 503 (7) $(M - OH - 3CO)^+$; 492 (55) $(M - 4CO)^+$; 475 (6) $(M - OH - 4CO)^+$; 464 (100) $(M - 5CO)^+$; 447 (8) $(M - OH - 5CO)^+$; 397 (60) $(M - H_2O - 4CO - C_6H_5)^+$; 321 (50) $(M - OH - 4CO - 2C_6H_5)^+$. Mass spectra (FAB−): m/z 603 (15) $(M - H)^-$; 342 (100) $(M - PPh_3)^-$; 314 (25) $(M - PPh_3 - CO)^-$; 286 (12) $(M - PPh_3 - 2CO)^-$. Disubstituted cluster **30**. ^{31}P NMR (CH_2Cl_2): δ 51.6, 50.0 (1:1 ratio). ^{13}C NMR (carbonyls) (CH_2Cl_2): δ 207.3 (single resonance). IR (CH_2Cl_2): ν_{CO} 2020 (m), 1990 (w), 1970 (s, br) cm^{-1}. Mass spectra (FAB+): m/z (%) 810 (2) ($(M - CO)^+$, $C_{44}H_{38}O_4P_2Co_2$); 782 (4) $(M - 2CO)^+$; 726 (22) $(M - 4CO)^+$; 642 (10) $(Co_2(PPh_3)_2)^+$; 565 (110) $(Co_2(PPh_3)_2 - C_6H_5)^+$; 520 (8) $(M - PPh_3 - 2CO)^+$; 492 (10) $(M - PPh_3 - 3CO)^+$; 46 (100) $(M - PPh_3 - 4CO)^+$. Mass spectra (FAB−): m/z (%) 837 (15) $(M - H)^-$; 576 (90) $(M - PPh_3)^-$; 314 (100) $(M - 2PPh_3)^-$. Minor diastereomer **29b**. ^{31}P NMR (CH_2Cl_2): δ 53.0 (single peak). ^{13}C NMR (CH_2Cl_2): δ 205.9, 205.2, 201.9 (carbonyls, 1:1:3); 134.5 (d, ipso *C*'s of phenyl rings, $^1J(^{13}C{-}^{31}P)$ = 41.6 Hz); 132.9 (d, ortho *C*'s of phenyl rings, $^2J(^{13}C{-}^{31}P)$ = 11.1 Hz); 130.4 (para *C*'s of phenyl rings); 128.6 (d, meta *C*'s of phenyl rings, $^3J(^{13}C{-}^{31}P)$ = 9.8 Hz); 96.4 (alkyne quaternary *C*); 72.7 (*C*H); 72.4 (alkyne *C*H); 32.3 (CH_2); 10.6 (CH_3). IR (CH_2Cl_2): ν_{CO} 2060 (m), 2005 (s), 1970 (sh) cm^{-1}. Mass spectra (FAB+): m/z (%) 587 (3) ($(M - OH)^+$, $C_{28}H_{22}O_5PCo_2$); 559 (3) $(M - OH - CO)^+$; 548 (15) $(M - 2CO)^+$; 531 (4) $(M - OH - 2CO)^+$; 520 (30) $(M - 3CO)^+$; 503 (6) $(M - OH - 3CO)^+$; 492 (49) $(M - 4CO)^+$; 475 (4) $(M - OH - 4CO)^+$; 464 (100) $(M - 5CO)^+$; 447 (9) $(M - OH - 5CO)^+$; 397 (62) $(M - H_2O - 4CO - C_6H_5)^+$; 321 (48) $(M - OH - 4CO - 2C_6H_5)^+$. Mass spectra (FAB−): m/z (%) 603 (15) $(M - H)^-$; 342 (100) $(M - PPh_3)^-$; 314 (27) $(M - PPh_3 - CO)^-$; 286 (14) $(M - PPh_3 - 2CO)^-$; 258 (11) $(M - PPh_3 - 3CO)^-$.

$[(C_5H_5)Mo(CO)_2Co(CO)_3][HC{\equiv}CCH(OH)Et]$, 31. A solution of $(C_5H_5)Mo(CO)_3^-Na^+$ and $[(OC)_3CoCo(CO)_3][HC{\equiv}CCH(OH)Et]$ (**27**, 0.556 g, 1.50 mmol) in THF (65 cm^3) was stirred at reflux for 0.5 h under an atmosphere of N_2. The reaction was monitored by TLC on Kieselgel (eluent, ether/hexane, 25/75), which showed the formation of the product as a red–orange band (R_f 0.15). Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/pentane, 15/85) yielded the product **31** as a red–orange oily material (0.460 g, 1.04 mmol, 69.3%) containing an approximately 70:30 mixture of the diastereomers. ^{13}C NMR (C_6D_6): δ 226.5, 225.4 (molybdenum carbonyls, 1:1 ratio); 204.6 (cobalt carbonyls); 92.6, *92.2 (alkyne quaternary *C*); 90.3, *90.0 (Cp ring *C*H's); 78.0, *79.2 (alkyne *C*H); 77.0, *77.2 (*C*H); 34.3, *33.1 (CH_2); 11.1 (CH_3). IR (CH_2Cl_2): ν_{CO} 2040 (m), 1990 (s), 1950 (sh), 1885 (sh) cm^{-1}. Mass spectra (FAB+): m/z (%) 446 (17) ($(M)^+$, $C_{15}H_{13}O_6CoMo$); 418 (40) $(M - CO)^+$; 390 (100) $(M - 2CO)^+$; 362 (50) $(M - 3CO)^+$; 334 (45) $(M - 4CO)^+$; 306 (30) $(M - 5CO)^+$; 288 (15) $(M - 5CO - H_2O)^+$. Mass spectra (FAB−): m/z (%) 445 (95) $(M)^-$; 418 (100) $(M - CO)^-$; 389 (40) $(M - H - 2CO)^-$. Anal. Calcd for $C_{15}H_{13}O_6CoMo$: C, 40.57; H, 2.95. Found: C, 40.36; H, 3.03.

$[(C_5H_5)W(CO)_2Co(CO)_3][HC{\equiv}CCH(OH)Et]$, 32. A solution of $(C_5H_5)W(CO)_3^-Na^+$ and $[(OC)_3CoCo(CO)_3][HC{\equiv}CCH(OH)Et]$ (**27**, 0.715 g, 1.93 mmol) in THF (60 cm^3) was stirred at reflux for 1.0 h under an atmosphere of N_2. The reaction was monitored by TLC on Kieselgel (eluent, ether/pentane, 20/80), which showed the formation of the product as a red–orange band (R_f 0.14). Removal of the solvent and flash chromatographic purification of the residue on silica gel (eluent, ether/pentane, 20/80) yielded the product **32** as a reddish oily material (0.311 g, 0.58 mmol, 30.1%) containing an approximately 60:40 mixture of the diastereomers. [Note: The major diastereomer could be isolated by flash chromatography on silica gel (eluent, ether/pentane, 5:95)] ^{13}C NMR (C_6D_6): 212.4, *213.4 (1 tungsten carbonyl); 211.0, *211.0 (1 tungsten carbonyl); 203.0 (cobalt carbonyls); 88.0, *88.2 (Cp ring *C*H's); 85.9 (alkyne quaternary *C*); 77.7, *77.2 (*C*H); 72.6, *71.3 (alkyne *C*H); 33.4, *34.7 (CH_2); 10.8, *11.2 (CH_3). IR (CH_2Cl_2): ν_{CO} 2040 (m), 2000 (s), 1985 (s, br), 1940 (sh) cm^{-1}. Mass spectra (FAB+): m/z (%) 532 (15) ($(M)^+$, $C_{15}H_{13}O_6CoW$); 515 (7) $(M - OH)^+$; 504 (40) $(M - CO)^+$; 487 (10) $(M - OH - CO)^+$; 476 (100) $(M - 2CO)^+$; 459 (10) $(M - OH - 2CO)^+$; 448 (43) $(M - 3CO)^+$; 431 (14) $(M - OH - 3CO)^+$; 420 (22) $(M - 4CO)^+$; 403 (21) $(M - OH - 4CO)^+$; 392 (32) $(M - 5CO)^+$; 375 (20) $(M - OH - 5CO)^+$. Mass spectra (FAB–): m/z (%) 531 (100) $(M)^-$; 504 (95) $(M - CO)^-$; 476 (30) $(M - 2CO)^-$; 448 (65) $(M - 3CO)^-$; 419 (56) $(M - H - 4CO)^-$; 392 (24) $(M - 5CO)^-$. Anal. Calcd for $C_{15}H_{13}O_6CoW$: C, 33.86; H, 2.46. Found: C, 33.30; H, 2.55.

X-ray Crystallography. Crystals of $[(Co(CO)_3)_2(C_{13}H_{19}OH)]$ were grown from CH_2Cl_2/hexane. The density was determined by suspension in an aqueous solution of $ZnCl_2$. Reddish-black prismatic crystals were examined under a polarizing microscope for homogeneity. A well-formed crystal, 0.64 × 0.42 × 0.26 mm, was selected and mounted on the tip of a glass fiber with use of epoxy cement. Unit cell parameters were obtained from a least-squares fit of χ, ϕ, and 2θ for 15 reflections in the range $21.6° < 2\theta < 28.7°$ recorded on a Nicolet P3 diffractometer with use of graphite monochromated Mo Kα radiation ($\lambda = 0.71069$ Å at 22 °C). Intensity data were also recorded on a Nicolet P3 diffractometer with a coupled θ(crystal)–2θ(counter) scan, for 4269 reflections in the quadrant $h,k,\pm l$ with $2\theta \leq 50°$. The method of selection of scan rates and initial data treatment have been described.[24,25] Corrections for Lorentz–polarization effects and absorption (ψ scans)[26] were applied to all reflections. Two standard reflections (0, 6, 7, 1.74%; and –1, 6, –3, 1.93%) monitored every 48 reflections showed no sign of crystal decomposition or instrument instability. Systematically absent reflections (31) were excluded, and 525 symmetry-equivalent data were then averaged ($R_{int} = 0.0175$) to give 3713 unique reflections. A summary of crystal data is given in Table III.

The coordinates of the cobalt atoms were found from a three-dimensional Patterson synthesis with use of the program SHELX-86.[27] Full-matrix least-squares refinement of these coordinates followed by a three-dimensional electron density synthesis revealed all the non-hydrogen atoms and confirmed the positional assignments for the heavy atoms. After refinement, the temperature factors of the non-hydrogen atoms, which were previously isotropic, were made anisotropic, and further cycles of refinement revealed the positional parameters for all of the hydrogen atoms. These were included in subsequent cycles of refinement (U fixed at 0.08 $Å^2$). Further refinement using full-matrix least-squares minimizing $\sum w(|F_o| - |F_c|)^2$ was terminated when the maximum shift/error reached 0.001. Correction for secondary extinction was made by the method in SHELX-76.[28] Final $R_1 = 0.0546$ and $R_2 = 0.0567$ for 3713 reflections. Alternative refinement where coordinates x,y,z were replaced by $-x,-y,-z$ gave $R_1 = 0.0626$, $R_2 = 0.0667$, and $S = 1.2812$ (for definition see Table III) for 3713 reflections, confirming the assignment for the correct hand of the structure. Throughout the refinement, scattering curves were taken from ref 29, and anomalous dispersion corrections from ref 30 were applied to the curve for cobalt. All calculations were performed on a VAX 8650 computer. Programs used were as follows: XTAL,[31] data reduction; TAPER,[26] absorption correction; SHELXS-86,[27] structure solution; SHELX-76,[28] structure refinement; MOLGEOM,[32] molecular geometry; and SNOOPI,[33] diagrams. Final atomic positional parameters are given in Table II, and selected bond lengths and bond angles are given in Table III.

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Supplementary Material Available: Tables SI–SV, listing full crystal data, least-squares mean planes and dihedral/torsional angles, hydrogen atom positional parameters, bond lengths and bond angles involving hydrogen atoms, and anisotropic temperature factors, respectively (9 pages); Table SVI, listing observed and calculated structure factor amplitudes (23 pages). Ordering information is given on any current masthead page.

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