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Regioselectivity of nucleophilic additions to substituted (η^4-diene)$Co(CO)_3BF_4$ complexes

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Abstract

The addition of several nucleophiles to a series of (η^4-diene)$Co(CO)_3BF_4$ complexes has been examined in order to probe the effect of diene substituents and the nature of the nucleophile on the regioselectivity of attack on the coordinated diene. The dienes include 1-substituted dienes: *trans*-1,3-pentadiene (piperylene), 1-trimethylsilyl-2,4-pentadiene; 2-substituted dienes: 2-methyl- (isoprene), 2-ethyl-, 2-phenyl-, 2-*para*-fluorophenyl-, and 2-trimethylsilylmethyl-1,3-butadiene; and the disubstituted diene 2-methyl-1,3-pentadiene. The set of nucleophiles includes $NaBH_3CN$, C_6H_5MgBr, $P(CH_3)_3$, C_5H_5N (pyridine), and $N(CH_2CH_3)_3$. The reactions occur generally with a high degree of regioselectivity according to the following trends: (1) addition of nucleophiles to most complexes occurs preferentially or exclusively at C(4) (terminal diene carbon remote from the substituent); (2) noteworthy exceptions include the isoprene complex, in which modest C(1) addition selectivity is observed with Nu = $NaBH_3CN$, C_6H_5MgBr, $P(CH_3)_3$ and the dimethyl derivative (for Nu = pyridine); and (3) the selectivity for C(4) attack is nucleophile dependent, decreasing in the order $N(CH_2CH_3)_3$ > pyridine > $P(CH_3)_3$ > C_6H_5MgBr > $NaBH_3CN$. A combination of steric and frontier molecular orbital effects is proposed to explain the observed regioselectivity.

Introduction

The addition of nucleophiles to π-complexed unsaturated hydrocarbon ligands is a reaction of considerable generality [1] which has found important utility in both stoichiometric and catalytic processes. The considerable regio- and stereo-selectivities associated with these reactions have invited increasing theoretical interest as well [2].

Recently we have become interested in the relatively little explored nucleophilic addition reactions of coordinated dienes. Our interest was originally piqued by contrasting reports of the regioselectivity of nucleophilic addition to dienes coordi-

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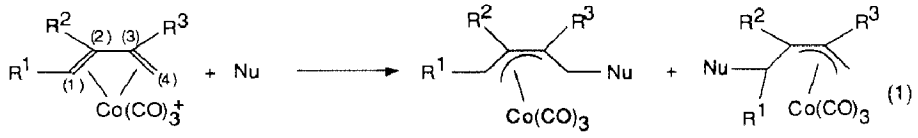
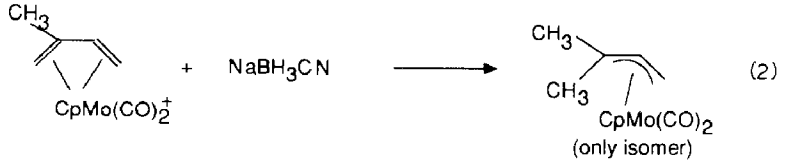
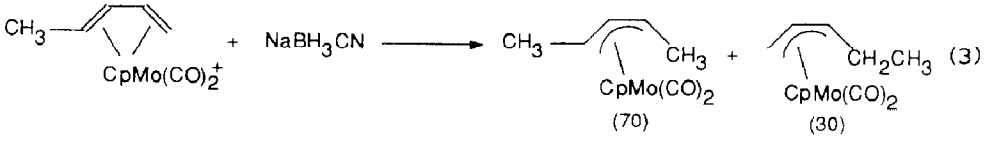
nated to different metal fragments: i.e. $MoCp(CO)_2^+$ [3], PdX_2 [4], and $Fe(CO)_3$ [5]. The first two systems undergo selective attack on the terminal diene carbon (C(1)) whereas the latter suffers attack at the internal carbon (C(2)). In exploring the origin of this apparent metal-dependent selectivity we found that (η^4-diene)$Co(CO)_3^+$ complexes, isoelectronic with the Fe complexes yet charged like the Mo derivatives, are attacked specifically at C(1) by a variety of carbon- and hetero-nucleophiles [6]. A recent theoretical analysis [7] has accounted for these observations in terms of a balance of frontier orbital interactions. For the more electron deficient Co^I, Mo^{II} and Pd^{II} complexes the dominant Nu/complex interaction is $HOMO_{Nu}$/$LUMO_{complex}$ which is maximized for most nucleophiles during attack at C(1). In the neutral Fe^0 complex this interaction is counterbalanced by a repulsive $HOMO_{Nu}$/$HOMO_{complex}$ interaction which favors attack at C(2) for many nucleophiles.

In attempting to further our understanding of the factors controlling the regioselectivity of nucleophilic additions to diene complexes, we now consider the question of the directing effects of diene substituents on the position of attack in unsymmetrical complexes as in eq. 1.



This issue is not only of fundamental interest but also of central importance to the future synthetic utilization of these complexes via the facile double nucleophilic additions which we have recently discovered [6,8]. At the outset of our study there were but a few examples of nucleophilic additions to unsymmetrically substituted diene complexes, these coming in the $CpMo(CO)_2(diene)^+$ system [3b] which are summarized in eq. 2, 3.

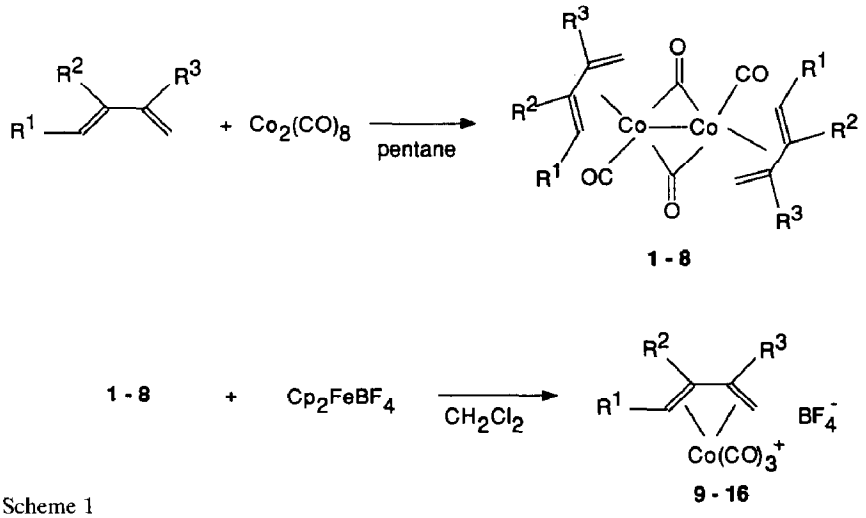




The highly selective C(1) addition to the isoprene complex (eq. 2) is especially intriguing because of its contrasteric nature. Interpretation of the origin of this interesting selectivity is complicated by the presence of equilibrating *endo*/*exo* isomers in both the diene and allyl complexes, a fact which Faller and coworkers suggested was important in determining the observed product ratios [3b].

Results

The first task at hand was the preparation of a series of 1- and 2-substituted diene complexes representing a range of steric and electronic properties. Complexes



Scheme 1

9–16 were prepared in a two step process via the dimeric precursors **1–8** according to Scheme 1. Using the method originally reported by the Fischer [9a] and Wilkinson [9b] groups, gentle heating of several alkyl- and aryl-substituted dienes with $Co_2(CO)_8$ produced the corresponding dimers **2–9** as orange-red somewhat air sensitive solids in generally good to excellent yields (68–95%). These were characterized spectroscopically and generally exist in solution as mixtures of *syn* and *anti* isomers. The general thermal and vacuum instability of these complexes, however, prevented us from obtaining analytically pure samples. We were unsuccessful in synthesizing stable complexes of some dienes containing strongly electron-withdrawing, -donating or sterically-demanding substituents, e.g. 2-chloro and 2-t-butyl.

Oxidation of the dimers **1–8** with ferricinium tetrafluoroborate [6] afforded the desired cationic diene complexes **9–16** in modest yield (20–45%) as yellow solids which were characterized by IR, ^1H NMR and FAB MS. Solution state lability of these species, however, prevented the acquisition of analytically pure samples.

A set of five nucleophiles: $NaBH_3CN$, C_6H_5MgBr, $P(CH_3)_3$, C_5H_5N (pyridine), and $N(CH_2CH_3)_3$, representing a variety of attacking atoms and electronic and steric properties was selected for reaction with complexes **9–16**. Each of these nucleophiles (1.0–1.1 equiv) reacts rapidly (minutes) with the diene complexes at or below 0 °C. Solvents for the reactions were chosen according to reagent solubility and complex stability/solubility: nitromethane (for $NaBH_3CN$ and $P(CH_3)_3$), diethyl ether (for PhMgBr), dichloromethane (for pyridine and $N(CH_2CH_3)_3$). Reaction progress was conveniently monitored by the disappearance of the high frequency M–C≡O IR stretching absorptions of the starting cationic complexes (ca. 2140, 2100 cm^{-1}) and the appearance of the corresponding lower frequency absorptions (ca. 2060, 1990 cm^{-1}) for the resulting neutral (η^3-allyl)cobalt adducts.

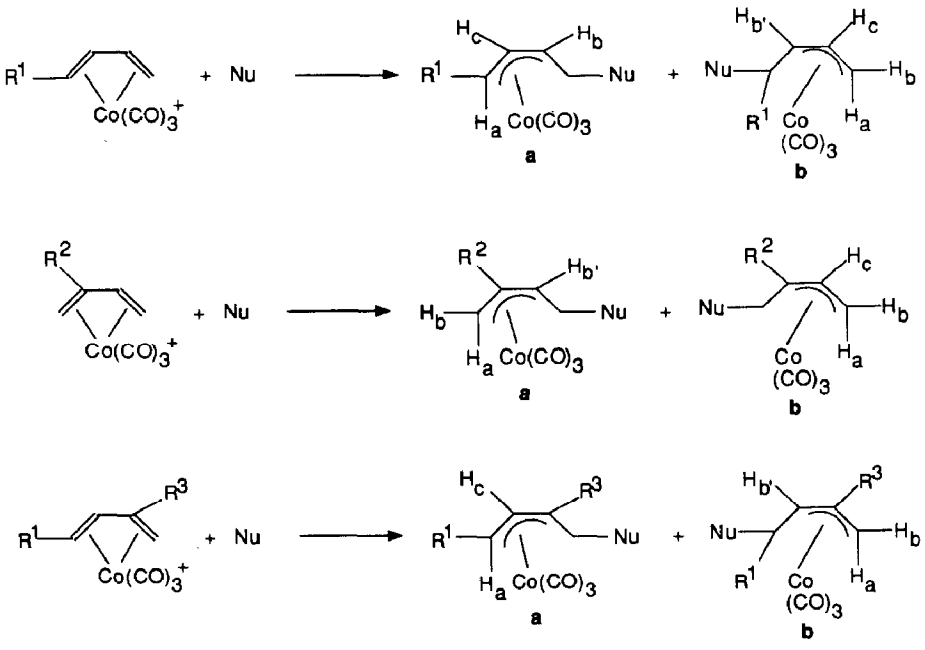
Because of the limited thermal and oxidative stability of most of the adducts and in an effort to minimize the possibility of product isomerization during isolation/purification, workup procedures were kept simple. Thus, the complex salts produced from the reactions with neutral nucleophiles ($P(CH_3)_3$, C_5H_5N (pyridine), and

Table 1

Regioselectivity of nucleophilic addition to substituted (η^4-Diene)$Co(CO)_3BF_4$ according to scheme 2 [a] (a : b)

Complex	R^1	R^2	R^3	$NaBH_3CN$	C_6H_5MgBr	$P(CH_3)_3$	pyridine	$N(CH_2CH_3)_3$
9	CH_3	H	H	3 : 1(56%, **17**)	> 20 : 1 (67%, **18**) [b,c]	> 20 : 1 (76%, **19**) [b]	> 20 : 1 (77%, **20**) [b]	> 20 : 1 (100%, **21**) [b]
10	CH_2SiMe_3	H	H	3 : 1 (45%, **22**)	> 20 : 1 (100%, **23**) [b,c]	> 20 : 1 (69%, **24**) [b]	> 20 : 1 (100%, **25**) [b]	> 20 : 1 (100%, **26**) [b]
11	H	CH_3	H	2 : 3 (70%, **27**)	1 : 3 (82%, **28**) [c]	2 : 3 (83%, **29**)	> 20 : 1 (91%, **30**) [b]	> 20 : 1 (100%, **31**) [b]
12	H	CH_2CH_3	H	2.3 : 1 (100%, **32**)	> 20 : 1 (100%, **33**) [c]	1 : 1 (100%, **34**)	> 20 : 1 (100%, **35**) [b]	> 20 : 1 (100%, **36**) [b]
13	H	C_6H_5	H	3 : 1 (90%, **37**)	2 : 1 (100%, **38**) [c]	> 20 : 1 (83%, **39**) [b]	> 20 : 1 (83%, **40**) [b]	> 20 : 1 (100%, **41**) [b]
14	H	*p*-FC_6H_4	H	4 : 1 (43%, **42**)	1.5 : 1 (100%, **43**) [c]	> 20 : 1 (86%, **44**) [b]	> 20 : 1 (75%, **45**) [b]	> 20 : 1 (100%, **46**) [b]
15	H	CH_2SiMe_3	H	> 20 : 1 (79%, **47**)	> 20 : 1 (100%, **48**) [b,c]	[d]	> 20 : 1 (100%, **49**) [b]	[d]
16	CH_3	H	CH_3	4 : 1 (100%, **50**)	> 20 : 1 (83%, **51**) [b,c]	> 20 : 1 (91%, **52**) [b]	1 : 1 (90%, **53**)	> 20 : 1 (100%, **54**) [b]

[a] Isolated yield in parenthesis. [b] Minor isomer not detected by NMR. [c] Product contaminated with biphenyl from C_6H_5MgBr decomposition. [d] Reaction not conducted.



Scheme 2

$N(CH_2CH_3)_3$) were isolated as yellow powders by direct precipitation from the reaction mixture with a large volume of diethyl ether. The neutral adducts from the reactions with $NaBH_3CN$ (yellow oils) were extracted into pentane and analyzed following solvent removal; the PhMgBr adducts (yellow oils or low melting solids) were isolated after rapid filtration of the reaction solution through alumina. No attempts were made to separate isomeric products (where obtained) but rather the mixtures were analyzed directly. The various products **18–50** (Table 1, vide infra) were characterized spectroscopically with a combination of IR, MS and ^1H NMR. Since the latter tool was routinely used to establish the regiochemical outcome of the reactions, we describe below generally how the isomeric product composition was determined from analysis of the product mixtures by NMR.

Earlier studies and the present examples indicate that *anti* → *syn* isomerization does not occur for (allyl)$Co(CO)_3$ complexes at these moderate temperatures [6,10] simplifying the NMR analysis. Thus, addition of a nucleophile to a 1-substituted diene complex (Scheme 2) can lead to two different regioisomers (**a** or **b**) depending upon which diene terminus is attacked.

Type **b** isomers typically exhibit a characteristic pattern (amongst other absorptions) for H_a at ca. 2.5 (d, J ca. 13 Hz) *, H_b at ca. 3.2 (d, J ca. 7 Hz) and H_c at ca. 4.5 (m) ppm, whereas type **a** isomers exhibit a complex multiplet for H_b. Regioisomeric adducts **a** and **b** derived from nucleophilic addition to the termini of 2-substituted diene complexes are distinguishable by the appearance of the H_a and H_b resonances of the former as singlets and of those the latter as doublets (J_{trans} ca. 12 Hz, J_{cis} ca. 7 Hz). Finally, adducts **a**, **b** derived from nucleophilic addition to a 1,3-disubstituted complex are distinguishable by the appearance of singlet absorp-

* Geminal coupling between $H_{a,b}$ is generally < 1 Hz.

tions for H_a and H_b in **b** and doublets for these proton resonances in **a**. Selective homonuclear decoupling experiments aided in spectral assignments where necessary. Regioisomer ratios ($\pm 10\%$) were then determined by comparative integration of one or more sets of signals associated with each isomer.

The results of the reactions of the set of five nucleophiles with complexes **9–16** are summarized in Table 1. In general the reactions were found to proceed in good to excellent yield. In considering the regiochemical course of the reactions it is convenient first to group these results according to the classes of substituted diene, i.e. 1- and 2-substituted and 1,3-disubstituted. The 1-substituted complexes **9** and **10** behaved identically, giving exclusively the products of C(4) attack with C_6H_5MgBr, $P(CH_3)_3$, C_5H_5N (pyridine), and $N(CH_2CH_3)_3$ and a predominance (3/1) of the same with $NaBH_3CN$. On the other hand the results for the 2-substituted diene complexes were found to be more sensitive to the diene substituent and the nature of the nucleophile. The isoprene complex **11** undergoes specific C(4) attack by pyridine and $N(CH_2CH_3)_3$ but exhibits a modest preference for C(1) attack with the other nucleophiles. The 2-ethyl-substituted complex **12** shows a greater propensity for C(4) attack, this pathway being the exclusive one in reactions with C_6H_5MgBr, pyridine and $N(CH_2CH_3)_3$ and relatively more important than for **11** with $NaBH_3CN$ and $P(CH_3)_3$ as nucleophiles. The 2-phenyl complex **13** was found to suffer C(4) attack primarily (with $NaBH_3CN$ and PhMgBr) or exclusively (with $P(CH_3)_3$, pyridine and $N(CH_2CH_3)_3$). Interestingly, the electronically perturbed *para*-FC_6H_4-derivative **14** was found to differ very little from the parent phenyl derivative in the regioselectivity of its reactions with our set of nucleophiles. The last of the 2-substituted complexes, the 2-trimethylsilylmethyl derivative **15**, reacts regiospecifically at C(4) with all three nucleophiles ($NaBH_3CN$, PhMgBr and pyridine) whose reactions were examined. Finally, the 1,3-dimethyl complex **16** undergoes regiospecific C(4) addition of C_6H_5MgBr, $P(CH_3)_3$, and $N(CH_2CH_3)_3$ but affords appreciable amounts of C(1) product with $NaBH_3CN$ and pyridine as nucleophiles.

Since the addition of nucleophiles to the substituted diene complexes shows a marked dependency on the nucleophile, it is also worthwhile to view briefly the results of Table 1 according to each nucleophile (i.e. proceeding vertically). In this way it can be seen that: (a) the addition of $N(CH_2CH_3)_3$ occurs regiospecifically at C(4) with each complex; (b) the attack of pyridine likewise is regiospecific at C(4) with each complex except with the disubstituted complex **16**; (c) $P(CH_3)_3$ also adds specifically at C(4) with two exceptions: the 2-methyl- and 2-ethyl-derivatives **11** and **12**; (d) C_6H_5MgBr adds specifically at C(4) with three exceptions: the 2-CH_3, 2-C_6H_5 and *p*-FC_6H_4 complexes; and (e) $NaBH_3CN$ provides mixtures of regioisomers in all cases but one (with **15**) with a moderate preference for C(4) attack in most cases. Thus a qualitative trend of C(4) selectivity with nucleophile is $N(CH_2CH_3)_3$ > pyridine > $P(CH_3)_3$ > C_6H_5MgBr > $NaBH_3CN$.

Before discussing the possible origins of the high regioselectivity observed in many of these reactions, it is important to address the question of whether product formation is kinetically or thermodynamically controlled. The nucleophiles which are most likely to add reversibly are the least basic (best leaving groups): $P(CH_3)_3$, pyridine and $N(CH_2CH_3)_3$. To test for reversibility the effect of different reaction temperatures on the regioselectivity was examined in a few cases. The reaction of the disubstituted complex **16** with pyridine (which gives a 1/1 isomer ratio at

$-78°C$) was carried out in an NMR tube starting at $-78°C$; the initial product composition was unchanged when the sample was warmed to room temperature over 1–2 h. Likewise, reactions of the *trans*-piperylene complex **9** (at 0 or $+20°C$) and the isoprene derivative **11** (at -40 or $0°C$) with $P(CH_3)_3$ did not exhibit any change in the isomer ratios. We believe, therefore, that the reactions of the (η^4-diene)$Co(CO)_3BF_4$ complexes with this set of nucleophiles are kinetically controlled, i.e. that the regioselectivities do not simply reflect the relative stability of the isomeric (η^3-allyl)$Co(CO)_3$ products.

Discussion

Several new $Co(CO)_3^+$ complexes of 1-, 2-, and 1,3-substituted dienes have been prepared for this study all of which undergo facile addition of a range of nucleophiles in good to excellent yields, thus further illustrating the generality of this scheme for cobalt-mediated activation of dienes. Unfortunately, to date we have been unsuccessful in attempts to use Scheme 1 to prepare complexes of diene possessing strongly electron donating/accepting or very bulky substituents, limiting somewhat the conclusions which can be drawn regarding the influence of the substituent's electronic character on regioselectivity. It is not clear if this reflects the inherent instability of such complexes but continuing efforts to develop alternate general routes to (η^4-diene)$Co(CO)_3Z$ may answer this question in the future.

At the outset it is important to establish whether the reactions under consideration are kinetically or thermodynamically controlled. Although this question has not been proven rigorously for all of the reactions presented, the temperature and time invariance of isomeric product ratios in several cases with nucleophiles which are relatively good leaving groups (i.e. $P(CH_3)_3$, C_5H_5N (pyridine), and $N(CH_2CH_3)_3$) leads us to conclude that these reactions are generally kinetically controlled. Furthermore, the following discussion presumes attack by the nucleophile "*anti*" to the metal (i.e. without precoordination or initial CO attack) based on the coordinatively saturated cobalt center, the absence of detectable intermediates by IR and NMR, and the *anti* stereochemistry observed in additions to the related $CpMo(CO)_2(diene)^+$ system [3b].

A number of factors, both steric and electronic, could play a role in determining the regiochemical outcome of the addition of nucleophiles to a π-complexed ligand. Steric factors derive from interactions of the approaching nucleophile with diene substituents in the transition state; for a late transition state interactions between adjacent substituents on the developing η^3-allyl unit should be considered. Analysis of the contributing electronic factors is more complex. Important considerations may include electrostatic interactions (i.e. both attractive and repulsive), orbital overlap (primarily $HOMO_{Nu}$ and $LUMO_{complex}$) and the related hard/soft character of the nucleophile and complex.

It is worthwhile at this point to recall the general regioselectivity features of the reactions of complexes **9–16** with the selected nucleophiles (Table 1): (1) addition of nucleophiles to C(1),C(2) and C(1),C(3) disubstituted complexes occurs preferentially or exclusively at C(4) in most cases, exceptions being the isoprene derivative **11** (where modest C(1) addition selectivity is observed with Nu = $NaBH_3CN$, C_6H_5MgBr, $P(CH_3)_3$) and the dimethyl derivative **16** (for Nu = pyridine); and (2)

C(4) attack selectivity is nucleophile dependent, generally decreasing in the order $N(CH_2CH_3)_3$ > pyridine > $P(CH_3)_3$ > C_6H_5MgBr > $NaBH_3CN$.

At first glance the general preference for attack at C(4) could be ascribed to steric factors alone since this position is the least hindered one in both the C(1) and C(2) substituted complexes. However, for reasons we will soon outline this appears to be an oversimplification and electronic factors clearly contribute as well. Clearcut examples of the influence of steric factors may be seen in comparing the regioselectivities observed in reactions of a common set of nucleophiles ($NaBH_3CN$, C_6H_5MgBr and $P(CH_3)_3$) with the 2-methyl- and 2-ethyl substituted diene complexes **11** and **12**: with a given nucleophile the bulkier ethyl derivative **12** undergoes less hindered C(4) attack to a greater extent than the methyl-substituted complex **11**. Other comparisons of pairs of complexes to evaluate steric effects alone generally are flawed by differences in the electronic properties of the substituents, e.g. the CH_3 vs. $CH_2Si(CH_3)_3$ derivatives, **9**/**10** and **11**/**15**; the trimethylsilylmethyl group is both bulkier and more strongly electron donating [11] than the methyl group. Examples illustrating the operation of electronic effects alone are similarly limited. The occurrence of preferential attack at C(1) with some nucleophiles in the isoprene complex **11** clearly is contrasteric and hence electronic in origin. Recall that the same selectivity was observed in the $CpMo(CO)_2(diene)^+$ system (eq. 2, 3 [3b]). The present Co system, however, lacks the conformational features of the former. On the other hand comparison of the *p*-FC_6H_4 and C_6H_5 groups in complexes **14** and **13** reveals a negligible effect on regioselectivity. Thus it appears that π-donation from the fluoro substituent into the coordinated diene unit is modest or that both C(1) and C(4) are affected equally.

A detailed discussion of the electronic influence of substituents on the regiochemical course of these reactions requires a knowledge of the electron distribution and energies/coefficients of the frontier molecular orbitals in the complexes and the nucleophiles. As indicated earlier such an analysis has been carried out at the extended Hückel level for the parent (1,3-butadiene)$Co(CO)_3^+$ [7]. According to this analysis the observed terminal attack regioselectivity can be rationalized in terms of a stabilizing interaction between $HOMO_{Nu}$ and $LUMO_{complex}$ (derived primarily from Ψ_2 of the diene and an e_a (d) metal orbital) which is maximized during attack at C(terminal) of the complexed diene. Attack of the nucleophile seems not to be strongly guided by electrostatics since electron density is calculated by a number of methods [7,12] to be greater at the terminal site. If we assume that the same orbital interactions dominate in the substituted diene complexes, one should look to the magnitude of the Ψ_2 orbital coefficients of the diene to predict regioselectivity. Various levels of calculations [13] indicate that these coefficients (in the free dienes) are largest at C(4) for 1-alkyl and -aryl substituted dienes and largest at C(1) for the corresponding 2-substituted dienes. The observed preferential C(1) attack of the isoprene complex **11** with some nucleophiles ($NaBH_3CN$, C_6H_5MgBr and $P(CH_3)_3$) may thus be the result of such frontier orbital control. The lesser preference for C(1) addition to the aryl substituted complexes **13** and **14** could reflect a smaller C(1) coefficient in LUMO of the latter [13b] or could be the result of the greater steric requirement of the aryl substituents. Similarly, the expectedly larger C(4) coefficient in the C(1) substituted complexes **9** and **10** could explain their highly selective C(4) attack by nucleophiles (except for $NaBH_3CN$). The preference for C(4) attack in the reactions of disubstituted complex **16** may

represent the contributions of the two methyl groups to the orbital coefficient at C(4) but we find the non-selective addition of pyridine to **16** inexplicable.

The origin of the marked regiochemical dependency on the nature of the nucleophile in these reactions is both intriguing and puzzling. For the C(2) substituted complexes it is interesting to note that the C- and H-nucleophiles prefer C(1) attack to a greater extent than the neutral, N-centered Lewis bases. Since the former pair would be considered softer than the latter [14], it is tempting to suggest that this tendency could be a hard/soft effect with orbital overlap interactions (greatest at C(1)) being more dominating for the softer nucleophiles. This explanation, however, fails to account for the somewhat lesser C(4) selectivity found for the reactions of the 1-substituted complexes **9** and **10** with $NaBH_3CN$. Of course there are significant differences in the steric bulk of our set of nucleophiles. The most unambiguous comparison is between the two amines and the phosphine where solvation and aggregation differences are probably small and the steric bulk increases in the order $P(CH_3)_3$, pyridine, $N(CH_2CH_3)_3$. This may contribute to the increasing tendency of the nucleophiles within this group to add remote to the diene substituent. The steric requirements of $NaBH_3CN$ and C_6H_5MgBr are difficult to assess because of uncertainty in the degree of ion separation (for the former) and solvent coordination (for the latter). Solvent separated ions pairing seems likely for $NaBH_3CN$ in nitromethane so that this species may represent the most compact of the nucleophiles. This could contribute to the relatively low sensitivity of this reagent to the steric character of the diene substituents.

Conclusions

The addition of nucleophiles to a series of 1-, 2- and 1,3-disubstituted diene-cobalt complexes proceeds in good yield and generally with a high degree of regioselectivity. Addition occurs preferentially or exclusively at C(4) (remote from the substituent) in most cases, exceptions being the isoprene derivative **11** (where modest C(1) attack occurs with Nu = $NaBH_3CN$, C_6H_5MgBr, $P(CH_3)_3$) and the dimethyl derivative **16** (for Nu = pyridine). The C(4) attack selectivity is nucleophile dependent, decreasing in the order $N(CH_2CH_3)_3$ > pyridine > $P(CH_3)_3$ > C_6H_5MgBr > $NaBH_3CN$. Although steric and electronic effects can be distinguished in certain of these reactions, most cases can be explained either by a predominant steric effect (directing incoming nucleophiles remote to the diene substituent) or by an optimum orbital interaction between $HOMO_{Nu}$ and $LUMO_{complex}$ (maximized at C(4) for both 1- and 2-substituted diene complexes). Future studies will seek to further elucidate the balance between steric and electronic effects and to exploit the regioselective coupling between (diene)$Co(CO)_3BF_4$ complexes and nucleophiles in the synthesis of complex organic molecules.

Experimental

All reactions and manipulations were carried out under a nitrogen atmosphere utilizing standard Schlenk line techniques. Solvents and common reagents were obtained commercially and used as received or purified as follows: methylene chloride and pentane were distilled under nitrogen from calcium hydride. IR spectra

were recorded on a Perkin Elmer model 1420 spectrophotometer. ^{1}H NMR spectra were recorded on Varian XL300 NMR spectrometer; resonances are reported relative to Me_4Si standard. FAB mass spectra were obtained on a VG ZAB-E mass spectrometer. The instability of most of the η^3-allyl adducts prevented the acquisition of analytically pure samples; products were generally judged to be $\geq 95\%$ pure based on their ^{1}H NMR spectra.

trans-Piperylene and *trans*-2-methyl-1,3-pentadiene were isolated from the mixture of *cis*- and *trans*-dienes via their SO_2 adducts [15]. 2-Phenyl-1,3-butadiene [16], 2-trimethylsilylmethyl-1,3-butadiene [17], and *trans*-1-trimethylsilylmethyl-1,3-butadiene [18] were synthesized according to literature methods; 2-(*p*-fluorophenyl)-1,3-butadiene [16] and 2-ethyl-1,3-butadiene [17] were prepared by direct extension of reported methods.

Representative procedure for the preparation of [(η^4-diene)Co(CO)$_2$]$_2$

Following the procedures described earlier [9,19] a 250 ml 3-neck round bottom flask was equipped with a condenser, nitrogen inlet tube and a magnetic stirring bar. Under a N_2 flush it was charged with 120 ml pentane, 6.75 g (0.02 mol) of dicobalt octacarbonyl and 0.04 mol of 2-(*p*-FC_6H_4)-1,3-butadiene and the mixture was refluxed for about 4 h. After cooling the solution to room temperature, the pentane was concentrated to half of its volume at reduced pressure and the resulting precipitate was filtered under nitrogen. The orange/red solid was washed with cold pentane twice and dried briefly in vacuo.

*[(η^4-1,3-Pentadiene)Co(CO)$_2$]$_2$ (**1**).* Orange red solid; 68% yield. IR (pentane): 2040, 2020, 2000, 1860, 1840, 1815 cm^{-1}. ^{1}H NMR (C_6D_6 exists as a mixture of *cis* and *trans* isomers): δ 4.63 (m, HC=CH(CH_3)), 4.53 (m, HC=CH_2), 4.38 (m, $H'C$=CH(CH_3)), 4.28 (m, $H'C$=CH_2), 2.27 (t, J 9 Hz, HHC=CH, *syn*, both isomers), 1.82 (m, $HC(CH_3)$=C, both isomers), 1.52 (br d, J 9 Hz, HHC=CH, *anti*, both isomers), 1.11 (d, J 9 Hz, (CH_3)HC=C, both isomers); MS (FAB): 279 (M − Co − CO, 8%), 211 (M − Co − CO − diene, 100%), 183 (M − Co − 2CO − diene, 23%), 127 (M − Co − 4CO − diene, 7%).

*[(η^4-1-Trimethylsilylmethyl-1,3-butadiene)Co(CO)$_2$]$_2$ (**2**).* This compound was not isolated in pure form due to its instability under vacuum. The complexation reaction was carried out in methylene chloride and the oxidation (vide infra) was carried out directly without isolation. IR (CH_2Cl_2): 2050, 2020, 2000, 1860, 1840, 1810 cm^{-1}; MS (FAB): 255 (M − diene − Co − 2CO, 5%), 227 (M − diene − Co − 3CO, 21%), 199 (M − diene − Co − 4CO, 4%).

*[(η^4-2-Methyl-1,3-butadiene)Co(CO)$_2$]$_2$ (**3**).* Orange solid, 80% yield. IR (pentane): 2080, 2040, 2000, 1840, 1810 cm^{-1} (identical to IR reported previously [19]). ^{1}H NMR (C_6D_6) (exists as a mixture of *cis* and *trans* isomers): δ 4.7 (dd, J 10, 7 Hz, H_2C=CH), 4.26 (dd, J 10, 7 Hz, HHC=CH'), 2.23 (d, J 7 Hz, HHC=CH, *syn*), 2.15 (d, J 7 Hz, HH'C=CH, *syn*), 2.09 (s, HHC=C(CH_3)), 1.69 (s, H'HC=C(CH_3) and HHC=C(CH_3)), 1.59 (s, CH_3'), 1.47 (s, CH_3), 1.32 (d, J 10 Hz, HHC=CH, *anti*, both isomers), 1.31 (s, HH'C=C(CH_3)); MS (FAB): 366 (M, 30%), 338 (M − CO, 30%), 298 (M − diene, 33%), 270 (M − diene − CO, 37%), 211 (M − diene − Co − CO, 34%), 127 (M − diene − Co − 4CO, 36%).

*[(η^4-2-Ethyl-1,3-butadiene)Co(CO)$_2$]$_2$ (**4**).* This compound was not isolated in pure form due to its instability under vacuum. IR (CH_2Cl_2): 2050, 2020, 2000, 1860, 1840, 1810 cm^{-1}; ^{1}H NMR (C_6D_6) (exists as a mixture of *cis* and *trans*

isomers): δ 4.78 (m, HHC=C*H'*), 4.35 (m, HHC=C*H*), 2.28 (d, *J* 7 Hz, H*H*C=CH, *syn*), 2.22 (d, *J* 7 Hz, H*H'*C=CH, *syn*), 2.16 (s, *H*HC=C(C_2H_5)), 2.13 (s, *H'*HC=C(C_2H_5)), 2.01–1.91 (m, H_2CCH_3, both isomers), 1.54 (d, *J* 10 Hz, *H*HC=CH, *anti*), 1.53 (s, H*H*C=C (C_2H_5)), 1.38 (d, *J* 12 Hz, *H'*HC=CH, *anti*), 1.37 (s, H*H'*C=C(C_2H_5)), 0.9 (m, CH_2CH_3, both isomers); MS (FAB): 366 (*M* − CO, 52%), 338 (*M* − 2CO, 100%), 284 (*M* − CO − diene, 57%), 256 (*M* − diene − 2CO, 23%), 169 (*M* − diene − 3CO − Co, 10%).

[(η^4-2-Phenyl-1,3-butadiene)Co(CO)$_2$]$_2$ (5). Orange solid, 91% yield. IR (pentane): 2080, 2030, 2020, 2000, 1860, 1840, 1815 cm^{-1}; ^{1}H NMR (C_6D_6) (exists as a mixture of *cis* and *trans* isomers) δ 7.6–7.2 (m, Ph, both isomers), 5.35 (t, *J* 9 Hz, HHC=C*H*), 4.29 (t, *J* 6 Hz, HHC=C*H'*), 2.96 (s, *H*HC=C(Ph)), 2.69 (s, *H'*HC=C(Ph), 2.44 (d, *J* 6 Hz, *H*HC=CH, *syn*), 2.33 (d, *J* 5 Hz, *H'*HC=CH, *syn*), 1.36 (d, *J* 9 Hz, H*H'*C=CH, *anti*), 1.23 (d, *J* 13 Hz, H*H*C=CH, *anti*), 1.23 (s, H*H'*C=C(Ph)), 1.04 (s, H*H*C=C(Ph)); MS (FAB): 332 (*M* − diene − CO, 32%), 245 (*M* − diene − Co − 2CO, 29%), 217 (*M* − diene − Co − 3CO, 23%), 189 (*M* − diene − Co − 4CO, 32%).

[(η^4-2-(p-FC_6H_4)-1,3-butadiene)Co(CO)$_2$]$_2$ (6). Brown-red solid, 80% yield. IR (KBr): 2060, 2020, 2000, 1850, 1830, 1795 cm^{-1}; ^{1}H NMR (C_6D_6) (exists as a mixture of *cis* and *trans* isomers): δ 7.6–7.2 (m, Ph, both isomers), 5.2 (dd, *J* 11, 8 Hz, HHC=C*H*), 4.16 (dd, *J* 11, 8 Hz, HHC=C*H'*), 2.79 (s, H*H*C=C(PhF), 2.5 (s, *H'*HC=C(PhF)), 2.43 (d, *J* 8 Hz, H*H*C=CH, *syn*), 2.18 (d, *J* 8 Hz, H*H'*C=CH, *syn*), 1.35 (s, H*H'*C=C(PhF)), 1.3 (d, *J* 11 Hz, *H'*HC=CH, *anti*), 1.2 (d, *J* 11 Hz, *H*HC=CH, *anti*), 0.98 (s, H*H*C=C(PhF)); MS (FAB): 378 (*M* − diene, 14%), 350 (*M* − diene − CO, 91%), 322 (*M* − diene − 2CO, 9%), 294 (*M* − diene − 3CO, 11%), 263 (*M* − diene − 2CO − Co, 11%), 235 (*M* − diene − 3CO − Co, 34%), 207 (*M* − diene − 4CO − Co, 42%).

[(η^4-2-Trimethylsilylmethyl-1,3-butadiene)Co(CO)$_2$]$_2$ (7). Red brown solid, 93% yield. IR (pentane) 2080, 2030, 2000, 1860, 1840, 1810 cm^{-1}; ^{1}H NMR (C_6D_6) (exists as a mixture of *cis* and *trans* isomers): δ 5.0 (dd, *J* 11, 8 Hz, HHC=C*H'*), 4.4 (dd, *J* 12, 9 Hz, HHC=C*H*), 2.36 (d, *J* 9 Hz, H*H*C=CH, *syn*), 2.27 (d, *J* 8 Hz, H*H'*C=CH, *syn*), 2.11 (s, *H*HC=C(CH_2SiMe_3), both isomers), 1.7 (m, H_2CSiMe_3, both isomers), 1.48 (m, *H*HC=CH, *anti*, both isomers, and H*H*C=C (CH_2SiMe_3), both isomers), 0.00 (s, CH_2SiMe_3, both isomers); MS (FAB): 370 (*M* − diene, 94%), 314 (*M* − diene − 2CO, 56%), 255 (*M* − diene − 2CO − Co, 65%), 227 (*M* − diene − 3CO − Co, 60%), 199 (*M* − diene − 4CO − Co, 52%).

[η^4-2-Methyl-1,3-pentadiene)Co(CO)$_2$]$_2$ (8). Light brown solid; 95% yield. IR (pentane) 2060, 2000, 1880, 1860 cm^{-1}; ^{1}H NMR (C_6D_6) (only one isomer); δ 4.27 (d, *J* 11 Hz, *H*HC=CH(CH_3)), 3.28 (m, *H*(CH_3)C=C), 2.21 (s, *H*HC=C, *syn*), 1.75 (s, H*H*C=C, *anti*), 1.64 (s, CH_3), 1.15 (d, *J* 6 Hz, H(CH_3)C=C); MS (FAB): 366 (*M* − CO, 10%) 338 (*M* − 2CO, 29%), 310 (*M* − 3CO, 5%), 197 (*M* − 4CO − diene, 8%).

Representative procedure for the synthesis of [(η^4-diene)Co(CO)$_3$](BF$_4$) complexes

A 250 ml side arm flask was charged with 1.9 g (3.6 mmol) of [(η^4-2-(*p*-FC_6H_4)butadiene)Co(CO)$_2$]$_2$ and 50 ml CH_2Cl_2 under nitrogen. To this solution, 7.2 mmol of (C_5H_5)$_2$Fe(BF$_4$) was added and the mixture stirred at room temperature overnight. Anhydrous diethyl ether (30 ml) was then added to the solution with stirring for 5 min. After removing the solvent via cannula, the resulting green solid

was washed with equal volumes of methylene chloride and diethyl ether two or three times. The yellow solid was then re-precipitated from 20 ml nitromethane/20 ml methylene chloride upon addition of 60 ml diethyl ether at 0 °C. Solvent was removed using a cannula and the yellow solid was dried under vacuo.

[(η^4-1,3-Pentadiene)Co(CO)$_3$](BF$_4$) (9). Yellow solid, 27% yield. IR (CH_3NO_2): 2140, 2100 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (CD_3NO_2): δ 6.58 (m, HHC=C*H* and H(CH_3)C=C*H*), 3.55 (dd, *J* 6, 3 Hz, H*H*C=CH, *syn*), 3.49 (m, *H*(CH_3)C=CH), 2.47 (dd, *J* 10, 3 Hz, *H*HC=CH, *anti*), 1.67 (d, *J* 7 Hz, H(C*H*$_3$)C=CH); MS (FAB): 211 (*M* − BF_4, 100%), 183 (*M* − BF_4 − CO, 76%), 155 (*M* − BF_4 − 2CO, 14%), 127 (*M* − BF_4 − 3CO, 7%).

[(η^4-1-Trimethylsilylmethyl-1,3-butadiene)Co(CO)$_3$](BF$_4$) (10). Yellow solid, 32% yield. IR (CH_2Cl_2): 2140, 2100 (C=O), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6): δ 6.83 (m, HHC=C*H* and H(Me_3SiCH_2)C=C*H*), 3.86 (m, *H*(Me_3SiCH_2)C=CH), 3.66 (d, *J* 8 Hz, H*H*C=CH, *syn*), 2.78 (d, *J* 11 Hz, *H*HC=CH, *anti*), 1.72 (d, *J* 6 Hz, C*H*$_2$SiMe$_3$), 0.00 (s, CH_2SiMe_3); MS (FAB): 227 (*M* − BF_4 − 2CO, 17%).

[(η^4-2-Methyl-1,3-butadiene)Co(CO)$_3$](BF$_4$) (11). Yellow solid, 27% yield. IR (KBr): 2120, 2080 (CO), 1045 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6): δ 6.52 (br m, HHC=C*H*), 3.44 (s, *H*HC=C(CH_3), *syn*), 3.33 (br s, *H*HC=CH, *syn*), 2.4 (s, C*H*$_3$), 2.28 (s, H*H*C=C(CH_3), *anti*), 2.16 (d, *J* 10 Hz, H*H*C=CH, *anti*); MS (FAB): 211 (*M* − BF_4, 100%), 183 (*M* − BF_4 − CO, 53%), 127 (*M* − BF_4 − 3CO, 21%).

[(η^4-2-Ethyl-1,3-butadiene)Co(CO)$_3$](BF$_4$) (12). Yellow solid, 12% yield. IR (CH_2Cl_2): 2170, 2100 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (CD_3NO_2): δ 6.7 (dd, *J* 6, 2 Hz, HHC=C*H*), 3.6 (s, *H*HC=C(C_2H_5), *syn*), 3.5 (d, *J* 6 Hz, *H*HC=CH, *syn*), 2.86 (m, *H*$_2$CCH_3), 2.4 (s, H*H*C=C(C_2H_5), *anti*), 2.3 (m, *H*HC=CH, *anti*), 1.44 (dd, *J* 5, 2 Hz, CH_2CH_3); MS (FAB): 225 (*M* − BF_4, 100%), 197 (*M* − BF_4 − CO, 58%), 169 (*M* − BF_4 − 2CO, 26%), 141 (*M* − BF_4 − 3CO, 3%).

[(η^4-2-Phenyl-1,3-butadiene)Co(CO)$_3$](BF$_4$) (13). Yellow solid, 38% yield. IR (CH_3NO_2): 2140, 2100 (C=O), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6): δ 8.2–7.8 (m, Ph), 6.99 (m, HHC=C*H*), 4.2 (s, *H*HC=C(Ph)), 3.99 (br s, H*H*C=CH, *syn*), 2.99 (d, *J* 11 Hz, *H*HC=CH, *anti*), 2.6 (s, H*H*C=C(Ph)); MS (FAB): 273 (*M* − BF_4, 82%), 245 (*M* − BF_4 − CO, 43%), 217 (*M* − BF_4 − 2CO, 69%), 189 (*M* − BF_4 − 3CO, 87%), 130 (diene, 8%).

[(η^4-2-(p-FC$_6$H$_4$)-1,3-butadiene)Co(CO)$_3$](BF$_4$) (14). Yellow solid, 39% yield. IR (CH_3NO_2): 2140, 2100 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6): δ 8.29 (2H, dd, *J* 8, 5 Hz, H_o), 7.57 (dd, *J* 10, 8 Hz, HHC=C*H*), 7.4 (2H, q, *J* 8 Hz, H_m), 4.37 (s, *H*HC=C(Ph)), 3.8 (d, *J* 5 Hz, *H*HC=CH, *syn*), 2.9 (br s, H*H*C=CH, *anti*, overlapping with signal at δ 2.85), 2.85 (s, H*H*C=C(Ph)); MS (FAB): 291 (*M* − BF_4, 51%), 263 (*M* − BF_4 − CO, 50%), 235 (*M* − BF_4 − 2CO, 56%), 207 (*M* − BF_4 − 3CO, 63%).

[(η^4-2-Trimethylsilylmethyl-1,3-butadiene)Co(CO)$_3$](BF$_4$) (15). Yellow solid, 46% yield. IR (CH_3NO_2): 2140, 2100 (C=O), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6): δ 6.75 (dd, *J* 10, 7 Hz, HHC=C*H*), 3.64 (m, *H*HC=CH, *syn*), 3.56 (s, *H*HC=C(CH_2SiMe_3)), 2.84 (d, *J* 12 Hz, C*H*HSiMe$_3$), 2.63 (m, H*H*C=CH, *anti*), 2.44 (s, H*H*C=C(CH_2SiMe_3)), 2.3 (d, *J* 12 Hz, CH*H*SiMe$_3$), 0.00 (9H, s, $SiMe_3$); MS (FAB): 283 (*M* − BF_4, 100%), 255 (*M* − BF_4 − CO, 73%), 227 (*M* − BF_4 − 2CO, 65%), 199 (*M* − BF_4 − 3CO, 27%).

*[(η^4-2-Methyl-1,3-pentadiene)Co(CO)$_3$](BF$_4$) (**16**).* Yellow solid, 28% yield. IR (CH_3NO_2): 2140, 2100 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6) δ 6.85 (d, J 11 Hz, H(CH_3)C=C*H*), 4.27 (s, H*H*C=C(CH_3), *syn*), 3.7 (m, *H*(CH_3)C=, overlapping with signal at δ 3.66), 3.66 (s, *H*HC=C(CH_3), *anti*)), 2.6 (s, CH_3), 1.75 (d, J 6 Hz, H(CH_3)C=); MS (FAB): 225 ($M - BF_4$, 100%), 197 ($M - BF_4 - CO$, 54%), 169 ($M - BF_4 - 2CO$, 11%).

Reactions of (η^4-diene)Co(CO)$_3$BF$_4$ with NaCNBH$_3$.

A 25 ml side arm round bottom flask equipped with a magnetic stir bar was charged with 4 ml nitromethane and cooled to 0 °C. After 10 min 33 mg (0.087 mmol) of [(η^4-2-(p-FC$_6$H$_4$)-butadiene)Co(CO)$_3$](BF$_4$) was added followed by 0.096 mmol of NaCNBH$_3$ and the mixture stirred for 30 min. The resulting green solution was extracted with three 5 ml portions of pentane. The pentane extracts were combined and the solvent was removed under vacuo to yield the η^3-allyl product as a thermally and oxidatively sensitive yellow oil.

*anti-(η^3-1,3-Dimethylpropenyl)Co(CO)$_3$ (**17a**) and (η^3-1-ethylpropenyl)Co(CO)$_3$ (**17b**):* Yellow oil; 56% yield. IR (CH_2Cl_2): 2050, 1975 (CO) cm^{-1}; ^1H NMR (C_6D_6) (values for **17b** in brackets): δ 4.17 (1H, dd, J 10, 8 Hz, H(2)), [4.29 (1H, m, H(2′))], 3.59 (1H, m, H(1)), [2.8 (1H, d, J 7 Hz, H(3′))], 3.31 (1H, m, H(3)), [2.34 (1H, d, J 12 Hz, H(3′))], 1.25 (3H, d, J 6 Hz, CH_3), [0.87 (2H, m, CH_2CH_3)], 0.76 (3H, d, J 7 Hz, CH_3), [0.68 (3H, q, J 7 Hz, CH_3')]; MS (FAB): 212 (M, 13%), 184 ($M - CO$, 12%). The NMR spectra were identical to those reported previously [10].

*anti-(η^3-1-Trimethylsilylmethyl-3-methylpropenyl)Co(CO)$_3$ (**22a**) and (η^3-1-trimethylsilylethyl-propenyl)Co(CO)$_3$ (**22b**):* Yellow oil, 45% yield. IR (CH_3NO_2): 2050, 1975 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) (values for **22b** in brackets): δ 4.77 (1H, dd, J 7, 3 Hz, H(2)), [4.94 (1H, m, H(2′)), 4.1 (1H, m, H(3))], [4.24 (1H, m, H(1′))], 3.82 (1H, m, H(1)), [3.32 (1H, d, J 6 Hz, H(3′))], 1.7 (2H, d, J 6 Hz, CH_2), [2.79 (1H, d, J 12 Hz, H(3′))], 1.18 (3H, d, J 7 Hz, CH_3), [1.35–1.2 (2H, m, CH_2)], [1.01 (2H, dd, J 9, 7 Hz, $CH_2'SiMe_3$)], 0.00 (18 H, s, Si(CH_3)$_3$, both isomers).

*anti-(η^3-1,2-Dimethylpropenyl)Co(CO)$_3$ (**27a**) and (η^3-1,1-dimethylpropenyl)Co(CO)$_3$ (**27b**).* Yellow oil; 70% yield. IR (CH_3NO_2): 2040, 1975 (CO) cm^{-1}; ^1H NMR (C_6D_6) (values for **27b** in brackets): δ 3.85 (1H, m, H(1)), [4.3 (1H, m, H(2))], 2.96 (1H, s, H(3)), [2.71 (1H, d, J 6 Hz, H(3′))], 2.5 (1H, s, H(3)), [2.14 (1H, d, J 11 Hz, H(3′))], 1.5 (3H, s, CH_3), [1.53 (3H, s, CH_3)], 0.82 (3H, d, J 6 Hz, CH_3), [0.87 (3H, s, CH_3)]; MS (FAB): 184 ($M - CO$, 8%). NMR data were comparable to those reported previously [10,20].

*anti-(η^3-2-Ethyl-1-methylpropenyl)Co(CO)$_3$ (**32a**) and η^3-(1-ethyl-1-methylpropenyl)Co(CO)$_3$ (**32b**).* Yellow oil, 100% yield. IR (pentane): 2060, 1990 (CO) cm^{-1}. ^1H NMR ($CDCl_3$) (values for **32b** in brackets): δ 4.26 (1H, dd, J 8, 6 Hz, H(1)), [4.82 (1H, dd, J 11, 7 Hz, H(2′))], 3.37 (1H, s, H(3)), [3.2 (1H, d, J 6 Hz, H(3′))], 2.89 (1H, s, H(3)), [2.6 (1H, d, J 10 Hz, H(3′))], 2.06 (2H, m, CH_2), [1.59 (3H, s, CH_3')], 1.25 (6H, m, CH_3, overlapping with CH_3') [1.09 (2H, t, J 7 Hz, CH(2′))], 0.87 (3H, d, J 7 Hz, CH_3); MS (FAB): 198 ($M - CO$, 7%), 142 ($M - 3CO$, 10%).

*anti-(η^3-1-Methyl-2-phenylpropenyl)Co(CO)$_3$ (**37a**) and η^3-(1-methyl-1-phenylpropenyl)Co(CO)$_3$ (**37b**).* Yellow oil, 90% yield, IR (CH_3NO_2): 2040, 1975 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) (values for **37b** in brackets): δ 7.62–7.27 (10H, m, Ph, both isomers), 4.72 (1H, dd, J 13, 7 Hz, H(1)), [5.67 (1H, dd, J 11, 7 Hz, H(2′))], 3.82 (1H, s, H(3)), [3.41 (1H, d, J 7 Hz, H(3′))], 3.05 (1H, s, H(3)), [2.84 (1H, d, J 11 Hz,

H(3′))], 1.4 (3H, d, *J* 7 Hz, CH_3, [1.63 (3H, s, CH_3')]; MS (FAB); 190 (*M* − 3CO, 13%), 131 (*M* − 3CO − Co, 9%).

*anti-(η^3-1-Methyl-2-(p-FC_6H_4)propenyl)Co(CO)$_3$ (**42a**) and η^3-(1-methyl-1-(p-FC_6H_4)propenyl)CO(CO)$_3$ (**42b**).* Yellow oil, 43% yield. IR (pentane): 2060, 2000 (CO) cm^{-1}; ^1H NMR ($CDCl_3$) (values for **42b** in brackets): δ 7.59–6.92 (8H, m, Ph, both isomers), 4.66 (1H, dd, *J* 7, 5 Hz, H(1)), [5.6 (1H, dd, *J* 7, 4 Hz, H(2′))], 3.75 (1H, s, H(3)), [3.41 (1H, d, *J* 7 Hz, H(3′))], 3.0 (1H, s, H(3), [2.85 (1H, d, *J* 11 Hz, H(3′))], 1.4 (3H, d, *J* 7 Hz, CH_3), [1.61 (3H, s, CH_3')]; MS (FAB): 292 (*M*, 12%), 264 (*M* − CO, 11%, 236 (*M* − 2CO, 12%), 208 (*M* − 3CO, 13%), 149 (*M* − 3CO − Co, 11%).

*anti-(η^3-Methyl-2-trimethylsilyl-allyl)Co(CO)$_3$ (**47a**).* Yellow oil; 79% yield. IR (pentane): 2060, 1990 (CO) cm^{-1}; ^1H NMR (acetone-d_6) δ 4.41 (1H, dd, *J* 13, 6 Hz, H(1)), 3.51 (1H, s, H(3)), 3.06 (1H, s, H(3)), 1.63 (2H, s, CH_2), 1.27 (3H, d, *J* 6Hz, CH_3), 0.0 9H, s, $Si(CH_3)_3$); MS (FAB): 200 (*M* − 3CO, 18%), 141 (*M* − 3CO − Co, 38%).

*anti-(η^3-1,1,3-Trimethylpropenyl)Co(CO)$_3$ (**50a**) and (η^3-1-ethyl-2-methylpropenyl)-Co(CO)$_3$ (**50b**).* Yellow oil, 100% yield, IR (CH_3NO_2); 2040, 1980 (CO) cm^{-1}; ^1H NMR (acetone-d_6) (values for **50b** in brackets): δ 4.82 (1H, d, *J* 10 Hz, H(2)), [4.4 (1H, m, H(1′))], 3.8 (1H, m, H(3)), [3.55 (1H, s, H(3′))], 1.78 (3H, s, CH_3), [3.29 (1H, s, H(3′))], 2.05 (3H, s, CH_3)], 1.68 (3H, d, *J* 6 Hz, CH_3), [1.1–0.98 (2H, m, CH_2)], 1.28 (3H, s, CH_3'), [0.85 (3H, m, CH_3')]; MS (FAB): 142 (*M* − 3CO, 6%).

Representative procedure for PhMgBr reactions with (η^4-diene)Co(CO)$_3$BF$_4$ complexes.

A 50 ml side arm round bottom flask equipped with a magnetic stir bar was charged with 70 mg (0.23 mmol) of [(η^4-2-methyl-1,3-butadiene)$Co(CO)_3$](BF_4) and 15 ml diethyl ether. After cooling the mixture to −78 °C, 0.258 mol (1.1 equiv.) of an ethereal solution of phenylmagnesium bromide was syringed in and the mixture stirred for about 1 h. The resulting brown solution was filtered through alumina (activity I). Solvent was removed under vacuo to yield an unstable yellow semisolid.

*anti-η^3-1-Phenyl-2-pentenyl)Co(CO)$_3$ (**18a**).* Yellow solid; 67% yield IR (Et_2O): 2050, 1980 (CO) cm^{-1}; ^1H NMR (C_6D_6): δ 7.6–7.2 (5H, m, *Ph*), 4.21 (1H, dd, *J* 11, 7 Hz, H(3)), 3.79 (1H, m, H(4)), 3.43 (1H, m, H(2)), 2.57 (1H, dd, *J* 14, 10 Hz, H(1)), 2.06 (1H, dd, *J* 14, 11 Hz, H(1)), 1.26 (3H, d, *J* 6 Hz, CH_3).

*anti-(η^3-1-Phenyl-5-trimethylsilyl-2-pentenyl)Co(CO)$_3$ (**23a**).* Yellow solid; 100% yield. IR (Et_2O): 2060, 1990 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.7–7.2 (5H, m, Ph), 4.82 (1H, dd, *J* 11, 7 Hz, H(3)), 4.1 (1H, m, H(2)), 3.97 (1H, m, H(4)), 2.9 (1H, dd, *J* 14, 5 Hz, H(1)), 2.38 (1H, dd, *J* 14, 11 Hz, H(1)), 1.75 (2H, d, *J* 6 Hz, H(5)), 0.0 (9H, S, $Si(CH_3)_3$); MS (FAB): 332 (*M* − CO, 3%), 217 (*M* − 3CO − Co, 3%).

*anti-(η^3-1-Phenyl-3-methyl-2-butenyl)Co(CO)$_3$ (**28a**) and anti-η^3-(1-phenyl-2-methyl-2-butenyl)Co(CO)$_3$ (**28b**).* Yellow solid; 82% yield. IR (Et_2O): 2050, 1985 cm^{-1}; ^1H NMR ($CDCl_3$) (values for **28b** in brackets): δ 7.6–7.1 (10H, m, Ph, both isomers), 4.33 (1H, dd, *J* 8, 4 Hz, H(2)), [4.88 (1H, q, *J* 7 Hz, H(3′))], 3.5 (1H, s, H(4)), 3.66 (1H, d, *J* 7 Hz, H(4′), 3.0 (1H, s, H(4)), 3.08 (1H, d, *J* 14 Hz, H(1′)) 2.95 (1H, dd, *J* 14, 10 Hz, H(1)), 2.77 (1H, d, *J* 11 Hz, H(4′)), 2.36 (1H, dd, *J* 14, 12 Hz, H(1)), [2.64 (1H, d, *J* 14 Hz, H(1′)], 1.96 (3H, s, CH_3), [1.63 (3H, s, CH_3')].

*anti-(η^3-1-Phenyl-3-ethyl-2-butenyl)Co(CO)$_3$ (**33a**).* Yellow solid; 100% yield. IR (Et_2O): 2060, 1990 cm^{-1} (CO); ^1H NMR ($CDCl_3$): δ 7.7–7.4 (5H, m, Ph), 4.23

(1H, dd, *J* 11, 4 Hz, H(2)), 3.45 (1H, s, H(4)), 3.0 (1H, s, H(4), overlapping with signal at 2.98), 2.98 (1H, d, *J* 10 Hz, H(1)), 2.33 (1H, dd, *J* 13, 12 Hz, H(1)), 2.04 (2H, br d, *J* 7 Hz, CH_2), 1.26 (3H, t, *J* 7 Hz, CH_3); MS (FAB): 218 (*M* − 3CO, 4%), 159 (*M* − 3CO − Co, 16%).

*anti-(η^3-1,3-Diphenyl-2-butenyl)Co(CO)$_3$ (**38a**) and anti(η^3-1,2-diphenyl-2-butenyl)Co(CO)$_3$ (**38b**).* Yellow solid; 100% yield. IR (Et_2O) 2060, 2000 (C≡O) cm^{-1}; ^1H NMR ($CDCl_3$) (values for ***38b*** in brackets): δ 7.8–7.2 (10H, m, Ph, both isomers), 4.7 (1H, br d, *J* 9 Hz, H(2)), [4.5 (1H, dd, *J* 11, 6 Hz, H(3′))], 3.9 (1H, s, H(4)), [2.55 (1H, d, *J* 12 Hz, H(4′), overlapping with signal at 2.58)], 3.3 (1H, s, H(4)), [2.1 (1H, d, *J* 12 Hz, H(4′))], 3.2 (1H, br d, *J* 15 Hz, H(1)), [1.85 (1H, d, *J* 7 Hz, H(1′)], 2.58 (1H, t, *J* 13 Hz, H(1)), [1.75 (1H, d, *J* 7 Hz, H(1′))] MS (FAB): 207 (*M* − 3CO − Co, 50%).

*anti-(η^3-1-Phenyl-3-(p-FC_6H_4)-2-butenyl)Co(CO)$_3$ (**43a**) and anti-(-η^3-1-phenyl-2-(p-FC_6H_4)-2-butenyl)Co(CO)$_3$ (**43b**).* Yellow solid; 100% yield. IR (Et_2O): 2060, 2000 (CO) cm^{-1}; ^1H NMR ($CDCl_2$) (values for **43b** in brackets): δ 7.8–7.2 (18H, m, Ph, both isomers), 4.6 (1, m, H(2)), [5.7 (1H, dd, *J* 11, 4 Hz, H(3′))], 3.84 (1H, s, H(4)), [2.23 (1H, d, *J* 8 Hz, H(4′))], 3.21 (1H, s, H(4)), [1.71 (1H, d, *J* 11 Hz, H(4′))], 3.16 (1H, dd, *J* 14, 4 Hz, H(1)), [1.43 (2H, m, H(1))], 2.52 (1H, dd, *J* 14, 11 Hz, H(1)); MS (FAB): 340 (*M* − CO, 21%), 312 (*M* − 2CO, 63%), 284 (*M* − 3CO, 100%).

*anti-(η^3-1-Phenyl-3-trimethylsilylmethyl-2-butenyl)Co(CO)$_3$ (**48a**).* Yellow solid; 100% yield. IR (Et_2O): 2060, 1990 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.6–7.2 (5H, m, Ph), 4.39 (1H, m, H(2)), 3.43 (1H, s, H(4)), 3.01 (1H, s, H(4)), 2.93 (1H, dd, *J* 14, 9 Hz, H(1)), 2.34 (1H, dd, *J* 14, 11 Hz, H(1)), 1.61 (2H, s, CH_2), 0.0 (9H, s, $Si(CH_3)_3$.

*anti-(η^3-1-Phenyl-2-methyl-2-pentenyl)Co(CO)$_3$ (**51**).* Yellow solid, 83% yield. IR (Et_2O): 2060, 1990 (CO) cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.8–7.4 (5H, m, Ph), 4.73 (1H, d, *J* 11 Hz, H(3)), 3.73 (1H, m, H(4)), 3.05 (1H, d, *J* 14 Hz, H(1)), 2.63 (1H, d, *J* 14 Hz, H(1)), 1.78 (3H, d, *J* 6 Hz, CH_3), 1.59 (3H, s, CH_3).

Representative procedure for PMe_3 reactions with (η^4-diene)Co(CO)$_3$BF$_4$

A 50 ml side arm round bottom flask was charged with 10 ml nitromethane and cooled to 0 °C. [(η^3-2-Methyl-1,3-butadiene)Co(CO)$_3$](BF_4) (0.234 mmol) was added and stirred to dissolve completely. One equivalent of trimethylphosphine in 2 ml nitromethane was then added dropwise. After 10–15 min diethyl ether (25 ml) was added to the solution to precipitate the product as a yellow solid. Solvent was removed using cannula and the solid was dried under vacuo.

*anti-[(η^3-1-Trimethylphosphonium-2-pentenyl)Co(CO)$_3$](BF$_4$) (**19a**).* Yellow solid, 76% yield. IR (CH_3NO_2): 2080, 1990 (CO), 1050 (BF_4^-) cm^{-1}. ^1H NMR (cold acetone-d_6); δ 5.24 (1H, m, H(3)), 4.27 (1H, m, H(4)), 3.12 (1H, m, H(1)), 2.35 (1H, m, H(1)), 2.05 (9H, d, *J* 14 Hz, $P(CH_3)_3$, overlapped with the solvent), 1.75 (3H, d, *J* 6 Hz, CH_3).

*anti-[(η^3-1-Trimethylphosphonium-5-trimethylsilyl-2-pentenyl)Co(CO)$_3$](BF$_4$) (**24a**).* Yellow solid; 69% yield. IR (acetone): 2060, 1990 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6): δ 5.3 (1H, m, H(3)), 4.3 (2H, m, H(2) and H(4)), 3.2 (1H, m, H(1)), 2.5 (1H, m, H(1)), 2.05 (9H, d, *J* 14 Hz, $P(CH_3)_3$, overlapped with solvent), 1.8 (2H, d, *J* 5 Hz, CH_2), 0.0 (9H, s, $Si(CH_3)_3$); MS (FAB); 359 (*M* − BF_4, 20%), 303 (*M* − BF_4 − 2CO, 37%), 275 (*M* − BF_4 − 3CO, 31%).

*anti-[(η^3-1-Trimethylphosphonium-3-methyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**29a**) and anti-[(η^3-1-trimethylphosphonium-2-methyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**29b**).* Yellow solid; 83% yield. IR (CH_3NO_2): 2060, 1990 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6) (values for **29b** in brackets): δ 4.45 (1H, dd, J 13, 8 Hz, H(2)), [5.38 (1H, m, H(3′))], 3.78 (1H, s, H(4)), [3.6 (1H, d, J 7 Hz, H(4′))], 3.26 (1H, m, H(1)), [3.52 (1H, d, J 11 Hz, H(1′))], 2.62 (1H, s, H(4)), [2.61 (1H, d, J 12 Hz, H(1′)), 2.42 (1H, m, H(1)), 2.18 (3H, s, CH_3')], 2.2 (3H, s, CH_3), 2.06 (18H, d, J 14 Hz, P(CH_3)$_3$, both isomers); MS (FAB): 374 (M, 13%), 287 ($M - BF_4$, 18%), 211 ($M - BF_4 - PMe_3$, 18%), 183 ($M - BF_4 - PMe_3 - CO$, 18%), 127 ($M - BF_4 - PMe_3 - 2CO$, 24%).

*anti-[(η^3-1-Trimethylphosphonium-3-ethyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**34a**) and anti-[(η^3-1-trimethylphosphonium-2-ethyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**34b**).* Yellow solid; 100% yield. IR (CH_3NO_2): 2080, 1990 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6) (values for **34b** in brackets): δ 4.43 (1H, m, H(2)), [6.91 (1H, dd, J 10, 7 Hz, H(3′))], 3.73 (1H, s, H(4)), [3.75 (1H, d, J 3 Hz, H(1′))], 3.28 (1H, s, H(4)), [3.66 (1H, dd, J 5, 3 Hz, H(4′))], 3.19 (1H, m, H(1)), [2.73 (1H, d, J 3 Hz, H(1′))], 3.0–2.8 (2H, m, CH_2), [2.65 (1H, dd, J 8, 3 Hz, H(4′))], 2.15 (1H, m, H(1)), 2.05 (18H, d, J 14 Hz, P(CH_3)$_3$, both isomers), [2.6–2.1 (2H, m, CH_2')], 1.47 (6H, t, J 8 Hz, CH_3, both isomers); MS (FAB): 301 ($M - BF_4$, 7%), 273 ($M - BF_4 - CO$, 7%), 217 ($M - BF_4 - 3CO$, 6%), 158 ($M - BF_4 - 3CO - Co$, 12%).

*anti-[η^3-(1-Trimethylphosphonium-3-phenyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**39a**).* Yellow solid; 83% yield. IR (CH_3NO_2): 2060, 2000 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6): δ 7.68–7.55 (5H, m, Ph), 5.35 (1H, dd, J 11, 8 Hz, H(2)), 3.92 (1H, s, H(4)), 3.71 (1H, d, J 8 Hz, H(1)), 2.74 (1H, d, J 11 Hz, H(1)), 2.27 (1H, s, H(4)), 2.05 (9H, d, J 14 Hz, P(CH_3)$_3$); MS (FAB): 321 ($M - BF_4 - CO$, 11%), 265 ($M - BF_4 - CO$, 9%), 206 ($M - BF_4 - 3CO - Co$, 20%).

*anti-[η^3-(1-Trimethylphosphonium-3-(p-FC$_6$H$_4$)-2-butenyl)Co(CO)$_3$](BF$_4$) (**44a**):* Yellow solid; 86% yield. IR (CH_3NO_2): 2070, 2010 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (acetone-d_6): δ 7.75–7.14 (4H, m, Ph), 4.93 (1H, m, H(2)), 4.25 (1H, s, H(4)), 3.35 (1H, m, H(1)), 2.59 (1H, m, H(1)), 2.1 (1H, s, H(4)), 2.08 (9H, d, J 14 Hz, P(CH_3)$_3$); MS (FAB): 367 ($M - BF_4$, 23%), 339 ($M - BF_4 - CO$, 62%), 311 ($M - BF_4 - 2CO$, 27%), 283 ($M - BF_4 - 3CO$, 100%).

*anti-[(η^3-1-Trimethylphosphonium-2-methyl-2-pentenyl)Co(CO)$_3$](BF$_4$) (**52a**).* Yellow solid; 100% yield. IR (CH_3NO_2): 2050, 1985 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone – d_6): δ 5.21 (1H, d, J 10 Hz, H(3)), 4.06 (1H, m, H(4)), 3.53 (1H, t, J 15 Hz, H(1)), 2.57 (1H, m, H(1)), 2.1 (9H, d, J 14 Hz, P(CH_3)$_3$), 1.96 (3H, s, CH_3), 1.76 (3H, d, J 6 Hz, CH_3); MS (FAB): 273 ($M - BF_4 - CO$, 1%), 158 ($M - BF_4 - 3CO - Co$, 15%).

Representative procedure for pyridine reactions with (η^4-diene)Co(CO)$_3$BF$_4$

A 50 ml side arm round bottom flask was charged with 50 mg (0.167 mmol) of η^4-(2-methyl-1,3-butadiene)Co(CO)$_3$BF$_4$ and 8 ml dichloromethane and cooled to −78° C. Pyridine (0.184 mmol) was added and the mixture stirred for 1 h. Then the solution was filtered into 50 ml cold diethyl ether using a cannula to form a yellow precipitate. Solvent was removed using a cannula and the solid dried in vacuo.

*anti-[(η^3-1-Pyridinium-2-pentenyl)Co(CO)$_3$](BF$_4$) (**20a**).* Yellow solid: 77% yield. IR (CH_2Cl_2): 2060, 2000 (CO), 1050 (BF_4^-) cm^{-1}; ^{1}H NMR (cold acetone-d_6): δ 9.15 (2H, d, J 5 Hz, H_o (C_5H_5N)), 8.75 (1H, t, J 8 Hz, H_p (C_5H_5N)), 8.27 (2H, t, J

6 Hz, H_m (C_5H_5N)), 5.18 (2H, m, H(3) and H(1)), 4.48 (2H, m, H(2) and H(4)), 4.36 (1H, dd, *J* 13, 12 Hz, H(1)), 1.8 (3H, d, *J* 6 Hz, CH_3); MS (FAB): 290 (*M* − BF_4, 5%), 206 (*M* − BF_4 − 3CO, 55%), 211 (M − BF_4 − C_5H_5N, 55%), 147 (*M* − BF_4 − 3CO − Co, 5%), 183 (*M* − BF_4 − C_5H_5N − CO, 11%).

*anti-[η^3-(1-Pyridinium-5-trimethylsilyl-2-pentenyl)Co(CO)$_3$](BF$_4$) (**25a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2070, 2000 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6): δ 9.19 (2H, d, *J* 6 Hz, H_o (C_5H_5N)), 8.78 (1H, dd, *J* 9, 7 Hz, H_p (C_5H_5N)), 8.3 (2H, dd, *J* 7, 5 Hz, H_m (C_5H_5N)), 5.2 (2H, m, H(1) and H(3)), 4.55 (1H, m, H(2)), 4.45 (1H, m, H(4)), 4.35 (1H, dd, *J* 13, 11 Hz, H(1)), 1.8 (2H, d, *J* 5 Hz, CH_2), 0.00 (9H, s, $Si(CH_3)_3$).

*anti-[η^3-(1-Pyridinium-3-methyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**30a**).* Yellow solid; 91% yield. IR (CH_2Cl_2): 2080, 2020 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6): δ 9.18 (2H, br s, H_o, C_5H_5N), 8.82 (1H, br s, H_p, C_5H_5N), 8.32 (2H, br s, H_m, C_5H_5N), 5.23 (1H, d, *J* 14 Hz, H(1)), 4.76 (1H, d, *J* 11 Hz, H(2)), 4.31 (1H, dd, *J* 14, 12 Hz, H(1)), 3.83 (1H, s, H(4), *syn*), 3.55 (1H, s, H(4), *anti*), 2.07 (3H, s, CH_3); MS (FAB): 211 (*M* − BF_4 − C_5H_5N, 100%), 183 (*M* − BF_4 − C_5H_5N − CO, 38%), 127 (*M* − BF_4 − C_5H_5N − 3CO, 8%).

*anti-[η^3-(1-Pyridinium-3-ethyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**35a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2080, 2000 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6): δ 9.16 (2H, d, *J* 5 Hz, H_o, C_5H_5N), 8.78 (1H, dd, *J* 9.8 Hz, H_p, C_5H_5N), 8.34 (2H, apparent t, *J* 7.7 Hz, H_m, C_5H_5N), 5.3 (1H, dd, *J* 13, 4 Hz, H(1)), 4.64 (1H, m, H(2)), 4.32 (1H, apparent t, *J* 12, 12 Hz, H(1)), 3.72 (1H, d, *J* 2 Hz, H(4)), 3.53 (1H, d, *J* 2 Hz, H(4)), 2.3–2.0 (2H, m, CH_2), 0.96 (3H, apparent t, *J* 7, 7 Hz, CH_3); MS (FAB): 304 (*M* − BF_4, 34%), 276 (*M* − BF_4 − CO, 2%), 161 (*M* − BF_4 − 3CO − Co, 7%), 146 (*M* − BF_4 − 3CO − Co − CH_3, 6%).

*anti-[η^3-(1-Pyridinium-3-phenyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**40a**).* Yellow solid; 83% yield. IR (CH_2Cl_2): 2060, 1995 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (acetone-d_6): δ 9.21 (2H, d, *J* 6 Hz, H_o, C_5H_5N), 8.78 (1H, t, *J* 8 Hz, H_p, C_5H_5N), 8.32 (2H, dd, *J* 7, 6 Hz, H_m, C_5H_5N), 7.47–7.29 (5H, m, Ph), 5.46 (1H, dd, *J* 14, 4 Hz, H(1)), 5.24 (1H, d, *J* 10 Hz, H(2)), 4.56 (1H, apparent t, *J* 13, 13 Hz, H(1)), 4.33 (1H, s, H(4)), 3.74 (1H, s, H(4)); MS (FAB): 352 (*M* − BF_4, 14%), 273 (*M* − BF_4 − C_5H_5N, 100%), 245 (*M* − BF_4 − C_5H_5N − CO, 25%), 217 (*M* − BF_4 − C_5H_5N − 2CO, 16%), 189 (*M* − BF_4 − C_5H_5N − 3CO, 21%).

*anti-[η^3-(1-Pyridinium-2-(p-FC_6H_6)-2-butenyl)Co(CO)$_3$](BF$_4$) (**45a**).* Yellow solid, 75% yield. IR (CH_2Cl_2): 2080, 2020 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (acetone-d_6): δ 9.2 (2H, d, *J* 5 Hz, H_o, C_5H_5N), 8.78 (1H, t, *J* 8 Hz, H_p, C_5H_5N), 8.3 (2H, apparent t, *J* 7, 7 Hz, H_m, C_5H_5N), 7.5–7.1 (4H, m, Ph), 5.44 (1H, dd, *J* 12, 4 Hz, H(1)), 5.23 (1H, m, H(2)), 4.55 (1H, apparent t, *J* 12, 12 Hz, H(1)), 4.33 (1H, s, H(4)), 3.7 (1H, s, H(4)); MS (FAB): 291 (*M* − BF_4 − C_5H_5N, 100%), 286 (*M* − BF_4 − 3CO, 45%), 263 (*M* − BF_4 − C_5H_5N − CO, 58%), 235 (*M* − BF_4 − C_5H_5N − 2CO, 58%), 207 (*M* − BF_4 − C_5H_5N − 3CO, 43%), 148 (*M* − BF_4 − C_5H_5 − N − 3CO − Co, 12%).

*anti-(η^3-1-Pyridinium-2-trimethylsilylmethyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**49a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2070, 2010 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (acetone-d_6): δ 9.26 (2H, d, *J* 5 Hz, H_o, C_5H_5N), 8.81 (1H, t, *J* 8 Hz, H_p, C_5H_5N), 8.39 (2H, t, *J* 7 Hz, H_o, C_5H_5N), 5.28 (1H, dd, *J* 14, 4 Hz, H(1)), 4.91 (1H, m, H(2)), 4.31 (1H, dd, *J* 14, 4 Hz, H(1)), 4.91 (1H, m, H(2)), 4.31 (1H, dd, *J* 14, 12 Hz, H(1)), 3.8 (1H, s, H(4)), 3.54 (1H, s, H(4)), 1.8 (1H, d, *J* 13 Hz, CH_2), 1.7 (1H,

d, J 13 Hz, CH_2), 0.00 (9H, s, $Si(CH_3)_3$); MS (FAB): 421 (M − CO, 31%), 334 (M − BF_4 − CO, 7%).

*anti-[η^3-(1-Pyridinium-2-methyl-2-pentenyl)Co(CO)$_3$](BF$_4$) (**53a**) and anti-[η^3-(2-pyridinium-4-methyl-2-pentenyl)Co(CO)$_3$](BF$_4$) (**53b**).* Yellow solid, 91% yield. IR (CH_2Cl_2): 2060, 2000 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6, values for **53b** in brackets): δ 9.3–8.3 (10 H, m, C_5H_5N, both isomers), 5.32 (1H, d, J 13 Hz, H(3)), [4.98 (1H, d, J 11 Hz, H(3′))], 5.15 (1H, d, J 11 Hz, H(1)), [4.49 (1H, m, H(2′))], 4.55 (1H, d, J 13 Hz, H(1)), [3.67 (1H, s, H(5′))], 4.31 (1H, m, H(4)), [3.52 (1H, s, H(5′))], 1.85 (3H, d, J 6 Hz, CH_3), [2.02 (3H, d, J 7 Hz, CH_3')], 1.65 (3H, s, CH_3), [1.97 (3H, s, CH_3')]; MS (FAB): 304 (M − BF_4, 17%), 307 (M − 3CO, 6%), 276 (M − BF_4 − CO, 5%), 161 (M − BF_4 − 3CO − Co, 4%).

Procedure for Et_3N reactions with [(η^4-diene)Co(CO)$_3$](BF$_4$)

A 25 ml side arm round bottom flask was charged with 15 mg (0.039 mmol) of [η^4-(2-(p-FC_6H_4)-1,3-butadiene)Co(CO)$_3$](BF_4) and 5 ml dichloromethane. After cooling the mixture to −78 °C, 1.1 equiv of triethylamine was syringed in and the mixture stirred for 1 h. The solution was filtered into 30 ml cold diethyl ether using a cannula to form a yellow precipitate. Solvent was removed via cannula and the solid was dried in vacuo.

*anti-[η^3-1-Triethylammonium-2-pentenyl)Co(CO)$_3$](BF$_4$) (**21a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2080, 2010 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6): δ 5.35 (1H, m, H(3)), 4.3 (2H, m, H(2) and H(4)), 3.81 (1H, d, J 14 Hz, H(1)), 3.5 (6H, q, J 7 Hz, CH_2), 2.95 (1H, d, J 15 Hz, H(1)), 1.73 (3H, d, J 7 Hz, CH_3), 1.37 (9H, t, J 7 Hz, CH_3); MS (FAB): 363 (M − 36, 5%), 35 (M − 36 − CO, 5%), 307 (M − 36 − 2CO, 8%).

*anti-[(η^3-1-Triethylammonium-5-trimethylsilyl-2-pentenyl)Co(CO)$_3$](BF$_4$) (**26a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2080, 2010 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6): δ 5.38 (1H, dd, J 10, 7 Hz, H(3)), 4.3 (2H, m, H(2) and H(4)), 3.79 (1H, d, J 14 Hz, H(1)), 3.5 (6H, br d, J 7 Hz, CH_2Si), 2.9 (1H, d, J 13 Hz, H(1)), 1.74 (2H, q, J 7 Hz, CH_2), 1.3 (9H, t, J 7 Hz, CH_3), 0.00 (9H, s, $Si(CH_3)_3$).

*anti-[(η^3-1-Triethylammonium-3-methyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**31a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2070, 2010 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6): δ 4.59 (1H, br d, J 8 Hz, H(1)), 3.85 (1H, dd, J 14, 12 Hz, H(2)), 3.69 (1H, s, H(4)), 3.5 (6H, q, J 7 Hz, CH_2), 3.4 (1H, br d, J 9 Hz, H_1), 3.33 (1H, s, H(4)), 2.2 (3H, s, CH_3), 1.39 (9H, t, J 7 Hz, CH_3); MS (FAB): 363 (M − 36, 10%), 335 (M − 36 − CO, 17%), 307 (M − BF_4 − 2CO, 31%).

*anti-[(η^3-1-Triethylammonium-3-methyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**31a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2070, 2010 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (cold acetone-d_6): δ 4.59 (1H, br d, J 8 Hz, H(1)), 3.85 (1H, dd, J 14, 12 Hz, H(2)), 3.69 (1H, s, H(4)), 3.5 (6H, q, J 7 Hz, CH_2), 3.4 (1H, br d, J 9 Hz, H(1)), 3.33 (1H, s, H(4)), 2.2 (3H, s, CH_3), 1.39 (9H, t, J 7 Hz, CH_3); MS (FAB): 363 (M − 36, 10%), 335 (M − 36 − CO, 17%), 307 (M − BF_4 − 2CO, 31%).

*anti-[(η^3-1-Triethylammonium-3-phenyl-2-butenyl)Co(CO)$_3$](BF$_4$) (**41a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2080, 2020 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (acetone-d_6): δ 7.73–7.53 (5H, m, Ph), 5.03 (1H, d, J 11 Hz, H(1)), 4.25 (1H, s, H(4)), 4.14 (1H, d, J 11 Hz, H(2)), 3.55 (6H, q, J 7 Hz, CH_2), 3.48 (1H, s, H(4)), 3.25 (1H, dd, J 14, 13 Hz, H(1)), 1.3 (9H, t, J 7 Hz, CH_3); MS (FAB), 425 (M − 36, 4 %), 397 (M − 36 − CO, 10%), 369 (M − 36 − 2CO, 14%).

anti-[η^3-(1-Triethylammonium-3-(p-FC_6H_4)-2-butenyl)Co(CO)$_3$](BF_4*) (**46a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2085, 2025 (CO), 1050 (BF_4^-) cm^{-1}; ^1H NMR (acetone-d_6): δ 7.81–7.14 (4H, m, Ph), 5.0 (1H, d, J 12 Hz, H(1)), 4.19 (1H, s, H(4)), 4.12 (1H, dd, J 12, 2 Hz, H(2)), 3.54 (6H, q, J 7 Hz, CH_2), 3.47 (1H, s, H(4)), 3.2 (1H, apparent t, J 13, 13 Hz, H(1)), 1.42 (9H, t, J 7 Hz, CH_3); MS (FAB): 443 (M − 36, 12%), 415 (M − 36 − CO, 10%), 387 (M − 36 − 2CO, 20%), 308 (M − 36 − 3CO, 6%).

anti-[η^3-(1-Triethylammonium-2-methyl-2-pentenyl)Co(CO)$_3$](BF_4*) (**54a**).* Yellow solid; 100% yield. IR (CH_2Cl_2): 2050, 1980 (CO), 1050 (BF_4^-) cm^{-1}. ^1H NMR (cold acetone-d_6): δ 6.82 (1H, m, H(3)), 3.63 (6H, q, J 7 Hz, CH_2), 3.44 (1H, m, H(4)), 2.7 (1H, d, J 2 Hz, H(1)), 2.54 (3H, s, CH_3), 2.52 (1H, d, J 2 Hz, H(1)), 1.69 (3H, d, J 6 Hz, CH_3), 1.4 (9H, t, J 7 Hz, CH_3). MS (FAB): 349 (M − 36 − CO, 5%), 321 (M − 36 − 2CO, 24%).

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References and notes

1 Reviews: J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke in Principles and Applications of Organotransition Metal Chemistry, Univ. Science Books, Mill Valley, CA., 1987, Chap. 17, 18; S.G. Davies in Organotransition Metal Chemistry: Applications to Organic Synthesis, Pergamon Press, Oxford, G.B., 1982, Chap. 4.

2 (a) S.G. Davies, M.L.H. Green and D.M.P. Mingos, Tetrahedron, 34 (1978) 3047; (b) L.A.P. Kane-Maguire, E.D. Honig and D.A. Sweigart, Chem. Rev., 84 (1984) 525; (c) O. Eisenstein, W.M. Butler and A.J. Pearson, Organometallics, 3 (1984) 887 and ref. therein; (d) D.A. Brown, N.J. Fitzpatrick and M.A. McGinn, J. Organomet. Chem., 293 (1985) 235 and ref. therein.

3 (a) M.L.H. Green, L.C. Mitchard and W.E. Silverthorn, J. Chem. Soc., Dalton, (1973) 1952; (b) J.W. Faller, A.M. Rosan, J. Am. Chem. Soc., 99 (1977) 4858; J.W. Faller, H.H. Murray, D.L. White and K.H. Chao, Organometallics 2 (1983) 400; (c) A.J. Pearson, M. Khan, J.C. Clardy and H. Cun-heng, J. Am. Chem. Soc., 107 (1985) 2748.

4 J.E. Backvall, J.E. Nystrom and R.E. Nordberg, J. Am. Chem. Soc., 107 (1985) 3676; B. Åkermark, A. Ljundqvist and M. Panunzio, Tetrahedron Lett., 22 (1981) 1055.

5 M.F. Semmelhack and J.W. Herndon, J. Organomet. Chem., 365 (1984) C15; M.F. Semmelhack, J.W. Herndon and J.P. Springer, J. Am. Chem. Soc., 105 (1983) 2497; M.F. Semmelhack and J.W. Herndon, Organometallics, 2 (1983) 363.

6 L.S. Barinelli, K. Tao and K.M. Nicholas, Organometallics, 5 (1985) 588.

7 P. Sautet, O. Eisenstein and K.M. Nicholas, Organometallics, 6 (1987) 1845.

8 L.S. Barinelli and K.M. Nicholas, J. Org. Chem., 53 (1988) 2114.

9 (a) E.O. Fischer, P. Kuzel and H.P. Fritz, Z. Naturforsch, B, 16 (1961) 138; (b) G. Winkhaus and G. Wilkinson, J. Chem. Soc., (1961) 602.

10 J.A. Bertrand, H.B. Jonassen and D.W. Moore, Inorg. Chem., 2 (1963) 601.

11 E.A. Colvin, Silicon Reagents in Organic Synthesis, Academic Press, London, 1988, Chap. 1.

12 A.A. El-Awady, J. Inorg. Nucl. CHem., 21 (1974) 223.

13 (a) K.N. Houk, J. Am. Chem. Soc., 95 (1973) 4092; (b) P.V. Alston and R.M. Ottenbrite, J. Org. Chem., 40 (1975) 1111.

14 R.G. Pearson, J. Am. Chem. Soc., 89 (193) 1827; I. Fleming in Frontier Orbitals and Organic Chemical Reactions, Wiley, New York, 1976, Chap. 3.

15 R.L. Frank, R.D. Emmick and R.S. Johnson, J. Am. Chem. Soc., 69 (1947) 2313.

16 C.S. Marvel and R.G. Woolford, J. Org. Chem., 23 (1958) 1658.
17 K. Tamao, K. Sumitani, Y. Kiso, M. Zembayashi, A. Fujidama, I. Nakajima, A. Minato and M. Kumada, Bull. Chem. Soc. Japan, 49 (1976) 1958.
18 D. Seyferth, J. Pornet and R.M. Weinstein, Organometallics, 1 (1982) 1651.
19 J. Newman and A.R. Manning, J. Chem. Soc. Dalton, (1978) 1593..
20 N. Chatini, Y. Yamasaki, S. Murai and N. Sonoda, Tetrahedron Lett., 24 (1983) 5649.