Diastereoselective Addition of Allyl- and Crotylstannanes to Dicobalt-Complexed Acetylenic Aldehydes

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In an endeavor to utilize metal carbonyl complexes of acetylenic aldehydes and ketones to control the stereoselectivity of nucleophilic acyl addition, the dicobalt hexacarbonyl and dicobalt pentacarbonyl(triphenylphosphine) complexes of 3-phenylpropynal and 2-hexynal were conveniently prepared. Crotyl transfer from either (*E*)- or (*Z*)-crotyltributylstannane to $Co_2(CO)_6$-complexed 3-phenylpropynal and 2-hexynal produced 3,4-disubstituted-1,5-enynes with high *syn* diastereoselectivity. Allyl and 2-methylallyl transfer to $Co_2(CO)_5PPh_3$-complexed aldehydes was also accomplished with high yields and diastereoselectivities. In all cases, decomplexation of the metal carbonyl moiety was effected, selectively, under very mild oxidative conditions. Exchange of a CO by PPh_3 led to decreased overall reactivity. Two competing kinetic processes were observed: stereoselective allylation was observed at low temperature, but at higher temperatures, the first formed allylic alcohol preferentially underwent elimination leading to dienynes.

Introduction

Methods for the introduction of nucleophiles at a propargyl carbon with simultaneous control of stereochemistry are invaluable for the construction of building blocks that contain multiple asymmetric centers and sites that are amenable to further transformation. The 1,5-enyne carbon skeleton is an extremely versatile fragment that continually finds application in total syntheses.[1] One approach to formation of the 1,5-enyne system, which allows the substituents at C2, C3, and C4 to be varied with concomitant control of their stereochemistry, involves allylic transposition from an allylmetal reagent to an acetylenic aldehyde or ketone. The allyl transfer reaction is of particular synthetic value, as the resulting homoallylic alcohol can be transformed into an aldol derivative upon oxidation of the double bond, thereby functioning as the synthetic equivalent of an aldol addition. Some common transformations that allow the 1,5-enyne carbon framework to be further extended are shown in Scheme 1.[2]

High levels of *syn* diastereoselectivity[3] of the C3−C4 substituents in 3,4-disubstituted-1,5-enynes have been obtained from the addition of chiral crotylboronates[4] and chiral γ-alkoxyallylboranes[5] to dicobalt hexacarbonyl-complexed acetylenic aldehydes. In both cases, since boron performs the dual function of coordinating to the carbonyl oxygen and delivering the allyl group, the diastereoselectivity can be attributed to a preferred orientation of the aldehyde, which minimizes 1,3-diaxial interactions, in a putative closed, Zimmerman-Traxler type transition state. Assuming that the dominant steric interaction is between the alkynyl moiety and the ligands on boron, the degree of stereoselection reported is based upon the large difference in steric bulk between the alkynyl group and the aldehydic proton. The dicobalt cluster plays a passive role, in that it simply serves to amplify this intrinsic difference in steric bulk. Consequently, reduced diastereoselectivity would be expected from the addition of crotylboranes and crotylboronates to ketones.

From our preliminary studies involving allyl transfer from functionalized allylsilanes onto dicobalt hexacarbonyl-complexed acetylenic aldehydes and ketones,[6] we

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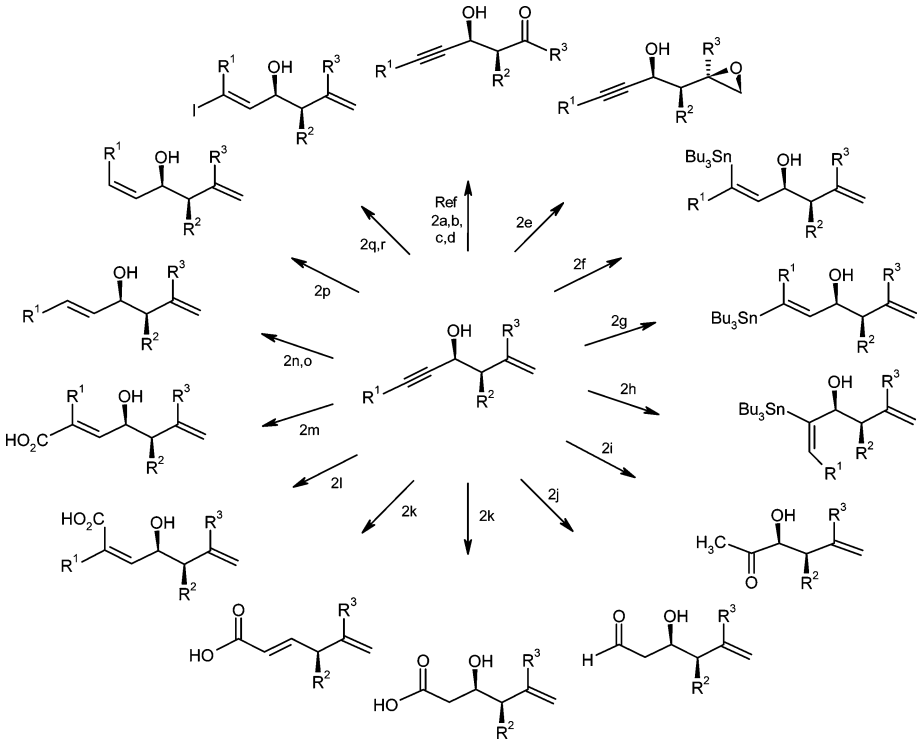
Scheme 1



recognized that the dicobalt cluster might be made to assume an active role in controlling the carbonyl facial selectivity during nucleophilic acyl addition. A general method to control the stereoselectivity of carbon−carbon bond formation that could be applied to acetylenic ketones as well as aldehydes would be synthetically advantageous. We chose silanes and stannanes as nucleophilic reactants for an investigation of nucleophilic addition to dicobalt-complexed acetylenic aldehydes and ketones. These allyl reagents have considerable synthetic utility since substitution at any of the allylic α, β, or γ positions provides a route to a wealth of compounds containing the 1,5-enyne system, they can be readily prepared in large quantities, and they are configurationally stable at room temperature.

We report herein the diastereoselectivities of 3,4-disubstituted-1,5-enynes obtained from the addition of crotyltributylstannanes to dicobalt hexacarbonyl-complexed aliphatic and aromatic acetylenic aldehydes. Also reported are the diastereoselectivities of allyl transfer to the corresponding chiral dicobalt pentacarbonyl(triphenylphosphine)-complexed propynals. To our knowledge, this is the first report of allyl and crotyl transfer to dicobalt-complexed aldehydes from reagents based on group 14 elements.

Results and Discussion

Allyl Transfer to Dicobalt Hexacarbonyl-Complexed Acetylenic Aldehydes. Initially, we examined BF_3-promoted allyl transfer from allyltributylstannane and (2-methylallyl)tributylstannane to the noncomplexed aldehydes 3-phenylpropynal and 2-hexynal. Formation of the homoallylic alcohols **4a**,**b** and **5a**,**b**, reported in Table 1, was complete in all cases within approximately 30 min at −78 °C.[7] The moderate yields of alcohol are the result of subsequent coupling, elimination, and double allylic transposition, leading, in the case of alcohol **4a**, to the isolated compounds **10** + **11**, **12**, and **13**, respectively. We found that the yields of homoallylic alcohol could be increased significantly by employing the corresponding dicobalt hexacarbonyl complexes of the acetylenic aldehydes. Under identical experimental conditions, the time required for complete conversion also increased to approximately 1−2 h at −78 °C, suggesting that the reactivity of the carbonyl group had been attenuated by the presence of the dicobalt cluster, which is well known to stabilize α-cationic sites.[8]

Table 1. Allyl Transfer to Noncomplexed and $Co_2(CO)_6$-Complexed Alkynals[a]

entry	aldehyde	allylstannane	alcohol	% yield[b]
1	**1**	**3a**	**4a**	70
2	**1**	**3b**	**4b**	71
3	**6**	**3a**	**8a**	95
4	**6**	**3b**	**8b**	96
5	**2**	**3a**	**5a**	68
6	**2**	**3b**	**5b**	65
7	**7**	**3a**	**9a**	94
8	**7**	**3b**	**9b**	93

[a] All reactions were carried out at −78 °C. [b] Yield after chromatography.

Interestingly, double allylic transposition was found to occur when 2 molar equiv of both allylstannane reagent and Lewis acid were added to the dicobalt-complexed aldehydes, whereas an excess of allyl reagent and Lewis acid did not change the ratio of products recovered from the corresponding noncomplexed alde-

(7) See Experimental Section for complete details.

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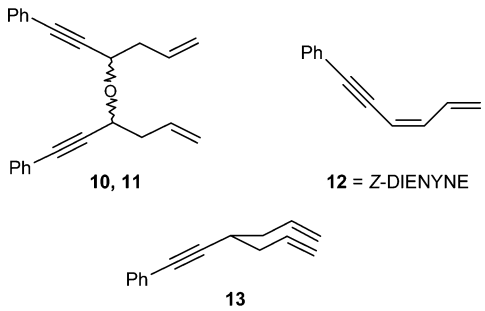

hydes. We presumed that the second allyl transfer proceeded via a dicobalt hexacarbonyl-stabilized secondary cation generated upon elimination of a propargyl alkoxy substituent from the initially formed homoallylic boron-trifluoride etherate. Indeed, treatment of **8a**, which had been independently synthesized, with 1 molar equiv of allyltributylstannane and $BF_3{\cdot}OEt_2$ yielded **14** in 87% yield. The structure of **14** was confirmed by spectroscopic characterization following oxidative decomplexation using $(CH_3)_3N(O)$. This reactivity introduces the possibility of incorporating two different nucleophiles at the propargylic site, possibly even as a one-pot procedure, giving rise to a trialkyl-substituted carbon atom from an acetylenic aldehyde, or a quaternary carbon from an acetylenic ketone.

Crotyl Transfer to Dicobalt Hexacarbonyl-Complexed Acetylenic Aldehydes. With a view toward constructing the 3,4-disubstituted-1,5-enyne carbon framework and controlling simple diastereoselectivity,[9] crotyl transfer to the dicobalt hexacarbonyl complex of 3-phenylpropynal and 2-hexynal was carried out using either (*E*)- or (*Z*)-crotyltributylstannane. Both crotyltin reagents led to a diastereomeric mixture in which the major isomer has C3 methyl and C4 hydroxyl substituents in a *syn* relationship to each other.[3] In contrast, only the *syn* diastereomer was obtained from crotyl transfer to the corresponding noncomplexed acetylenic aldehydes, irrespective of the stereochemistry of the crotyltin reagent, as has previously been observed for the addition of enolsilanes.[10] The yields and ratios are given in Table 2. The relative stereochemistry of **4c** was determined by comparison with a previously reported ^{1}H NMR spectrum.[11] $LiAlH_4$ was used to reduce compound **5c** to the diene **15** (Scheme 5), whose relative stereochemistry was assigned by comparison with previously published ^{1}H NMR[12] and ^{13}C NMR[13] spectra, respectively.

Two different open acyclic transition state models, termed antiperiplanar[14] and synclinal,[15] have been advanced for understanding the observed stereoselectivities of addition reactions between trigonal centers. The two models differ in the relative orientation of the participating π-bonds. Whereas the reacting π-bonds are oriented at an angle of 180° to each other in the antiperiplanar model, they are positioned approximately 30° apart in the synclinal model. The various factors that are believed to influence the preferred orientation of π-bonds include steric repulsion,[16] orbital control,[17] metal chelation,[18] and Coulombic attraction.[19] Both models predict a preference for formation of the *syn* diastereomer from Lewis acid-promoted crotyl transfer to simple aldehydes, such as 3-phenylpropynal and 2-hexynal. The stereoconvergent *syn* diastereoselectivity derives from the π-bond facial selectivity of the crotylmetal reagent, which leads to fewer steric interactions between itself and the aldehyde, which, upon comparison of (*E*)- and (*Z*)-crotylmetal reagents, is found to be diametrical. Thus, the exclusive recovery of **4c** from **1**, and **5c** from **2**, is in accord with this postulate.

Table 2. Crotyl Transfer to Noncomplexed and $Co_2(CO)_6$-Complexed Alkynals[a]

entry	aldehyde	allylstannane	alcohol	% yield[b]	*syn*:*anti*[c]
1	**1**	**3c**	**4c**	88	100:0
2	**1**	**3d**	**4c**	86	100:0
3	**6**	**3c**	**8c** + **8d**	95[d]	75:25
4	**6**	**3d**	**8c** + **8d**	97[d]	86:14
5	**2**	**3c**	**5c**	85	100:0
6	**2**	**3d**	**5c**	82	100:0
7	**7**	**3c**	**9c** + **9d**	96[d]	73:27
8	**7**	**3d**	**9c** + **9d**	94[d]	85:15

[a] All reactions were carried out at −20 °C. [b] Yield after chromatography. [c] The diastereomeric ratios of alcohols were determined by ^{1}H NMR analysis of the mixtures. [d] Yield of the diastereomeric mixture of alcohols after chromatography.

By virtue of the tetrahedral geometry of the dicobalt cluster, comprised of two cobalt vertexes and two acetylene carbon atoms, the aldehydes **6** and **7** possess a plane of symmetry that bisects the cobalt−cobalt bond. This makes equivalent the two enantiotopic faces of the carbonyl group in dicobalt hexacarbonyl-complexed acetylenic aldehydes, as is the case in the analogous noncomplexed acetylenic aldehydes. As a result, the diastereoselectivity of homoallylic alcohol formation should be determined only by the relative π-bond facial selectivity of the dicobalt-complexed aldehyde and the crotyltin reagent during allyl transfer. The predominant steric interaction that controls this relative facial selectivity is expected to be identical to that which operates in the case of noncomplexed aldehydes. Therefore, the dicobalt-complexed aldehydes should give rise to the same degree of diastereoselectivity as the noncomplexed aldehydes.

The ability of a $Co(CO)_3$ vertex to interact with and provide stabilization for positive charge that develops at a propargyl carbon[20] introduces an additional factor,

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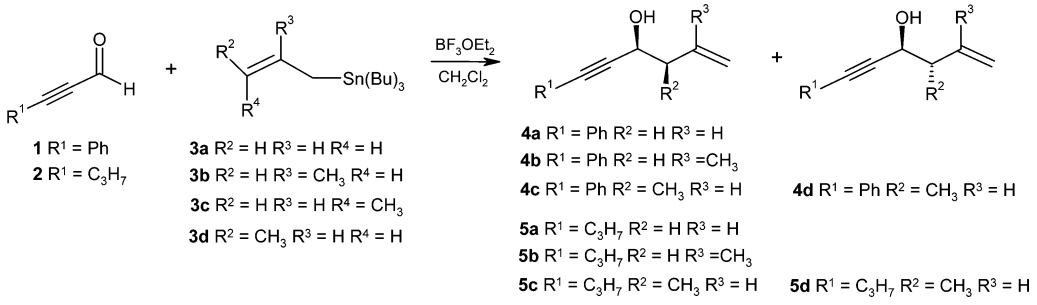
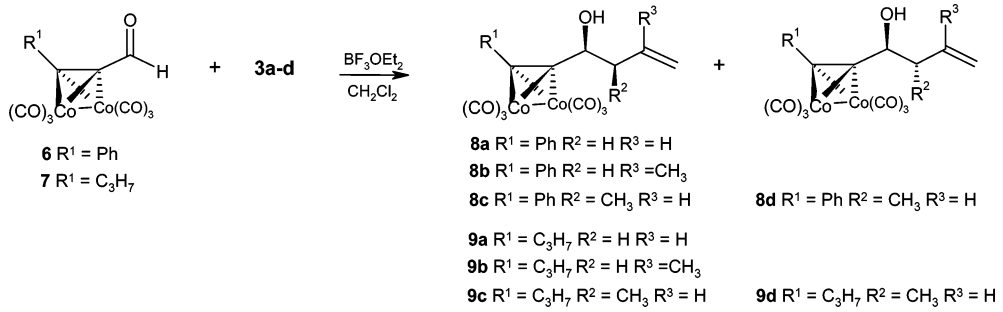
Scheme 2



Scheme 3



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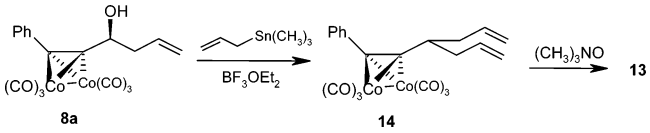
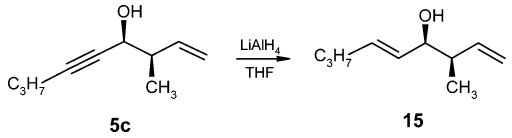


Scheme 5



specific to the complexed aldehydes, that can affect the stereoselectivity of crotyl transfer. When the two metal vertexes provide a comparable degree of charge delocalization, two different dynamic processes can occur, as evidenced by variable-temperature NMR studies on cations generated in solution from dicobalt hexacarbonyl-complexed propargyl alcohols.[21] The higher energy process, termed suprafacial migration, exchanges the environment of the substituents bonded directly to a propargyl carbon. A mechanism that is consistent with the spectroscopic findings involves migration of the vinylidene group from one cobalt vertex to the other. This is depicted in the interconversion of structures **16** and **18** in Figure 1. By comparison, the spectroscopic evidence of a lower energy process, termed antarafacial migration, is consistent with an exchange of the different environments *within* the propargyl substituents. This has been rationalized to involve migration of the vinylidene group from one cobalt vertex to the other with a concomitant inversion of the π-bond facial selectivity, depicted in the interconversion of **16** and **17**.

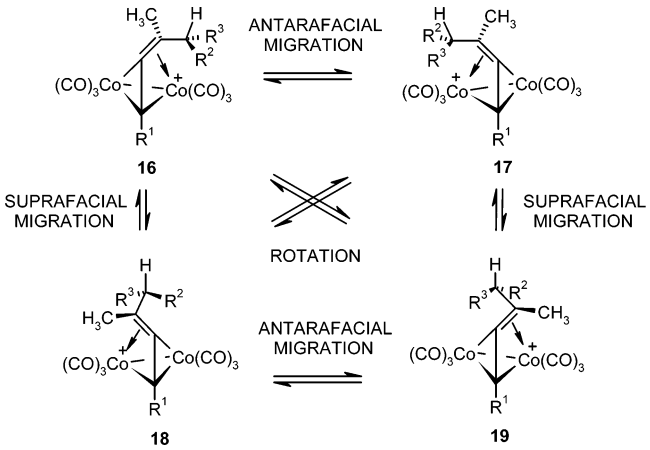


Figure 1.

We have reasoned that the cationic character, which develops at a carbonyl carbon in a $Co_2(CO)_6$-complexed acetylenic aldehyde upon coordination of a Lewis acid, could be stabilized through an interaction with the cobalt vertexes in a similar manner. Furthermore, since the two cobalt vertexes in $Co_2(CO)_6$-complexed aldehydes are equivalent, they could both participate in charge delocalization, giving rise to fluxionality of the molecule. Antarafacial migration would then expose both faces of the compound's π-bond during crotyl transfer, and it is this process that would lead to a reduction in the degree of stereoselectivity of nucleophilic addition, as compared with noncomplexed aldehydes. Antarafacial migration of aldehyde **6** coordinated to BF_3 is illustrated in structures **20** and **22**, in Figure 2.

The loss of diastereospecificity with complexed, versus uncomplexed, propynals could also be attributed to an increased facility for racemization of the product, as has previously been reported.[22] Erosion of diastereoselec-

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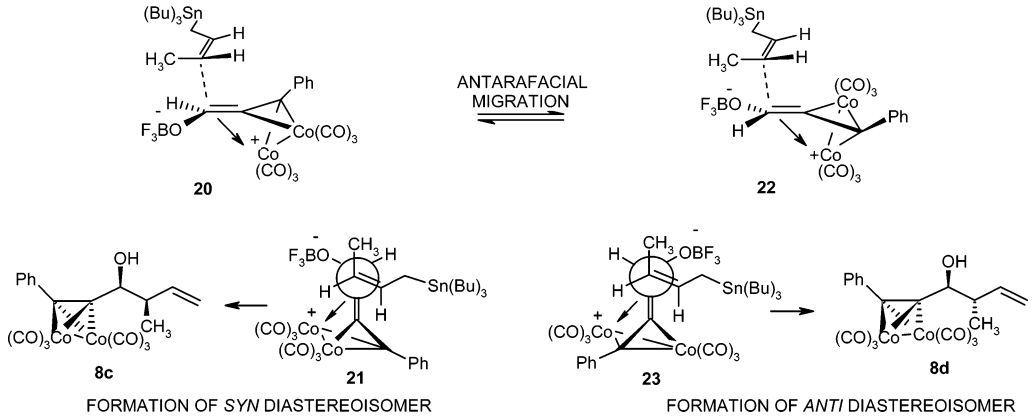

Figure 2.

tivity, accompanied by elimination reactions, was observed if reaction temperatures were allowed to arise above 0 °C before quenching. However, in these reactions there was no observed time-dependent change in diastereoselectivity as would be anticipated from a racemization process. Thus, we interpret the changeover in stereoselectivity with complexed materials to arise from the initial formation of the homoallylic alcohol, rather than subsequent racemization.

By analogy with the noncomplexed aldehydes, the dicobalt cluster determines the π-bond facial selectivity of the crotyltin reagent since, in the putative open transition state, the two reactants can approach each other via a pathway that minimizes steric interactions. An analysis of both the antiperiplanar and synclinal models reveals that the latter provides a more cogent rationale for the observed *syn* diastereoselectivity, as it allows placement of the smallest substituent of the crotylstannane—that being the hydrogen bonded to the γ-carbon—at the most sterically demanding site in the transition structure—that being nearest to a $Co(CO)_3$ vertex. The synclinal orientation and the π-bond facial selectivity of (*Z*)-crotyltributylstannane, which is thought to participate in crotyl transfer, is illustrated in the Newman projections **21** and **23**, in Figure 2.

Allyl Transfer to Chiral Dicobalt Pentacarbonyl-(triphenylphosphine)-Complexed Acetylenic Aldehydes. The dynamic processes described above were observed in homobimetallic[23] cluster compounds, where the two vertexes provide comparable stabilization of adjacent positive charge. In contrast, when one metal vertex can delocalize the charge to a greater extent, as in heterobimetallic[24] or mixed trimetallic[25] cluster compounds, the same processes have not been detected on the NMR time scale. This condition has been applied to Co_2-complexed propargyl alcohols, wherein one of the cobalt vertexes was made to provide greater charge stabilization by replacing a weakly σ-donating/strongly π-accepting CO ligand with the stronger σ-donating/

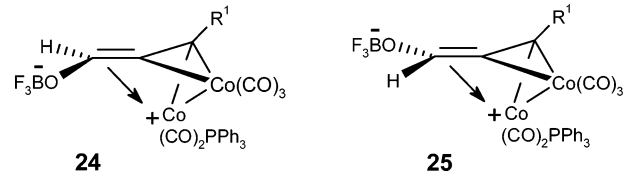

Figure 3.

weaker π-accepting PPh_3 ligand, by Nicholas and coworkers.[22,26] Upon protonation, the resulting $Co_2(CO)_5$-PPh_3-complexed propargyl cations were judged to be more electron-rich than the parent cationic $Co_2(CO)_6$ complexes and to have the charge preferentially localized onto the phosphine-bearing cobalt vertexes. Only one diastereomeric cation was formed from complexes possessing a bulky substituent at the propargyl carbon, such as isopropyl or *tert*-butyl. Its conformation was determined, by difference NOE NMR experiments, to have the bulky substituent flanking the less sterically encumbered cobalt−cobalt bond, rather than the cobalt−carbon bond. As with bimetallic clusters, fluxionality was not detected by variable-temperature NMR monitoring of the cation.

We anticipated that this phenomenon could be utilized to synthetic advantage if it provides a means by which the dicobalt-complexed acetylenic aldehyde's π-bond facial selectivity could be controlled during allyl and crotyl transfer. Our observed diastereoselectivities of crotyl transfer to $Co_2(CO)_6$-complexed aldehydes provide evidence for an interaction between the carbonyl carbon and both cobalt vertexes of a fluxional cluster. By inducing preferential delocalization of positive charge onto one cobalt vertex only, the dynamic process that exposes both faces of the compound's π-bond would be precluded. We predicted that the replacement of a CO ligand in aldehydes **6** and **7**, with PPh_3, would produce a compound in which fluxionality of the cluster was absent or slow relative to the rate of allyl transfer. Then, the ratio of diastereomeric homoallylic alcohols formed would reflect the relative stabilities of the two possible conformational isomers of the Lewis acid-coordinated dicobalt-complexed acetylenic aldehydes,[27] illustrated in Figure 3.

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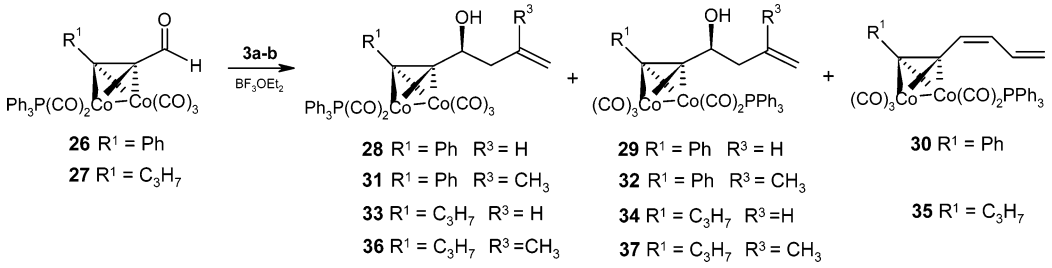
Table 3. Allyl Transfer to $Co_2(CO)_5PPh_3$-Complexed Propynals

				products (mol %)[a]			homoallylic alcohols		
entry	allyl reagent	aldehyde	reaction temp (°C)	ald.[b]	alc.[c]	dien.[d]	alc.[c]	ratio[e]	% yield[f]
1	**3a**	**26**	−78 to 25	16	70	14	**28**, **29**	70:30[g]	63
2	**3a**	**26**	−78 to 25	16	25	59	**28**, **29**	60:40	18
3	**3a**	**26**	−78 to 25	0	23	77	**28**, **29**	5:95	15
4	**3a**	**26**	−10	0	90	10	**28**, **29**	74:26	87
5	**3a**	**26**	−20	0	100	0	**28**, **29**	90:10	96
6	**3a**	**26**	−30	0	100	0	**28**, **29**	86:14	98
7	**3a**	**27**	−20	0	100	0	**33**, **34**	84:16[h]	95
8	**3b**	**26**	−20	0	100	0	**31**, **32**	100:0[i]	92
9	**3b**	**27**	−20	0	100	0	**36**, **37**	85:15[j]	93

[a] Composition of the crude reaction mixture. [b] Unreacted aldehyde. [c] Homoallylic alcohols. [d] (*Z*)-Dienyne **30**. [e] The diastereomeric ratios of alcohols were determined by ^1H NMR analysis of alcohol mixtures. The absolute stereochemical assignment of the major diastereomer has been inferred. [f] Yield of the diastereomeric mixture of alcohols after chromatography. [g] Alcohols **28**, **29** given as X:Y where X and Y correspond to the diastereomer having a chemical shift of C4−H at 3.92 and 4.07 ppm, respectively. [h] Alcohols **33**, **34** given as X:Y where X and Y correspond to the diastereomer having a chemical shift of C4−H at 3.89 and 4.05 ppm, respectively. [i] Alcohols **31**, **32**. [j] Alcohols **36**, **37** given as X:Y where X and Y correspond to the diastereomer having a chemical shift of C4−H at 4.14 and 4.30 ppm, respectively.

Scheme 6



The dicobalt pentacarbonyl(triphenylphosphine) complexes of 3-phenylpropynal and 2-hexynal were prepared by gently refluxing aldehydes **6** and **7** in the presence of triphenylphosphine. All the reactions described below were carried out with a racemic mixture of the chiral compounds **26** and **27**. The product mixtures and diastereoselectivities of the homoallylic alcohols obtained from allyl transfer reactions carried out with aldehyde **26**, while the cooling bath temperature had been allowed to warm from −78 °C to 25 °C, are given in entries 1 to 3 in Table 3 and shown in Scheme 6.

The temperature at which allyl transfer was performed proved to be the most critical variable in determining the yield and product mixture. At cooling bath temperatures above −10 °C, elimination from the homoallylic boron-trifluoride etherate took place in competition with allyl transfer, giving rise to the (*Z*)-dienyne **30**. These results are noteworthy, as they show a correlation between large quantities of the (*Z*)-dienyne and a seeming "reversal" of diastereoselectivity (compare entries 1 and 3). After having monitored the progress of the reaction over time, using TLC and ^1H NMR, we attribute this "reversal" to the occurrence of two competing kinetic processes. At lower temperatures, a diastereoselective allylation of the complexed aldehyde favors the formation of one isomer, such as **28**. However, as the bath temperature increases, elimination takes place from **28** preferentially, leaving **29** as the major homoallylic alcohol product. Judicious manipulation of the reaction conditions thus allows the reaction to be directed to either the *syn* or *anti* isomer. Also reported in Table 3 are the improved yields and diastereoselectivities obtained at constant cooling bath temperatures of −30, −20, and −10 °C, in the absence of elimination. The optimal reaction temperature seems to lie somewhere between −30 and −20 °C; the rate was found to be sluggish at temperatures below −40 °C.

Whereas allyltrimethylsilane could be used to effect allyl transfer to $Co_2(CO)_6$-complexed aldehydes, the more nucleophilic allyltributylstannane was required for $Co_2(CO)_5PPh_3$-complexed aldehydes; in this case the reaction time was increased 3-fold under otherwise identical conditions. The second allylic transposition did not occur when two or more molar equivalents of allylstannane and Lewis acid were added to $Co_2(CO)_5$-PPh_3-complexed aldehydes, unlike the parent $Co_2(CO)_6$-complexed aldehydes (vide supra). On the basis of the results reported in Table 3, and allyl transfer studies carried out with the less sterically encumbered Co_2-$(CO)_5P(CH_3)_3$-complexed 3-phenylpropynal,[28] the attenuated reactivity of the phosphine-bearing compounds suggests that they are more electron-rich than the parent compounds and have positive charge delocalized onto the $Co(CO)_2PR_3$ vertex, as shown in Figure 3.

The thermodynamically favorable conformation of Lewis acid-coordinated $Co_2(CO)_5PPh_3$-complexed aldehydes is expected to be that which places the smallest propargyl substituent—a hydrogen—flanking the more sterically hindered cobalt−carbon bond, as depicted in **24**. Nicholas and co-workers have carried out magnetization transfer experiments to probe the existence of dynamic processes in related $Co_2(CO)_5PPh_3$-complexed cations generated in CD_2Cl_2.[26] On the basis of their report that antarafacial migration was not detected on the NMR time scale, and our recovery of a single

(27) This corresponds to the condition of "kinetic quenching", derived from a kinetic treatment of second-order reactions involving two interconverting substances. Seeman, J. I. *Chem. Rev*. **1983**, *83*, 83. This postulate will only be valid if the π-bond facial selectivity of the allylstannane is the same for both isomers **24** and **25**.

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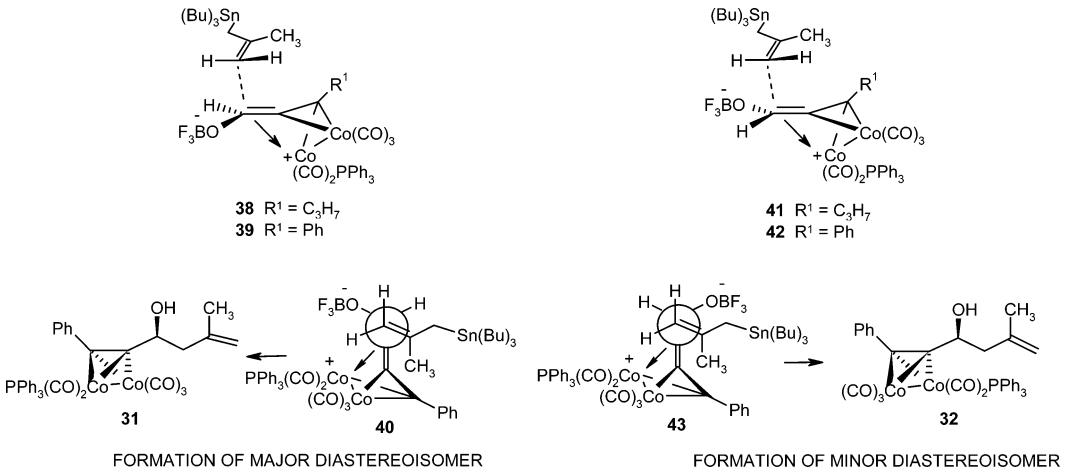

Figure 4.

diastereomeric homoallylic alcohol from the addition of **3b** to **26**, we surmise that isomers **24** and **25** were not interconverted by a dynamic process under the reaction conditions used.

We can extend our synclinal transition state model to BF_3-coordinated $Co_2(CO)_5PPh_3$-complexed aldehydes in order to illustrate how the conformation of the cluster itself could be the origin of stereochemical control. The thermodynamically favorable conformation of BF_3-coordinated complexed aldehydes is believed to have given rise to **31**[29] and the major diastereomeric alcohol in the case of **28/29**, **33/34** and **36/37**, as depicted in Figure 4.

Crotyl Transfer to Chiral Dicobalt Pentacarbonyl(triphenylphosphine)-Complexed Acetylenic Aldehydes. If the diastereoselectivity of allyl transfer derives from the conformation of the Lewis acid-coordinated phosphine-bearing compound, which consequently determines the π-bond facial selectivity of allylmetal reagents, there exists the potential to effect crotyl transfer diastereospecifically, under experimental conditions that favor crotyl addition to one conformational isomer exclusively. In a parallel set of experiments, we examined crotyl transfer to **26** and **27**.

Electrophilic substitution of allylsilanes and their derivatives has been studied extensively, and the widely accepted S_E2' mechanism has also been extended to allylstannanes and allylgermanes.[30] On the basis of the previously reported increased reactivity of (*E*)- and (*Z*)-crotyltrimethylsilane, relative to allyltrimethylsilane, with cations generated in solution,[31] we initially expected (*E*)- and (*Z*)-crotyltributylstannane to be similarly more reactive than allyltributylstannane. From the addition of each of allyltributylstannane, (*E*)-crotyltributylstannane and (*Z*)-crotyltributylstannane, to a separate solution of **6** and $BF_3{\cdot}OEt_2$ under identical conditions, we learned that the crotylstannanes are actually less reactive than allyltributylstannane and required twice as much time for complete conversion to be achieved. Nevertheless, we attempted crotyl transfer to **26** using (*E*)- and (*Z*)-crotyltributylstannane and $BF_3{\cdot}OEt_2$, $TiCl_4$, or $SnCl_4$ as Lewis acid at both −20 and 0 °C. In all cases, however, only starting material was recovered. Thermal decomplexation of the dicobalt cluster occurred at temperatures above 0 °C.

According to Mayr's reactivity scales,[32] the electrophilicity of the propargyl cation derived from $Co_2(CO)_6$-complexed propargyl alcohol is reduced by almost an order of magnitude when the acetylenic proton is substituted with a phenyl group.[33] We speculated that the electrophilicity of **26** might be increased by replacing the acetylenic phenyl group with a proton or an aliphatic group and attempted crotyl transfer to **27** using (*E*)- and (*Z*)-crotyltributylstannane. Disappointingly, only starting material was again recovered.

The electrophilicity of BF_3-coordinated $Co_2(CO)_5PPh_3$-complexed aldehydes can now be quantified in the context of Mayr's reactivity scales. The parameters *E* and *N* in eq 1 correspond to values of electrophilicity and nucleophilicity, respectively, obtained from numerous "constant selectivity" correlations between cationic electrophiles and neutral nucleophiles.[32] For a given nucleophile, eq 1 can be used to predict the *E* value that an electrophile must possess in order for a reaction to proceed at 20 °C by setting log *k* to −5 s (corresponding to a minimum rate constant of 10^{-5} L mol^{-1} s^{-1}). Since allyltrimethylsilane was found to be unreactive toward $Co_2(CO)_5PPh_3$-complexed aldehydes, it sets an approximate upper limit on the electrophilicity of the phosphine-bearing aldehydes. Similarly, since allyltributylstannane and (2-methylallyl)tributylstannane did undergo allyl transfer, the former sets an approximate lower limit on their electrophilicity. The *N* values of 1.62 and 5.72, reported for allyltrimethylsilane and allyltributylstannane, respectively, were used to calculate *E* values of −6.62 and −10.72. Therefore, the electrophilicity of BF_3-coordinated aldehydes **26** and **27** falls within the range of −6.62 and −10.72, as defined by Mayr. This allows one to predict that a reaction should occur between BF_3-coordinated aldehyde **26** or **27** and silyl enol ethers, hydride donors, alkoxy-substituted arenes, amines, and other nucleophiles of comparable or greater strength.

(29) The absolute configuration at C4 and the dicobalt cluster is unknown in the absence of X-ray diffraction data and has been inferred. An *R* or *S* configuration can be assigned to a metal cluster according to the Cahn−Ingold−Prelog selection rules. See ref 21b.

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$$\log k = s(E + N) \quad (1)$$

Summary

The yields and diastereoselectivities of allyl and crotyl transfer to $Co_2(CO)_6$-complexed aldehydes support the proposal that the development of positive charge at a carbonyl carbon is stabilized by an interaction with both cobalt vertexes, which leads to a loss of stereochemical integrity at that site through dynamic processes. We have shown that allyl and 2-methylallyl transfer to $Co_2(CO)_5PPh_3$-complexed aldehydes can be effected with high yields and good diastereoselectivities. The reduced reactivity of the latter complexes suggests they are more electron-rich than the parent complexes and lends further support to the proposal of charge stabilization by a cobalt vertex, particularly $Co(CO)_2PPh_3$. We speculate that a single diastereomeric homoallylic alcohol **31** was formed from 2-methylallyl transfer to the thermodynamically favored conformational isomer of a static complex. If the diastereoselection originates from steric interactions that exist *within* the dicobalt-complexed aldehyde itself, it should be possible to control the stereoselectivity of nucleophilic addition to dicobalt-complexed acetylenic ketones in a similar manner.

Experimental Section

^{1}H NMR spectra were recorded on a Bruker AC-300 spectrometer at 300.130 MHz or on a Bruker AC-200 spectrometer at 200.20 MHz, using $CDCl_3$ as solvent and internal standard. ^{13}C NMR were recorded on the same instrument at 75.467 MHz or at 50.340 MHz, also using $CDCl_3$ as solvent. Infrared spectra were recorded on a Bio Rad FTS-40 Fourier transform spectrometer. Liquid samples were used as neat films on NaCl disks, and solid samples were prepared as KBr pellets. Chemical ionization (CI), with ammonia as the reagent gas, and electron impact (EI) mass spectra were recorded at 70 eV with a source temperature of 200 °C on a VG Analytical ZAB-R mass spectrometer equipped with a VG 11-250 data system. Flash chromatography was performed using Silicycle silica gel (230−400 mesh). Analytical thin-layer chromatography (TLC) was performed on aluminum sheets precoated with silica gel (Merck, Kieselgel 60 F_{254}).

Allyltrimethylsilane, allyltributylstannane, *n*-butyllithium in hexanes, tributyltin chloride, 2-butyn-1-ol, *trans*-crotyl chloride, 3-chloro-2-methylpropene, *N*-formyl morpholine, hexachloroacetone, lithium wire, Lindlar catalyst, phenylacetylene, 1-pentyne, triphenylphosphine, trimethylamine *N*-oxide, $TiCl_4$, $BF_3{\cdot}OEt_2$, and $SnCl_4$ were purchased from Aldrich and used without purification. Dicobalt octacarbonyl was purchased from Strem Chemicals and used without further purification. CH_2Cl_2 was distilled from CaH_2 prior to use; THF and diethyl ether were distilled from sodium prior to use. Aldehydes **1** (lit.[34] bp 65 °C (0.1 mmHg)) and **2** (lit.[35] bp 56−62 °C (20 mmHg)) were prepared by formylation of the organolithium derivatives of phenylacetylene and 1-pentyne, using *N*-formylpiperidine, as described by Olah.[34]

(2-Methyl-2-propenyl)tributylstannane (3b). This allyltin reagent was prepared by coupling 2-methyl-2-propenylmagnesium chloride and Bu_3SnCl with external irradiation of ultrasound, following the procedure of Naruta.[36] ^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.66 (br s, 2H), 1.95 (s, 2H), 1.84 (s, 3H), 1.6−1.0 (m, 18H), 0.91 (m, 9H).

(*Z*)-2-Butenyltributylstannane (3c). This compound was prepared in three steps starting from 2-butyn-1-ol. A mixture of 2-butyn-1-ol (10.0 g, 142.6 mmol) and Lindlar catalyst (1.0 g) in CH_3OH (150 mL) was stirred at 25 °C under 1.0 atm of H_2 for approximately 2 h, at which time the alkyne was judged, using TLC, to have been completely consumed. The mixture was then filtered through a pad of Celite and concentrated. Purification by distillation yielded 9.77 g (135.5 mmol, 95%) of (*Z*)-2-buten-1-ol (lit.[37] bp 123.6 °C). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.60 (m, 2H), 4.19 (d, J = 4.7 Hz, 2H), 1.72 (br s, 1H), 1.66 (d, J = 5.2 Hz, 3H).

(*Z*)-2-Buten-1-ol was converted to the chloride by treating a solution of the alcohol in hexachloroacetone with PPh_3.[38] Purification by distillation yielded (*Z*)-1-chloro-2-butene (lit.[39] bp 84.1 °C (758 mmHg)). ^{1}H NMR ($CDCl_3$, 200 MHz): δ 5.69 (m, 2H), 4.11 (d, J = 6.8 Hz, 2H), 1.72 (d, J = 5.7 Hz, 3H).

The procedure described by Matarasso-Tchiroukhine was followed for the preparation of the (*Z*)-crotyltin reagent.[40] To a stirred suspension of finely cut lithium wire (1.26 g, 182.6 mmol) in dry THF (60 mL) under N_2 at 25 °C was added Bu_3SnCl (19.84 g, 60.96 mmol). When the reaction had begun, as evidenced by the evolution of heat and the formation of a tan color, an additional 90 mL of THF was added and stirring at 25 °C was continued for 8 h. After allowing the mixture to stand for 1 h, it was filtered through a plug of glass wool under N_2 into a dry flask, which was then cooled to −40 °C. To this flask was added a solution of (*Z*)-1-chloro-2-butene (5.52 g, 60.96 mmol) in THF (6 mL). The mixture was stirred at −40 °C for 30 min, then quenched by adding a saturated aqueous solution of NH_4Cl, which had been cooled to 0 °C. The solution was brought to room temperature, and the aqueous phase was extracted twice with ether. The organic phases were combined, dried over Na_2SO_4, filtered, and concentrated under reduced pressure. The residue was purified by distillation to yield 16.42 g (43.28 mmol, 71%) of (*Z*)-2-butenyltributylstannane, a colorless oil (lit.[41] bp 100−110 °C (1.0 mmHg)). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 129.6, 118.2, 29.3, 27.5, 27.4, 13.8, 12.5, 9.4.

(*E*)-2-Butenyltributylstannane (3d). This compound was prepared from (*E*)-crotyl chloride and Bu_3SnCl, using the procedure described above. ^{13}C NMR ($CDCl_3$, 50 MHz): δ 130.5, 120.3, 29.3, 27.5, 27.4, 17.9, 13.8, 9.2.

General Procedure for Preparation of Dicobalt Hexacarbonyl-Complexed Aldehydes: (3-Phenylpropynal)dicobalt Hexacarbonyl Complex (6). To a solution of dicobalt octacarbonyl (0.31 g, 0.91 mmol) in CH_2Cl_2 (18 mL) was added 3-phenylpropynal (0.10 g, 0.76 mmol) in CH_2Cl_2 (15 mL) at 0 °C under N_2. Stirring was continued for 4 h, followed by concentration of the solvent under reduced pressure and purification by flash chromatography (19:1 pentane/diethyl ether) to yield 0.31 g (0.74 mmol, 97%) of a red solid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.50 (s, 1H), 7.57 (m, 2H), 7.33 (m, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 197.6, 190.8, 136.3, 129.7, 129.0, 128.8, 92.1, 85.6. IR (KBr) 2101, 2065, 2032, 1666, 1484, 1442, 1019 cm^{-1}; MS (EI, *m/z*) 388 (M^+ − CO, 21), 360 (M^+ − 2 CO, 31), 332 (M^+ − 3 CO, 29), 304 (M^+ − 4 CO, 53), 276 (M^+ − 5 CO, 68), 248 (M^+ − 6 CO, 75); MS (CI, NH_3, *m/z*) 417 (M + H^+, 100), 389 (M + H^+ − CO, 56).

(2-Hexynal)dicobalt Hexacarbonyl Complex (7). Purification by flash chromatography (19:1 pentane/diethyl ether) yielded 96% of a red solid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 10.29 (s, 1H), 2.87 (t, J = 5.9 Hz, 2H), 1.70 (m, 2H), 1.07 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50 MHz) δ 198.3, 190.6, 100.7, 87.4,

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36.4, 25.3, 13.9; IR (KBr) 2968, 2938, 2879, 2809, 2691, 2101, 2059, 2028, 1670, 1580, 1097, 1086 cm^{-1}; MS (EI, *m/z*) 382 (M^+, 10), 354 ($M^+ - CO$, 100), 326 ($M^+ - 2\ CO$, 89), 298 ($M^+ - 3\ CO$, 54), 270 ($M^+ - 4\ CO$, 39), 242 ($M^+ - 5\ CO$, 24); MS (CI, NH_3, *m/z*) 383 ($M + H^+$, 100), 389 ($M + H^+ - CO$, 51); MS (+ve ES, *m/z*) 382.3 (8) [M^+].

General Procedure for Preparation of Dicobalt Pentacarbonyl(triarylphosphine)-Complexed Aldehydes: (3-Phenylpropynal)dicobalt Pentacarbonyl(triphenylphosphine) Complex (26). To a solution of (3-phenylpropynal)-dicobalt hexacarbonyl (0.19 g, 0.45 mmol) in diethyl ether (4.5 mL) and THF (4.5 mL) at 50 °C was added a solution of triphenylphosphine (0.12 g, 0.45 mmol) in diethyl ether (4.5 mL) and THF (4.5 mL). After gentle reflux for 4 h, the solution was cooled to room temperature, and the solvent concentrated under reduced pressure. Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 0.24 g (0.37 mmol, 81%) of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 9.93 (s, 1H), 7.21 (m, 20H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 204.9, 203.7, 199.5, 190.9, 137.9, 133.7, 133.1, 133.0, 132.9, 132.8, 130.3, 130.1, 128.6, 128.5, 128.3, 127.3, 88.2, 79.6; IR (KBr) 2068, 2022, 2005, 1971, 1652, 1480, 1438, 1098, 753, 699 cm^{-1}; MS (+ve ES, *m/z*) 651.0 (7) [$M + 1H]^+$.

(2-Hexynal)dicobalt Pentacarbonyl(triphenylphosphine) Complex (27). Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 84% of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 9.75 (s, 1H), 7.43 (m, 15 H), 2.06 (m, 2H), 1.30 (m, 2H), 0.75 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 205.2, 203.8, 200.4, 191.1, 134.5, 133.7, 133.2, 133.1, 132.9, 130.5, 128.7, 128.5, 97.4, 81.9, 35.0, 24.9, 13.9; IR (KBr) 3061, 2962, 2932, 2875, 2808, 2067, 2011, 1972, 1653, 1436, 1093, 747, 696 cm^{-1}; MS (+ve ES, *m/z*) 617.1 (20) [$M + 1H]^+$.

General Procedure for Allyl and Crotyl Transfer to Noncomplexed and Dicobalt Hexacarbonyl-Complexed Propynals. To a solution of 3-phenylpropynal (0.2 g, 1.53 mmol) and activated crushed 4 Å molecular sieves (0.04 g) in CH_2Cl_2 (30 mL) was added $BF_3{\cdot}OEt_2$ (0.20 mL, 1.58 mmol) at −78 °C under N_2. After stirring for 20 min, allyltributylstannane (0.48 mL, 1.53 mmol) was added. Stirring was continued at −78 °C until the starting material was completely consumed, as determined by TLC. The mixture was then quenched at 0 °C by the addition of a cold aqueous solution of $NaHCO_3$, and the organic layer was separated, extracted with a saturated aqueous NaCl solution, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to give a yellow oil. Separation by flash chromatography (19:1 to 8:2 pentane/diethyl ether) yielded the products **4a**, **10**, **11**, **12**, and **13**.

6-Phenyl-1-hexen-5-yn-4-ol (4a).[42] Isolated 0.184 g (1.07 mmol) of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.42 (m, 2H), 7.29 (m, 3H), 5.94 (m, 1H), 5.22 (m, 2H), 4.64 (t, $J =$ 6.1 Hz, 1H), 2.56 (m, 2H), 2.11 (br s, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 133.0, 131.5, 128.2, 128.1, 122.4, 118.7, 89.4, 85.0, 61.9, 42.0; IR (neat) 3397, 3080, 2981, 2913, 2232, 1642, 1490, 1442, 1031, 757, 692 cm^{-1}; MS (EI, *m/z*) 131 ($M^+ - CH_2CH{=}CH_2$, 100), 77 ($C_6H_5^+$, 36); MS (CI, NH_3, *m/z*) 190 ($M + NH_4^+$, 48), 172 (M^+, 62), 155 ($M^+ - OH$, 100).

2-Methyl-6-phenyl-1-hexen-5-yn-4-ol (4b).[43] Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 71% of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.43 (m, 2H), 7.28 (m, 3H), 4.94 (br s, 1H), 4.91 (br s, 1H), 4.73 (t, $J =$ 6.6 Hz, 1H), 2.55 (d, $J = 6.6$ Hz, 2H), 2.40 (br s, 1H), 1.84 (s, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 140.9, 131.5, 128.2, 128.1, 122.6, 114.2, 60.8, 46.0, 22.6.

***syn*-3-Methyl-6-phenyl-1-hexen-5-yn-4-ol (4c).**[11] Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 88% of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.44 (m, 2H), 7.30 (m, 3H), 5.94 (m, 1H), 5.24 (m, 2H), 4.50 (d, $J = 4.9$ Hz, 1H), 2.54 (m, 1H), 1.19 (d, $J = 6.9$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 138.8, 131.7, 128.3, 128.2, 122.6, 117.2, 88.2, 85.9, 66.4, 44.5, 15.7.

1-Nonen-5-yn-4-ol (5a). Purification by flash chromatography (7:3 pentane/diethyl ether) yielded 68% of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.90 (m, 1H), 5.20 (m, 2H), 4.41 (m, 1H), 2.45 (m, 2H), 2.19 (dt, $J = 1.9$, 7.0 Hz, 2H), 1.48 (m, 2H), 1.25 (br s, 1H), 0.97 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 133.3, 117.7, 84.9, 80.6, 61.4, 42.2, 21.7, 20.3, 13.0; IR (neat) 3398, 3079, 2965, 2874, 2230, 1708, 1642, 1460, 1434, 1032, 916 cm^{-1}.

2-Methyl-1-nonen-5-yn-4-ol (5b). Purification by flash chromatography (8:2 pentane/diethyl ether) yielded 65% of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 4.89 (br s, 1H), 4.83 (br s, 1H), 4.48 (m, 1H), 2.41 (d, $J = 6.6$ Hz, 2H), 2.18 (dt, $J =$ 1.8, 7.0 Hz, 2H), 1.89 (d, $J = 4.4$ Hz, 1H), 1.79 (s, 3H), 1.53 (m, 2H), 0.96 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 141.3, 114.0, 85.4, 80.9, 60.5, 46.5, 22.5, 22.0, 20.6, 13.4; IR (neat) 3387, 3078, 2965, 2936, 2875, 2232, 1649, 1454, 1378, 1051, 1022, 891 cm^{-1}; MS (EI, *m/z*) 137 ($M^+ - CH_3$, 20), 97 ($M^+ - CH_2C(CH_3){=}CH_2$, 100); MS (CI, NH_3, *m/z*) 170 ($M + NH_4^+$, 54), 153 ($M + H^+$, 31), 152 (M^+, 35), 135 ($M^+ - OH$, 100); HRMS (*m/z*) calcd for $C_9H_{13}O$ ($M^+ - CH_3$) 137.0966, found 137.0964.

***syn*-3-Methyl-1-nonen-5-yn-4-ol (5c).** Purification by flash chromatography (8:2 pentane/diethyl ether) yielded 85% of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.82 (m, 1H), 5.12 (m, 2H), 4.25 (m, 1H), 2.43 (m, 1H), 2.19 (dt, $J = 1.7$, 7.0 Hz, 2H), 1.86 (d, $J = 6.8$ Hz, 1H), 1.52 (m, 2H), 1.09 (d, $J = 6.8$ Hz, 3H), 0.97 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 139.1, 116.7, 86.4, 79.2, 66.1, 44.4, 22.0, 20.6, 15.5, 13.4; IR (neat) 3411, 3081, 2967, 2935, 2875, 2247, 1641, 1458, 1380, 1015, 913, 734 cm^{-1}; MS (EI, *m/z*) 137 ($M^+ - CH_3$, 4), 97 ($M^+ - CH_2C(CH_3){=}CH_2$, 100); MS (CI, NH_3, *m/z*) 170 ($M + NH_4^+$, 21), 152 (M^+, 17), 135 ($M^+ - OH$, 19) 97 ($M^+ - CH_2C(CH_3){=}CH_2$, 100); HRMS (*m/z*) calcd for $C_{10}H_{20}NO$ ($M + NH_4^+$) 170.1545, found 170.1543.

(6-Phenyl-1-hexen-5-yn-4-ol)dicobalt Hexacarbonyl Complex (8a). Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 95% of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.55 (m, 2H), 7.35 (m, 3H), 5.99 (m, 1H), 5.26 (m, 2H), 5.08 (m, 1H), 2.68 (m, 1H), 2.46 (m, 1H), 2.22 (d, $J = 3.8$ Hz, 1H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 199.3, 137.6, 134.1, 129.6, 128.8, 127.9, 118.9, 100.2, 90.8, 71.5, 43.9; IR (KBr) 3467, 3080, 2092, 2053, 2021, 1612, 1483, 1442, 1050, 760, 692 cm^{-1}; MS (EI, *m/z*) 430 ($M^+ - CO$, 5), 402 ($M^+ - 2\ CO$, 35), 374 ($M^+ - 3\ CO$, 12), 346 ($M^+ - 4\ CO$, 26), 318 ($M^+ - 5\ CO$, 48), 290 ($M^+ - 6\ CO$, 100); MS (CI, NH_3, *m/z*) 441 ($M^+ - OH$, 100), 413 ($M^+ - OH - CO$, 68), 385 ($M^+ - OH - 2\ CO$, 80), 346 ($M^+ - 4\ CO$, 63), 290 ($M^+ - 6\ CO$, 72); MS (−ve ES, *m/z*) 456.9 (100) [$M - 1H]^-$, 457.9 (24) [M].

(2-Methyl-6-phenyl-1-hexen-5-yn-4-ol)dicobalt Hexacarbonyl Complex (8b). Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 96% of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.57 (m, 2H), 7.35 (m, 3H), 5.16 (m, 1H), 5.01 (br s, 1H), 4.97 (br s, 1H), 2.64 (m, 1H), 2.40 (m, 1H), 2.34 (s, 1H) 1.89 (s, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 199.5, 141.8, 137.6, 129.6, 128.8, 127.8, 114.6, 100.2, 90.4, 69.5, 48.2, 22.2; IR (KBr) 3079, 3019, 2925, 2856, 2093, 2055, 2025, 1217, 1067, 759 cm^{-1}; MS (EI, *m/z*) 416 ($M^+ - 2\ CO$, 22), 388 ($M^+ - 3\ CO$, 13), 360 ($M^+ - 4\ CO$, 20), 332 ($M^+ - 5\ CO$, 46), 304 ($M^+ - 6\ CO$, 100); MS (CI, NH_3, *m/z*) 455 ($M^+ - OH$, 100), 427 ($M^+ - OH - CO$, 53), 399 ($M^+ - OH - 2\ CO$, 79); MS (−ve ES, *m/z*) 471.1 (100) [$M - 1H]^-$, 507.1 (22) [$M + {}^{35}Cl]^-$, 509.1 (7) [$M + {}^{37}Cl]^-$.

(*syn*-3-Methyl-6-phenyl-1-hexen-5-yn-4-ol)dicobalt Hexacarbonyl Complex (8c). Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 83% of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.51 (m, 2H), 7.31 (m, 3H), 5.90 (m, 1H), 5.12 (m, 2H), 4.98 (m, 1H), 2.56 (m, 1H), 2.13 (d, $J = 4.6$ Hz, 1H), 1.17 (d, $J = 6.8$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 199.6, 140.4, 137.7, 129.8, 128.8, 127.8, 116.1, 99.4, 92.5, 76.5,

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45.6, 14.9; IR (KBr) 3444, 3081, 2972, 2933, 2091, 2052, 2023, 1596, 1487, 1444, 1029, 920, 758 cm^{-1}; MS (EI, *m/z*) 416 ($M^+ - 2$ CO, 30), 388 ($M^+ - 3$ CO, 10), 360 ($M^+ - 4$ CO, 28), 332 ($M^+ - 5$ CO, 48), 304 ($M^+ - 6$ CO, 100); MS (CI, NH_3, *m/z*) 455 ($M^+ - OH$, 100), 427 ($M^+ - OH - CO$, 91), 399 ($M^+ - OH - 2$ CO, 58); MS (−ve ES, *m/z*) 471.1 (100) $[M - 1H]^-$, 507.1 (16) $[M + {}^{35}Cl]^-$, 509.1 (5) $[M + {}^{37}Cl]^-$.

(*anti*-3-Methyl-6-phenyl-1-hexen-5-yn-4-ol)dicobalt Hexacarbonyl Complex (8d). ^1H NMR ($CDCl_3$, 200 MHz): δ 7.51 (m, 2H), 7.31 (m, 3H), 5.90 (m, 1H), 5.20 (m, 2H), 4.78 (m, 1H), 2.37 (m, 1H), 2.35 (d, $J = 3.7$ Hz, 1H), 1.06 (d, $J = 6.8$ Hz, 3H).

(1-Nonen-5-yn-4-ol)dicobalt Hexacarbonyl Complex (9a). Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 94% of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.93 (m, 1H), 5.24 (m, 2H), 4.82 (m, 1H), 2.80 (m, 2H), 2.46 (m, 2H), 2.01 (d, $J = 4.3$ Hz, 1H), 1.65 (m, 2H), 1.07 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 199.8, 134.0, 118.7, 100.3, 98.6, 71.5, 43.8, 35.9, 25.2, 14.1; IR (KBr) 3468, 3083, 2966, 2937, 2878, 2090, 2045, 2019, 1642, 1611, 1434, 1380, 1046, 997, 920 cm^{-1}; MS (EI, *m/z*) 396 ($M^+ - CO$, 7), 368 ($M^+ - 2$ CO, 65), 340 ($M^+ - 3$ CO, 54), 312 ($M^+ - 4$ CO, 84), 284 ($M^+ - 5$ CO, 90), 256 ($M^+ - 6$ CO, 100); MS (CI, NH_3, *m/z*) 424 (M^+, 6), 407 ($M^+ - OH$, 100), 379 ($M^+ - OH - CO$, 30), 351 ($M^+ - OH - 2$ CO, 18); MS (−ve ES, *m/z*) 423.2 (100) $[M - 1H]^-$, 459.1 (15) $[M + {}^{35}Cl]^-$, 461.1 (5) $[M + {}^{37}Cl]^-$.

(2-Methyl-1-nonen-5-yn-4-ol)dicobalt Hexacarbonyl Complex (9b). Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 93% of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 4.93 (m, 2H), 4.89 (m, 1H), 2.81 (m, 2H), 2.49 (m, 1H), 2.30 (m, 1H), 2.07 (d, $J = 3.5$ Hz, 1H), 1.85 (s, 3H), 1.68 (m, 2H), 1.07 (t, $J = 7.3$ Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 200.0, 141.7, 114.3, 100.4, 98.5, 69.4, 48.0, 35.8, 25.2, 22.2, 14.1; IR (KBr) 3478, 3081, 2966, 2937, 2878, 2090, 2047, 2018, 1649, 1611, 1456, 1378, 1059, 898 cm^{-1}; MS (EI, *m/z*) 410 ($M^+ - CO$, 8), 382 ($M^+ - 2$ CO, 71), 354 ($M^+ - 3$ CO, 65), 326 ($M^+ - 4$ CO, 84), 298 ($M^+ - 5$ CO, 100), 270 ($M^+ - 6$ CO, 83); MS (CI, NH_3, *m/z*) 421 ($M^+ - OH$, 100), 393 ($M^+ - OH - CO$, 26), 365 ($M^+ - OH - 2$ CO, 24); MS (-ve ES, *m/z*) 437.2 (100) $[M - 1H]^-$, 473.2 (26) $[M + {}^{35}Cl]^-$, 475.2 (9) $[M + {}^{37}Cl]^-$.

(*syn*-3-Methyl-1-nonen-5-yn-4-ol)dicobalt Hexacarbonyl Complex (9c). Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 80% of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.85 (m, 1H), 5.15 (m, 2H), 4.57 (dd, $J =$ 5.5, 7.2 Hz, 1H), 2.79 (m, 2H), 2.42 (m, 1H), 1.86 (d, $J = 5.4$ Hz, 1H), 1.62 (m, 2H), 1.23 (d, $J = 6.8$ Hz, 3H), 1.06 (t, $J =$ 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 199.9, 139.9, 116.2, 100.2, 99.2, 76.1, 46.2, 36.3, 25.2, 17.1, 14.1; IR (KBr) 3479, 3081, 3021, 2962, 2930, 2875, 2089, 2032, 2010, 1460, 1217, 1024, 924, 773 cm^{-1}; MS (EI, *m/z*) 410 ($M^+ - CO$, 16), 382 ($M^+ - 2$ CO, 100), 354 ($M^+ - 3$ CO, 34), 326 ($M^+ - 4$ CO, 44), 298 ($M^+ - 5$ CO, 32), 270 ($M^+ - 6$ CO, 47); MS (CI, NH_3, *m/z*) 421 ($M^+ - OH$, 100), 393 ($M^+ - OH - CO$, 66), 365 ($M^+ - OH - 2$ CO, 55), 337 ($M^+ - OH - 3$ CO, 22); MS (-ve ES, *m/z*) 437.2 (74) $[M - 1H]^-$, 517.1 (42) $[M + {}^{79}Br]^-$, 519.1 (40) $[M + {}^{81}Br]^-$.

(*anti*-3-Methyl-1-nonen-5-yn-4-ol)dicobalt Hexacarbonyl Complex (9d). Purification by flash chromatography (9:1 pentane/diethyl ether) yielded 14% of a red solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 5.91 (m, 1H), 5.24 (m, 2H), 4.46 (dd, $J =$ 3.9, 7.5 Hz, 1H), 2.79 (m, 2H), 2.33 (m, 1H), 2.15 (d, $J = 3.9$ Hz, 1H), 1.65 (m, 2H), 1.14 (d, $J = 6.8$ Hz, 3H), 1.07 (t, $J =$ 7.4 Hz, 3H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 200.2, 139.8, 117.5, 99.7, 98.6, 75.1, 47.2, 36.3, 25.2, 17.0, 14.2.

Di-4-(6-phenyl-1-hexen-5-yn) Ether (enantiomers (4*R*,4′*R* and 4*S*,4′*S*) or meso compound) (10). Isolated 0.027 g (0.17 mmol) of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.47 (m, 4H), 7.33 (m, 6H), 6.00 (m, 2H), 5.20 (m, 4H), 4.79 (t, $J =$ 6.5 Hz, 2H), 2.63 (m, 4H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 133.6, 131.7, 128.2, 128.1, 122.7, 117.6, 87.5.0, 86.2, 67.4, 40.1; IR (neat) 3079, 2980, 2918, 2865, 2231, 1642, 1599, 1490, 1443, 1341, 1070, 917, 756, 691 cm^{-1}; MS (EI, *m/z*) 285 ($M^+ - CH_2CH{=}CH_2$, 10), 155 ($M^+ - C_6H_5C_2CH(O)CH_2CH{=}CH_2$, 100), 77 ($C_6H_5^+$, 16); MS (CI, NH_3, *m/z*) 344 ($M + NH_4^+$, 33), 285 ($M^+ - CH_2CH{=}CH_2$, 16), 172 ($M + H^+ - C_6H_5C_2CHCH_2CH{=}CH_2$, 58), 155 ($M^+ - C_6H_5C_2CH(O)CH_2CH{=}CH_2$, 100).

Di-4-(6-phenyl-1-hexen-5-yn) Ether (enantiomers (4*R*,4′*R* and 4*S*,4′*S*) or meso compound) (11). Isolated 0.029 g (0.18 mmol) of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.43 (m, 4H), 7.28 (m, 6H), 5.99 (m, 2H), 5.20 (m, 4H), 4.63 (t, $J =$ 6.5 Hz, 2H), 2.63 (m, 4H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 133.5, 131.7, 128.3, 128.2, 122.7, 117.9, 88.0, 86.2, 68.6, 40.1; MS (EI, *m/z*) 285 ($M^+ - CH_2CH{=}CH_2$, 8), 155 ($M^+ - C_6H_5C_2CH(O)CH_2CH{=}CH_2$, 100), 77 ($C_6H_5^+$, 63); MS (CI, NH_3, *m/z*) 344 ($M + NH_4^+$, 69), 285 ($M^+ - CH_2CH{=}CH_2$, 21), 172 ($M + H^+ - C_6H_5C_2CHCH_2CH{=}CH_2$, 65), 155 ($M^+ - C_6H_5C_2CH(O)CH_2CH{=}CH_2$, 100).

(*Z*)-6-Phenyl-1,3-hexadien-5-yne (12).[44] Isolated 0.013 g (0.07 mmol) of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.44 (m, 2H), 7.30 (m, 3H), 6.97 (ddd, $J = 16.6$, 10.6, 10.0 Hz, 1H), 6.43 (dd, $J = 10.8$, 10.6 Hz, 1H), 5.68 (d, $J = 10.8$ Hz, 1H), 5.40 (dd, $J = 16.6$, 1.4 Hz, 1H), 5.31 (dd, $J = 10.0$, 1.4 Hz, 1H).

4-(Phenylacetylene)-1,6-heptadiene (13). Isolated 0.004 g (0.02 mmol) of a colorless oil: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.37 (m, 2H), 7.26 (m, 3H), 5.94 (m, 2H), 5.10 (m, 4H), 2.69 (quintet, $J = 4.5$ Hz, 1H), 2.31 (dd, $J = 4.5$, 4.5 Hz, 4H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 135.8, 131.6, 128.1, 127.5, 123.8, 116.7, 92.2, 82.4, 38.6, 32.0; IR (neat) 3079, 2962, 2928, 1724, 1642, 1599, 1490, 1442, 1262, 1070, 1030, 997, 916, 756 cm^{-1}; MS (EI, *m/z*) 196 (M^+, 7), 168 ($M^+ - CH_2{=}CH_2$, 26), 155 ($M^+ - CH_2CH{=}CH_2$, 79), 129 ($M^+ - HC{\equiv}CH - CH_2CH{=}CH_2$, 45), 77 ($C_6H_5^+$, 44), 43 ($C_3H_7$, 100); MS (CI, NH_3, *m/z*) 197 ($M + H^+$, 40), 155 ($M^+ - CH_2CH{=}CH_2$, 25), 76 ($C_6H_4^+$, 100).

(4-(Phenylacetylene)-1,6-heptadiene)dicobalt Hexacarbonyl Complex (14). To a solution of (3-phenylpropynal)-dicobalt hexacarbonyl (0.22 g, 0.52 mmol) and $BF_3{\cdot}OEt_2$ (0.15 mL, 1.19 mmol) in CH_2Cl_2 (11 mL) at −78 °C under N_2 was added allyltributylstannane (0.37 mL, 1.19 mmol). Stirring at −78 °C was continued until the starting material could no longer be detected by TLC. After quenching the reaction mixture at 0 °C by adding a cold aqueous solution of $NaHCO_3$, the organic layer was separated, extracted with aqueous NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure. The mixture was purified by flash chromatography (9:1 pentane/diethyl ether) to yield 0.21 g (0.45 mmol, 87%) of a brown solid: ^1H NMR ($CDCl_3$, 200 MHz) δ 7.39 (m, 2H), 7.27 (m, 3H), 5.84 (m, 2H), 5.05 (m, 4H), 3.23 (quintet, $J = 6.6$ Hz, 1H), 2.44 (dd, $J = 6.6$, 6.1 Hz, 4H).

General Procedure for Oxidative Decomplexation of the Dicobalt Cluster. To a solution of **14** (0.21 g, 0.45 mmol) in CH_3OH (4 mL) at 25 °C was added trimethylamine *N*-oxide (0.30 g, 3.99 mmol). The reaction mixture was stirred at 25 °C until the starting material could no longer be detected by TLC. It was then filtered through glass wool and brought to a volume of approximately 20 mL by the addition of diethyl ether. The organic layer was extracted with a saturated aqueous solution of NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield 0.075 g (0.38 mmol, 85%) of a yellow oil. The product was confirmed to be 4-(phenylacetylene)-1,6-heptadiene (**13**) by comparing its ^1H NMR spectrum with that previously obtained.

***syn*-(5*E*)-3-Methyl-1,5-nonadien-4-ol (15).**[12,13] To a solution of *syn*-3-methyl-1-nonen-5-yn-4-ol (**5c**) (0.050 g, 0.32 mmol) in THF (3.5 mL) was added $LiAlH_4$ (0.018 g, 0.47 mmol) at 25 °C. The reaction mixture was refluxed for 12 h, then cooled to 0 °C and quenched by the dropwise addition of 10 mL of a cold aqueous solution of 2 N H_2SO_4. Diethyl ether (5

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mL) was added to the flask, and the organic layer was separated, extracted with a saturated aqueous solution of NaCl, dried over $MgSO_4$, filtered, and concentrated under reduced pressure to yield 0.045 g of a mixture of **5c** and **15**. Compound **15**: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 5.82 (m, 1H), 5.70−5.39 (m, 2H), 5.11 (br s, 1H), 5.05 (br s, 1H), 3.97 (m, 1H), 2.41 (m, 1H), 2.02 (m, 2H), 1.40 (m, 2H), 1.03 (d, J = 6.8 Hz, 3H), 0.89 (t, J = 7.3 Hz, 3H).

General Procedure for Allyl Transfer to Dicobalt Pentacarbonyl(triarylphosphine)-Complexed Propynals. Entries 1 to 3 of Table 3 correspond to reactions in which the reagents were all added to a flask immersed in a cooling bath at a temperature of −78 °C, as described for the preparation of 6-phenyl-1-hexen-5-yn-4-ol (**4a**). The temperature of the cooling bath was allowed to warm to 25 °C over a period of approximately 4, 6, and 12 h, for entries 1, 2, and 3, respectively. Entries 4 to 9 correspond to reactions in which the reagents were added, and the cooling bath was maintained, at the temperature specified for the duration of the reaction. The reaction mixtures were all quenched at 0 °C by the addition of a cold aqueous solution of $NaHCO_3$ and worked up as described for **4a**.

(6-Phenyl-1-hexen-5-yn-4-ol)dicobalt Pentacarbonyl(triphenylphosphine) Complex (28, 29). Major Diastereomer. Purification by flash chromatography (8:2 pentane/diethyl ether) yielded 87% of a red solid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.27 (m, 20H), 5.74 (m, 1H), 5.09 (m, 2H), 3.92 (m, 1H), 2.29 (m, 1H), 2.10 (m, 1H), 1.97 (d, J = 4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 200 MHz) δ 205.0, 205.1, 201.4, 139.3, 135.3, 134.4, 133.6, 133.1, 133.0, 130.3, 130.1, 128.4, 128.4, 128.2, 128.2, 126.5, 117.1, 96.1, 83.9, 70.0, 44.1; IR (KBr) 3311, 3078, 3059, 2908, 2858, 2058, 2008, 1961, 1642, 1593, 1488, 1438, 1182, 1120, 1069, 997, 916, 756, 723, 694 cm^{-1}; MS (−ve ES, *m/z*) 726.8 (62) [M + ^{35}Cl]$^-$, 728.8 (27) [M + ^{37}Cl]$^-$.

(6-Phenyl-1-hexen-5-yn-4-ol)dicobalt Pentacarbonyl(triphenylphosphine) Complex (28,29). Minor Diastereomer. Purification by flash chromatography (8:2 pentane/diethyl ether) yielded 13% of a red solid: ^{1}H NMR ($CDCl_3$, 500 MHz) δ 7.27 (m, 20H), 5.74 (m, 1H), 5.14 (m, 2H), 4.06 (m, 1H), 2.65 (m, 1H), 2.29 (m, 1H), 1.64 (d, J = 4.7 Hz, 1H); ^{13}C NMR ($CDCl_3$, 500 MHz) δ 205.5, 205.4, 201.3, 139.3, 135.1, 134.1, 133.8, 132.9, 132.8, 130.3, 130.0, 128.4, 128.4, 128.3, 128.3, 126.5, 117.8, 93.9, 86.8, 70.1, 44.0.

(*Z*)-6-Phenyl-1,3-hexadien-5-yne)dicobalt Pentacarbonyl(triphenylphosphine) Complex (30). Isolated by flash chromatography (8:2 pentane/diethyl ether) from the reactions described in entries 1 to 3 in Table 3. After oxidative decomplexation using trimethylamine *N*-oxide, the compound was confirmed to be (*Z*)-6-phenyl-1,3-hexadien-5-yne by comparison of its ^{1}H NMR spectrum with that previously obtained.

(2-Methyl-6-phenyl-1-hexen-5-yn-4-ol)dicobalt Pentacarbonyl(triphenylphosphine) Complex (31, 32). Purification by flash chromatography (8:2 pentane/diethyl ether) yielded 92% of a red solid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.25 (m, 20H), 4.80 (br s, 1H), 4.72 (br s, 1H), 4.0 (m, 1H), 2.25 (m, 1H), 2.03 (m, 1H), 1.71 (d, J = 3.5 Hz, 1H) 1.58 (s, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 206.8, 206.7, 201.8, 142.5, 139.4, 134.3, 133.5, 133.2, 133.0, 130.1, 130.1, 128.3, 128.3, 128.1, 128.1, 126.5, 113.2, 96.3, 83.1, 67.7, 48.3, 22.3; IR (KBr) 3380, 3077, 3062, 2968, 2917, 2857, 2059, 2007, 1963, 1647, 1489, 1438, 1179, 1120, 1059, 1027, 849, 757, 723, 693 cm^{-1}; MS (−ve ES, *m/z*) 705.3 (4) [M − 1H]$^-$, 741.2 (7) [M + ^{35}Cl]$^-$, 743.2 (3) [M + ^{37}Cl]$^-$.

(1-Nonen-5-yn-4-ol)dicobalt Pentacarbonyl(triphenylphosphine) Complex (33, 34). Major Diastereomer. Purification by flash chromatography (7:3 pentane/diethyl ether) yielded 80% of a red solid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.56 (6H), 7.42 (m, 9H), 5.64 (m, 1H), 5.00 (m, 2H), 3.91 (m, 1H), 2.15 (m, 2H), 1.61 (m, 2H), 1.46 (m, 2H), 0.79 (t, J = 7.1 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 205.8, 205.7, 202.0, 135.2, 135.1, 134.2, 133.0, 132.8, 130.3, 130.3, 128.6, 128.4, 117.2, 95.1, 94.4, 70.5, 43.6, 33.7, 25.1, 13.9; IR (KBr) 3583, 3062, 3011, 2961, 2934, 2875, 2057, 1996, 1959, 1482, 1436, 1092, 918, 758, 697 cm^{-1}; MS (−ve ES, *m/z*) 656.9 (100) [M − 1H]$^-$.

(1-Nonen-5-yn-4-ol)dicobalt Pentacarbonyl(triphenylphosphine) Complex (33, 34). Minor Diastereomer. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 205.8, 205.7, 202.0, 135.3, 135.2, 134.5, 133.0, 132.8, 130.3, 130.3, 128.6, 128.4, 117.6, 96.3, 94.6, 71.2, 44.1, 34.6, 25.2, 14.0.

(2-Methyl-1-nonen-5-yn-4-ol)dicobalt Pentacarbonyl(triphenylphosphine) Complex (36, 37). Major Diastereomer. Purification by flash chromatography (7:3 pentane/diethyl ether) yielded 79% of a red solid: ^{1}H NMR ($CDCl_3$, 200 MHz) δ 7.55 (m, 6H), 7.42 (m, 9H), 4.78 (br s, 1H), 4.68 (br s, 1H), 4.14 (m, 1H), 2.09 (m, 2H), 1.65 (m, 2H), 1.57 (m, 2H), 1.55 (s, 3H), 0.82 (t, J = 7.3 Hz, 3H); ^{13}C NMR ($CDCl_3$, 50.3 MHz) δ 205.7, 205.5, 201.4, 142.3, 135.1, 134.3, 133.1, 132.9, 130.3, 130.3, 128.6, 128.4, 113.1, 95.2, 94.2, 68.5, 47.7, 33.6, 25.0, 22.3, 13.9; IR (KBr) 3344, 3062, 2961, 2931, 2873, 2055, 1998, 1959, 1437, 1185, 1120, 1092, 746, 723, 696 cm^{-1}; MS (−ve ES, *m/z*) 671.3 (100) [M − 1H]$^-$, 707.3 (50) [M + ^{35}Cl]$^-$, 709.3 (22) [M + ^{37}Cl]$^-$.

(2-Methyl-1-nonen-5-yn-4-ol)dicobalt Pentacarbonyl(triphenylphosphine) Complex (36,37). Minor Diastereomer. ^{13}C NMR ($CDCl_3$, 50.3 MHz): δ 205.7, 205.5, 201.4, 142.7, 135.3, 134.5, 133.1, 132.9, 130.3, 130.3, 128.6, 128.4, 113.3, 96.6, 94.3, 69.5, 48.3, 34.7, 25.2, 22.6, 14.1.

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