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Activator-Free Single-Component Co(I)-Catalysts for Regio- and Enantioselective Heterodimerization and Hydroacylation Reactions of 1,3-Dienes. New Reduction Procedures for Synthesis of [L]Co(I)-Complexes and Comparison to *in-situ* Generated Catalysts

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Although cobalt(I) bis-phosphine complexes have been implicated in many selective C-C bond-forming reactions, until recently relatively few of these compounds have been fully characterized or have been shown to be intermediates in catalytic reactions. In this paper we present a new practical method for the synthesis and isolation of several cobalt(I)-bis-phosphine complexes and their use in Co(I)-catalyzed reactions. We find that easily prepared (in situ generated or isolated) bis-phosphine and (2,6-*N*-aryliminoethyl)pyridine (PDI) cobalt (II) halide complexes are readily reduced by 1,4-*bis*-trimethylsilyl-1,4-dihydropyrazine or commercially available lithium nitride (Li_3N), leaving behind only innocuous volatile byproducts. Depending on the structures of the bis-phosphines, the cobalt(I) complex crystallizes as a phosphine-bridged species [(**P**~**P**)(X)Co^{I}[μ-(**P**~**P**)]Co^{I}(X)(**P**~**P**)] or a halide-bridged species [(**P**~**P**)Co^{I}[μ-(X)]$_2$Co^{I}(**P**~**P**)]. Because the side-products are innocuous, these methods can be used for the in-situ generation of catalytically competent Co(I) complexes for a variety of low-valent cobalt-catalyzed reactions of even sensitive substrates. These complexes are also useful for the synthesis of rare cationic [(**P**~**P**)Co^{I}-η^4-diene]$^+$ X$^-$ or [(**P**~**P**)Co^{I}-η^6-arene]$^+$ X$^-$ complexes, which are shown to be excellent single-component catalysts for the following regioselective reactions of dienes: heterodimerizations with ethylene or methyl acrylate, hydroacylation and hydroboration. The reactivity of the single-component catalysts with the in situ generated species are also documented.

Introduction

The Use of low-valent cobalt complexes for organic synthesis has received enormous attention recently as highlighted by several topical review articles[1] and a steady stream of impactful original publications. Representative examples include a broad range of carbon-carbon bond-forming reactions such as cross-coupling reactions,[2] heterodimerizations of alkenes[3] cycloaddition reactions,[4] hydroacylation reactions,[5] functionalizations via C-H activation,[6] and reductive coupling of alkenes and alkynes.[7] Until recently, with few exceptions,[3d, 4c, 8] the oxidation state of cobalt and the nature of the intermediates (radicals or low-valent organometallic C-Co species) in many of these reactions have remained open to speculation. For most C-C bond-forming reactions that involve low-valent cobalt species, the reactive catalysts were often generated in situ by reduction of the corresponding Co^{II} species with reducing agents such as Zn, Mn, Na/Hg, NaEt$_3$BH, alkyl aluminum, alkyl lithium or Grignard reagents (Figure 1). It is conceivable that the metal salts these reducing agents leave behind[9] can be deleterious for sensitive substrates, might interact with the catalytic metal producing extraneous species, or, sometimes even interfere with the targeted catalytic reaction, promoting alternate paths. Further, reductions with M^0 reagents can be capricious due the heterogeneous nature of the reaction conditions, leading to long induction periods as we have documented,[10] and, even over-reduction of Co^{II} to Co^0.[11] Lewis acidic nature of the metal byproducts can also interfere with an intended reaction. In addition, depending on the reaction conditions, a stable, yet catalytically inactive tetradentate Co^{I} species such as [(DPPP)$_2$Co^{I}]$^+$ [ZnBr$_3$]$^-$ (Figure 1, DPPP = 1,3-*bis*-diphenylphosphinopropane) can also be formed under the reaction conditions.[10]

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Electronic Supplementary Information (ESI) available: Experimental procedures, syntheses and isolation of all intermediates, and Tables with details of several optimization studies. Spectroscopic and chromatographic data showing identities and compositions of products under various reaction conditions.
Crystallographic Information and data for the new Co-complexes have been deposited at the Cambridge Crystallographic Data Centre under accession numbers shown. [(dppp)(Cl)Co[μ-(dppp)]Co(Cl)(dppp)] (**12**) [CCDC 1873380], [(dppe)(Cl)Co[μ-(dppe)]Co(Cl)(dppe)] (**13**) [CCDC 1966496], complex {[(*R,R*)-QuinoxP*]cobalt(I)(μ-Br)}$_2$ (**18**) [CCDC 1966498], {[(*S,S*)-Ph-BPE]cobalt(I)(μ-Br)}$_2$ (**19**) [CCDC 1966499], [*bis*(*N*-aryliminoethyl-*k*N,N')pyridine-*k*N]CoCl (**22**) [CCDC 1966500], {[(*R,R*)-QuinoxP*]cobalt(I)(η^6-C$_6$D$_6$)}$^+$[BARF]$^-$ (**23**) [CCDC 2016105], {[(*R,R*)-*i*Pr-DuPhos]cobalt-η^4-(2,3-dimethylbutadiene)]}$^+$ [BARF]$^-$ (**25**) [CCDC 2016106]. See DOI: 10.1039/x0xx00000x

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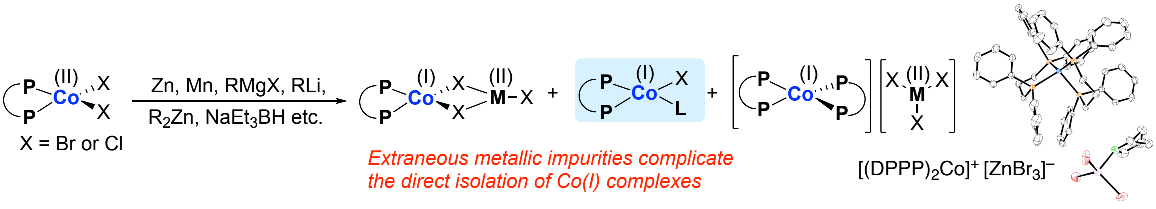
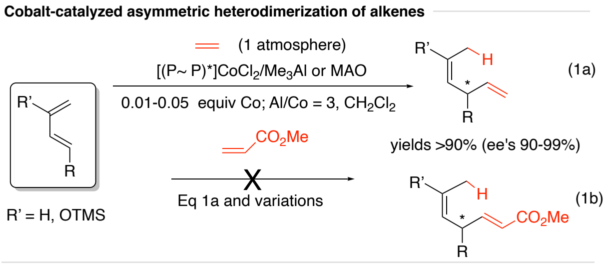


Extraneous metallic impurities complicate the direct isolation of Co(I) complexes

Figure 1. Reduction of (**P**~**P**)CoX_2 for synthesis of Co^I precatalysts

We encountered such problems in the in situ reduction of Co^{II} reagents in initial efforts to expand the scope of an enantioselective version of the hydrovinylation reaction (addition of ethylene) to 1,3-dienes (eq 1a) by substitution of ethylene by methyl acrylate as a reaction partner (eq 1b). Our originally used hydrovinylation conditions (eq 1a)[3c, 12] using catalysts generated from (**P**~**P**)CoX_2 and Me_3Al [**P**~**P** = chelating phosphines (e.g., *bis*-1,3-diphenylphosphinopropane (DPPP), *bis*-1,4-diphenylphosphinobutane (DPPPB), (*S,S*)-2,4-*bis*-diphenylphosphinopentane (BDPP)]) gave no detectable dimerization products with the acrylate partner under a variety of conditions (eq 1b).



In our attempts to overcome the substrate limitations in the diene/acrylate dimerization reaction, we wondered whether consideration of alternate mechanistic scenarios that are described for the olefin dimerization reaction[13] might offer some clues to solving the problems, especially as they relate to the incompatibility of the reagents with the reaction partners. Two principal mechanisms (Figure 2) have been advanced for this reaction: (a) metal-hydride route in which there are no oxidation changes in the metal, or (b) an oxidative cyclization route involving a Co^I/Co^{III} cycle.

Based on anecdotal observations in the literature[1c] and our own early results, we decided to explore in greater detail the oxidative dimerization route starting with synthesis of discrete (**P**~**P**)$Co^{(I)}X$ complexes and checking their viability as catalysts. An added incentive for this work when we first initiated this work (2015) was a dearth of reports in the literature that dealt with preparation and properties of these rare species, especially those containing synthetically useful chiral chelating bis-phosphines. Since then, our group[3d, 14] and Chirik's group[11b, 15] have published syntheses and structures of several Co^I bisphosphine complexes. Yet, in view of the versatility of these complexes as catalysts, there is still a need for facile, broadly applicable methods for the synthesis of such complexes. In this paper, in an approach complementary to the one published by the Chirik group,[11b] we report the applications of lithium nitride (Li_3N)[16] and an organic reducing agent, 1,4-*bis*-trimethylsilyl-dihydropyrazine (Mashima's Reagent, Figure 3)[17] for the synthesis of Co^I-complexes. In the cases of the neutral bis-phosphine complexes we find that the structures of the Co^I products (as determined by X-ray crystallography) depend on the ancillary ligands and the nature of the bis-phosphines. The halide-bearing complexes crystallize in one of two forms, either as a ligand-bridged (**I**) or a halide-bridged (**II**) structure (Figure 3). Furthermore, applications of such isolated complexes and their cationic versions (**III**) as catalyst for highly selective reactions of 1,3-dienes are reported.[18] Documented comparisons of the performance of in situ generated species with that of isolated complexes (including activator-free single-component cationic Co^I-complexes), enable more user-friendly procedures for carrying out these fundamental reactions.

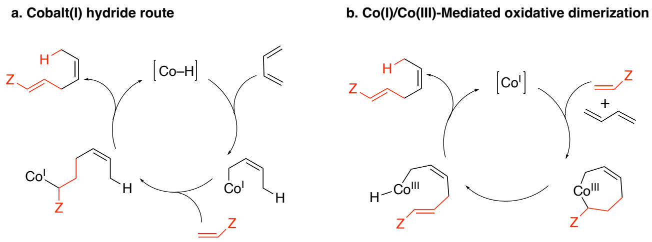


Figure 2. Possible mechanisms of heterodimerization of dienes and alkenes

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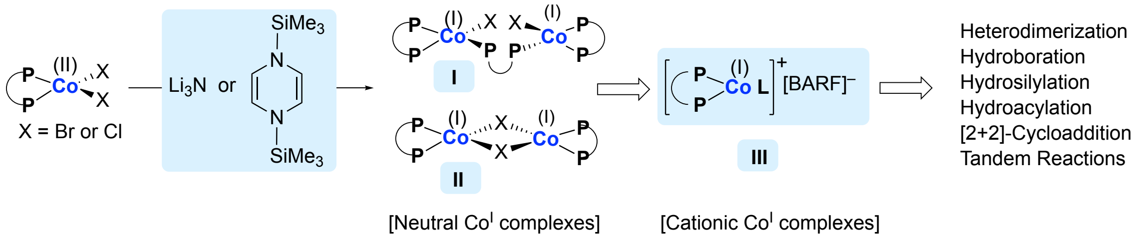


Figure 3. Synthesis of ligand-bridged (**I**) or halide-bridged (**II**) Co^I bimetallic complexes and their cationic variants (**This work**)

Results and discussion

The rarity of bis-phosphine Co(I) complexes was somewhat surprising since there were numerous examples of fully characterized Co^I complexes of non-phosphine ligands such as 2,6-diiminopyridine (PDI),[19] 1,2-bis-imine[20] and 2,6-*bis*-(*N*-heterocyclic carbene)-arylpincer[8b] ligands. Among phosphorus-containing complexes, those with monophosphines (**1**) (**P**$_3$CoX),[21] and chelating tripodal tris-phosphines (**2**, **3**)[22] were also known when we initiated this work (Figure 4 **A**).

Our initial approach for the preparation of discrete Co^I-bisphosphine complexes relied on a rarely used Co^I complex, **4** [(η^3-cyclooctenyl)Co^I(1,5-cyclooctadiene)],[23] which gave stable 16-electron (η^3-cyclooctenyl)Co^I(1,n-*bis*-diphenylphosphonoalkane) complexes by displacement of the COD ligand (Figure 4 **B**). Several complexes (**5a-5d**) were prepared *in situ* for use in reactions, and, the (*S*)-BINAP complex **5e** was recrystallized and fully characterized by X-ray crystallography.[3d] These complexes were used successfully in prototypical heterodimerization reactions of (*E*)-1,3-dodecadiene (**6**) with ethylene (eq 3, Table 1, entries 1-3), and subsequently with methyl acrylate, to give products **7** and **8** respectively.[3d] These studies established, for the first time, that neutral complexes [e.g., (**P~P**)Co^IX (X = η^3-cyclooctenyl)] were *not* competent to effect the dimerization (Table 1, entry 1) and they need a Lewis acid such as $(C_6F_5)_3B$ or a halide sequestering agent like sodium *tetrakis*-3,5-*bis*-trifluorophenylborate (NaBARF) to effect the dimerization reaction. Presumably these activators generate a cationic Co^I species which were responsible for the highly regio- and stereo-selective reactions.

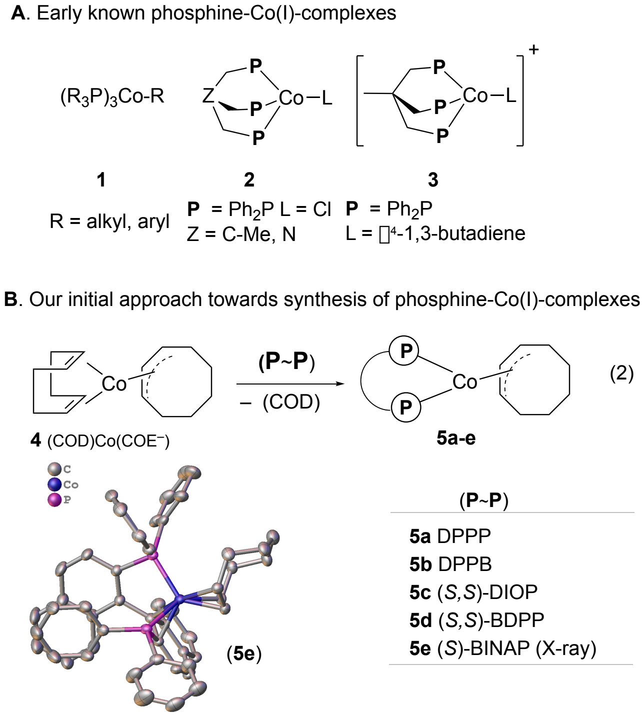
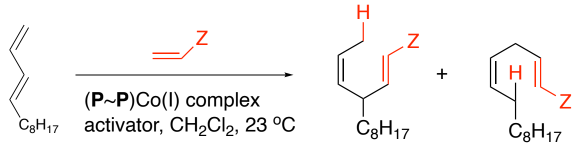


Figure 4. Early examples of Co^I phosphine complexes. Solid-state structure for **5e** is shown at 50% probability ellipsoid with hydrogens omitted for clarity.

Table 1. Heterodimerizations of (*E*)-1,3-dodecadiene with ethylene or methyl acrylate using Co^{I} complexes. Effect of additives[a]



(3)

6 **a** Z = H; **b** Z = CO$_2$Me **7** **8** (1,4-adduct)

Entry (Z)	Co(I) source (mol%)	Activator (mol%)	Temp (°C), Time (h)	Conv. (%)	**7**:**8**
1 (H)	**5b** (DPPP)Co(COE$^-$) (10)	none	23, 2	0	
2 (H)	**5b** (DPPB)Co(COE$^-$) (10)	$(C_6F_5)_3B$ (30)	23, 1	100	71/3
3 (H)	**5d** [(*S,S*)-BDPP]Co(COE$^-$) (10)	$(C_6F_5)_3B$ (30)	0 to 23, 2	100	77[b]/21
4 (H)	**10** (DPPP)$_3$Co$_2$Br$_2$ (5)	none	23, 2	<5	--
5 (H)	**10** (DPPP)$_3$Co$_2$Br$_2$ (5)	$(C_6F_5)_3B$ (60)	23, 1	100	80/20
6 (H)	**10** (DPPP)$_3$Co$_2$Br$_2$ (5)	NaBARF (20)	23, 1	>99	82/17
7 (CO$_2$Me)[c]	**10** (DPPP)$_3$Co$_2$Br$_2$ (3)	NaBARF (14)	23, 15	74	75:15[d]

[a] See eq 3 for procedure and ref. 3d for other similar examples. Products from ethylene are **7a** and **8a** and those from methyl acrylate are **7b** and **8b**. [b] Enantiomeric ratio for **7a** was 90:10. [c] Methyl acrylate used instead of ethylene. [d] Ratio of 4,1:1,4 adducts from methyl acrylate (**7b**:**8b**). For a striking effect of counter ion on the rate of heterodimerization of 2,3-butadiene and methyl acrylate, see Supplementary Information, p. S22.

Even though we found the Otsuka complex **4** to be quite useful in initially establishing the crucial role of a cationic Co^{I} for these heterodimerization reactions, large scale preparation of this highly sensitive precursor was quite inconvenient, and we sought alternate methods for the preparation of structurally simpler generic (**P**~**P**)Co^{I}X complexes. Scouting experiments quickly revealed that among the classical reduction procedures, reduction of (**P**~**P**)Co^{II}X$_2$ complexes with activated zinc[21] was the most convenient and we resorted to this method to prepare the first Co^{I} complexes. Thus, the treatment of (dppp)Co^{II}Br$_2$ (**9**)[12] with Zn (5 equiv) in THF at room temperature gave a green solid that was recrystallized to get X-ray quality crystals of **10**. The same solid could be isolated (and identified as equivalent by X-ray crystallography by crystal unit parameters) by reduction of a THF solution of (DPPP)Co^{II}Br$_2$ with 3M EtMgBr in ether (eq 4). In the event, the facile isolation of the discrete Co^{I}-complex (DPPP)$_3$Co$_2$Br$_2$ (**10**) allowed us to study in detail the effect of various additives (Lewis acids and halogen sequestering agents such as various Ag-salts and NaBARF) in the heterodimerization reactions of 1,3-dienes with ethylene and also with alkyl acrylates (Table 1, entries 4-7).[3d]

New Procedures for the Preparation of Chiral (*bis*-Phosphine)Co$^{(I)}$X Complexes. Our repeated attempts to prepare a chiral Co^{I} complex from highly crystalline [(*S,S*)-BDPP]CoBr$_2$,[12] via reduction with common reducing agents (Zn, Mg, RMgBr, hydride reagents) under conditions including the ones that yielded the complex (dppp)$_3$Co$_2$Br$_2$ (Figure 5) returned no crystalline products that could be fully characterized by X-ray crystallography. These high-spin Co^{I} complexes typically give only poorly resolved ^{1}H, and ^{31}C NMR spectra, and thus are not useful for identification.

While it is not clear why some Co^{II} complexes (**P**~**P**)CoX$_2$ such as the (DPPP)-complex **9** readily yielded clean, *isolable* Co(I) reduction products (**10**, Figure 5) upon treatment with reducing agents like Zn or RMgX, others did not, it is not unreasonable to assume that the contaminant byproducts from these reducing agents (Figure 1) play a role here, as has been observed in the reduction of other transition metal halides.[9] We reasoned that one solution to the problem is to use *cleaner reduction procedures* that leave only innocuous byproducts or those that can be easily removed. Further, absence of extraneous Lewis acidic metal salts such as ZnX$_2$ or MnX$_2$ could be advantageous in reactions of sensitive substrates (e.g., silyloxy-1,4-dienes, vide infra) where the Co^{I}-catalyst could be generated in situ. For this, first we turned to lithium nitride,[16] which was a little known reducing agent giving byproducts N$_2$ and LiCl (Figure 6, eq 5), and to 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine and its analogs (**11a, b**),[17a] from which the volatile byproducts can be readily removed (Figure 6, eq 6).

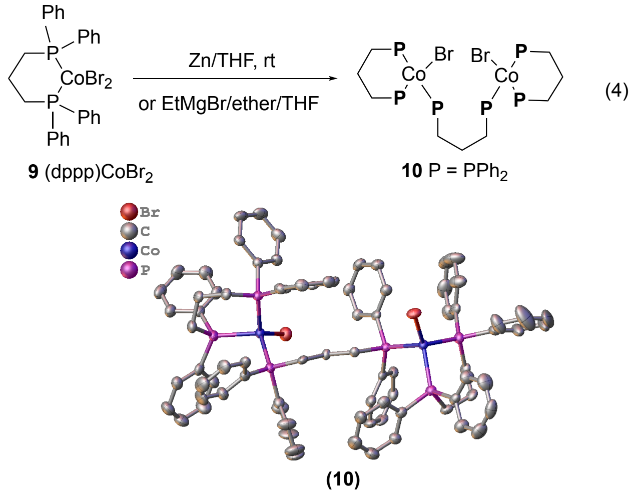


Figure 5. Synthesis of a ligand-bridged Co^I bis-phosphine complex. Solid-state structure for **10** is shown at 50% probability ellipsoid with hydrogens omitted for clarity.

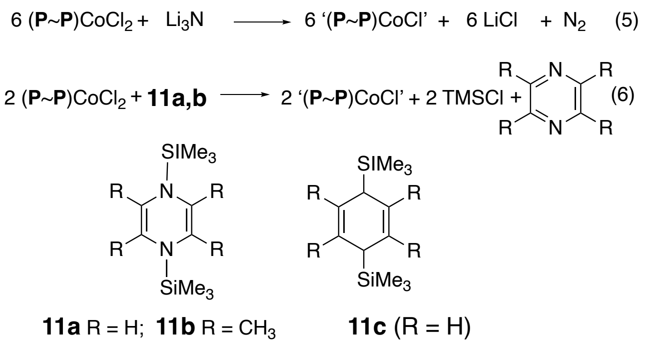
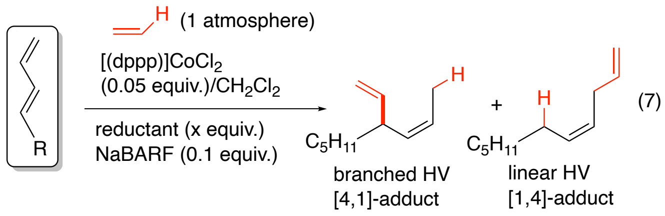


Figure 6. Reduction of (**P~P**)CoCl$_2$ with lithium nitride and 1,4-dihydro-1,4-bis-trimethylsilylpyrazine

For an initial evaluation of the viability of these reagents for the in situ generation and catalysis by a Co^I-species we turned to a prototypical hydrovinylation, that of a 1,3-nonadiene (eq 7, Table 2), a reaction familiar to us from previous studies.[12,24] It was quickly established that a catalytically competent low valent Co^I reagent was readily generated in solution either by Li$_3$N or the 1,4-*bis*(trimethylsilyl)-1,4-dihydropyrazine reagents, **11a** and **11b** (Table 2). Excellent yields of the adducts were obtained with both these reagents (Entries 2, 3 and 5). We found that a carbocyclic analog of **11a**, 1,4-*bis*-trimethylsilylcyclohexa-2,5-diene (**11c**) was not suitable for this reaction. Even though Li$_3$N was an excellent reagent for the in situ reduction of the Co^{II}-complexes (Table 2, Entry 5, See also Supplementary Information for further details including additional examples using Li$_3$N, pp. S23-25), in the enantioselective heterodimerizations of 1,3-dienes, we pursued the dihydropyrazine reagents **11a** and **11b** for further studies because of the potential hazards associated with the nitride reagent.[25]

Table 2. A test reaction to check the viability of the in situ reduction methods for generation of [(dppp)Co^I]$^+$ [a]



entry	reductant (x)	t (h)	conver. (%)	[4:1]:[1:4]
1	Zn (0.5)	0.5	100	78:22
2	**11a**^{b} (0.05)	1.25	100	79:20
3	**11b**^{b} (0.05)	0.75	100	80:20
4	**11c**^{b} (0.05)	24	4	-
5	Li$_3$N 0.10)	1.5	100	80:20

a. See Supplementary Information for experimental details. b. See Figure 6 for structures.

Synthesis, isolation, and characterization of ligand-bridged Co(I) complexes, [(P~P)(Cl)Co^I[μ-(P~P)]Co^I(Cl)(P~P)]. In the optimized procedure for the synthesis of the ligand-bridged complexes (**12**-**14**, Figure 7), the corresponding (**P~P**)CoX$_2$ [prepared in situ by stirring a mixture of the ligand (~1.55 equiv.) with CoX$_2$ in THF] was treated with 2 equivalents of **11a** for 18-24 h (eq 8 and 9). The volatile products were removed, and the residual solid was *readily recrystallized (inside a glovebox) in high yield* from a concentrated THF solution with slow diffusion of hexane. We found that it is important to keep the stoichiometry of cobalt(II) halide to the ligand at 1.00:1.55 since it was noticed that at 1:1 stoichiometry part of the cobalt salt was sacrificed (possibly through disproportionation of the resulting Co(I) complex to Co(II) and metallic Co(0)?) resulting in lower overall yields.

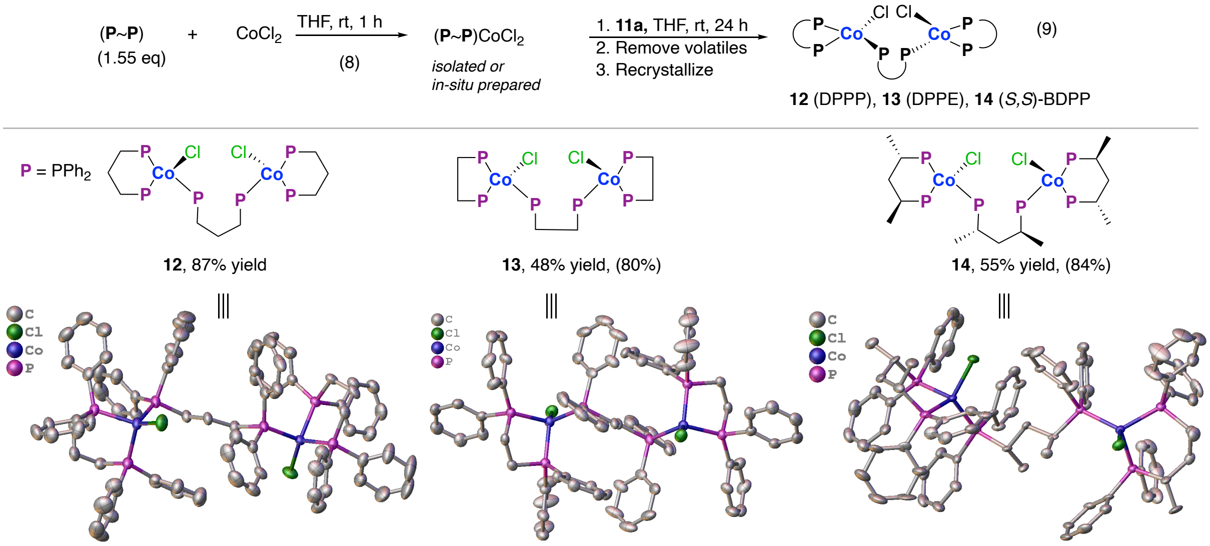


Figure 7. **A.** Synthesis of (**L**)Co(I) complexes via reduction of the Co^{II}-complex with 1,4-*bis*-(TMS)-1,4-dihydropyrazine (**11a**). Yields are reported after recrystallization. In brackets are the isolated yields before recrystallization. **B.** Solid-state structures: [(dppp)(Cl)Co[μ-(dppp)]Co(Cl)(dppp)] (**12**) [Geometry around Co- tetrahedral, P-Co-P = 95.5°, 95.7°, Cl-Co-Co-Cl = -140.98°, Co-P = 2.23Å, Co-P (bridging)= 2.27Å]; [(dppe)(Cl)Co[μ-(dppe)]Co(Cl)(dppe)] (**13**) [Geometry around Co- tetrahedral, P-Co-P = 87.96°, Cl-Co-Co-Cl = -180° Co-P = 2.258Å, Co-P (bridging)= 2.264Å]; and [(*S,S*)-(BDPP)(Cl)Co[μ-[(*S,S*)-(BDPP)]]Co(Cl)(*S,S*)-(BDPP)] (**14**) [Geometry around Co- tetrahedral, P-Co-P = 95.67°, 96.61°, Cl-Co-Co-Cl = 96.08°, Co-P = 2.25Å, Co-P(bridging) = 2.31Å]. Structure of **14** has been previously disclosed in the literature (ref 14). Structures are shown at 50% probability ellipsoid with hydrogens omitted for clarity.

[[(dppp)(Br)Co[μ–(dppp)]Co(Br)(dppp)] (10*).* This complex was prepared using the same general procedure (eq 8, 9, Figure 7) using the *bis*-TMS-dihydropyrazine reagent **11a**. An alternate preparation using LiN$_3$ instead of **11a** was also successful, even though the yield of the final product was found to be lower (~ 46%) in this case. The products from both of these reactions were identified via unit cell parameters of a compound we have previously reported (**10**, Figure 5) via Zn reduction of the corresponding cobalt (II) complex (CCDC # 1814337).[3d]

[(dppp)(Cl)Co[μ-(dppp)]Co(Cl)(dppp)] (12). This paramagnetic complex (CCDC # 1873380) has a tetrahedral geometry around cobalt and is characterized by a bridging ligand connecting the two coordinately unsaturated 16-electron cobalt(I) atoms. These complexes were tested for hydrovinylation and give excellent reaction. See SI (p. S27, Figure S4) for details.

(dppe)(Cl)Co[*μ*-(dppe)]Co(Cl)(dppe)] (13). Reduction of 1,2-*bis*-(diphenylphosphinoethane)CoCl$_2$ also gives a bridged structure very similar to what was obtained from the (dppp)CoX$_2$ complexes. In this case, the starting Co^{II}Cl$_2$ complex is known to be an intricate mixture of various structures and depending on the condition of generation, at least 3 different forms have been characterized.[26] But in situ generation of the presumed mixture of Co^{II}-halides followed by reduction with **11a** gave a single compound whose structure, **13,** is depicted in Figure 7.

[(*S,S*)-(BDPP)(Cl)Co[*μ*-[(*S,S*)-(BDPP)]]Co(Cl)(*S,S*)-(BDPP)] (14). One of the simplest chiral analogs of 1,3-*bis*-diphenylphosphinopropane is (*S,S*)-*bis*-2,4-diphenylphosphinopentane, and, cobalt complex of this ligand, and as mentioned earlier, has been used extensively in enantioselective catalysis. The Co^{I} complex is best prepared by the dihydropyrazine-mediated reduction of the pre-formed [(*S,S*)-BDPP]CoCl$_2$. The solid-state structure (**14**, (CCDC # 1885713) is shown in Figure 7. This complex has been previously reported.[14]

The structure of **12** is very similar to **10**[3d] with the main differences caused by the halogen used and the fact that **10** is a tris-THF solvate, whereas **12** is a neat structure with two molecules in the asymmetric unit. In both structures there is some amount of Ph-H … halogen bonding. With the reduction of the bridging chain by 1 carbon in **13**, the structure becomes symmetrical and sits on an inversion center. With the introduction of the methyl's in 14, one side of the ligand-bridged species is similar to those in **10** and **12** but the other side with Cl1 in close proximity to C33 forces the complex to expand to allow for the added group. Looking at the angle between the plane of the phosphine bridge and the plane of the metal and other phosphines shows this difference to be quite significant and closer to that of the contracted bridging species (**13**).

Synthesis, isolation, and characterization of halide-bridged Co(I) complexes, [(P~P)Co(*μ*-X)$_2$Co(P~P)]. In sharp contrast to the complexes of the 1,n-*bis*-diphenylphosphinoalkane (n = 2, 3) ligands, the complexes of the more sterically demanding chiral ligands (Figure 8) crystallize in a dimeric form with a halide bridge rather than a ligand bridge. These compounds could also be prepared by chemical reduction of the corresponding (**P~P**)CoX$_2$ complexes, used as isolated solids or prepared in situ as described earlier (Figure 7, eq 8, eq 9). Structures of three such complexes derived from the ligands, (*R,R*)-2,3-*bis*(*tert*-butylmethylphosphino)quinoxaline [(*R,R*)-QuinoxP*, **15**][27], 1,2-*bis*-(2*S*,5*S*)-2,5-diphenylphospholano)ethane [(*S,S*)-Ph-BPE,

16][28] and (2*R*,5*R*)-1-[2-[(2*R*,5*R*)-2,5-diisopropylphospholan-1-yl]phenyl]-2,5-diisopropylphospholane [(*R,R*)-^{i}Pr-DuPhos, **17**],[29] are shown in the Figure 8 (**18**-**20**). The solid-state structure of the complex **20** has been previously reported (CCDC #1586348).[11b] These complexes crystallize with tetrahedral geometry around the central Co^{I} ions. The structure of **18** is symmetrical with both Br's sitting on a two fold rotation axis but instead of a planar geometry, the structure is bent with angle of 151.38 between the planes of the ligands. The metal-halogen planes on **18** and **19** are almost flat with **19** nearly isostructural to the previously reported Cl analog,[11b] although the inverted configuration. Interestingly, the metal-halogen planes on **20** are far from planar with an angle of almost **24** degrees.

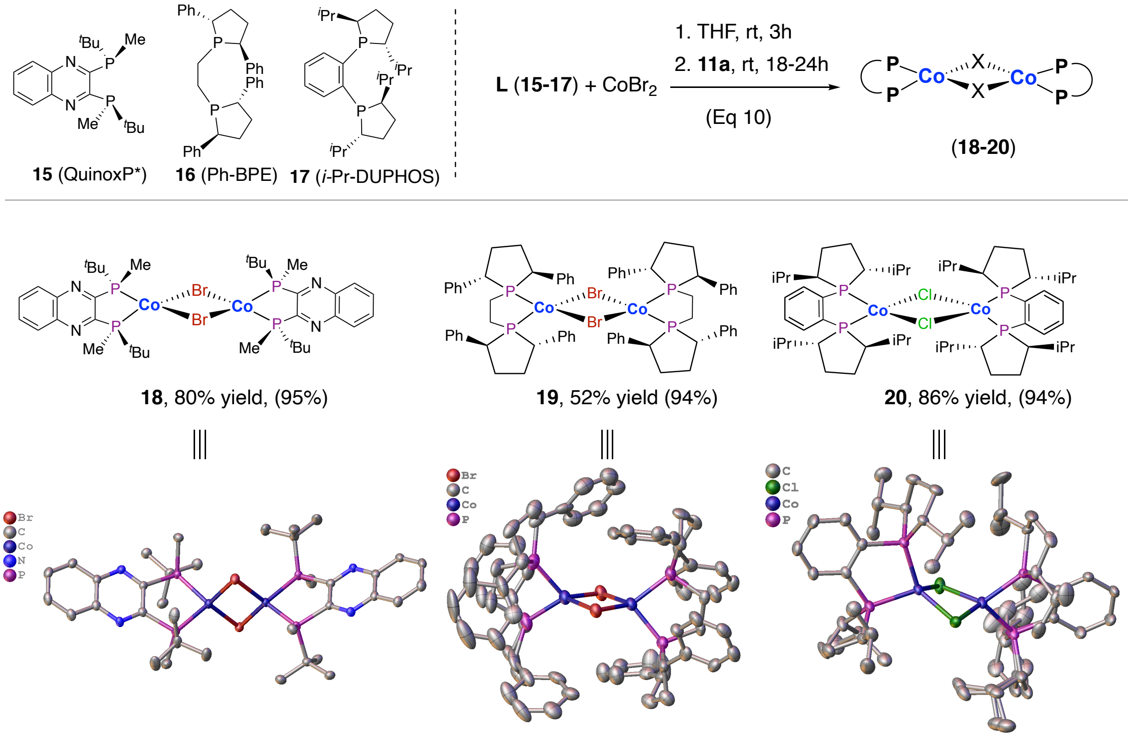
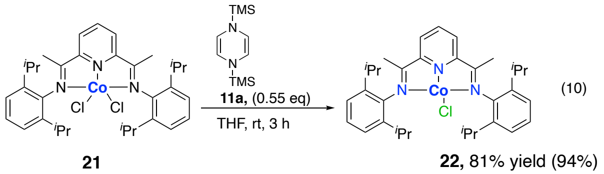


Figure 8. Co(I) complexes of chiral ligands **15, 16** and **17**: {[(*R,R*)-QuinoxP*]Co^{I}(μ-Br)}$_2$ (**18**) [Geometry around Co- tetrahedral, P-Co-P = 91.29°, Br-Co-Br = 111.50°, Co-P = 2.20 Å Co-Br (bridging) = 2.43, 2.44 Å; [[(*S,S*)-Ph-BPE]Co^{I}(μ-Br)}$_2$ (**19**) [Geometry around Co- tetrahedral P-Co-P = 88.70°, 89.05°, Br-Co-Br = 105.58°,105.60°, Co-P = 2.21Å, 2.23 Å, Co-Br(bridging) = 2.43Å 2.45Å]; {[(*R,R*)- ^{i}Pr-DuPhos]cobalt(μ-Cl)}$_2$ (**20**) [Geometry around Co- tetrahedral, P-Co-P = 89.02°, Cl-Co-Cl = 99.81°, 99.96°, Co-P = 2.21Å, Co-Cl (bridging) = 2.32Å, 2.34 Å]. Yields are reported after recrystallization. In brackets are the isolated yields before recrystallization. The Cl analog of **19** and the complex **20** has already been described in the literature (CCDC # 1586348, ref. 11b). At 50% probability ellipsoid with hydrogens omitted for clarity.

A 2,6-*bis*-Aryliminoethylpyridine Co(I) complex. Incidentally, the chemical reduction procedure using the pyrazine agent **11a** is equally applicable for the synthesis of widely used pyridine-diimine Co^{I} complexes (eq 9). Thus, the Co$^{(I)}$-complex of a ligand **21**, [*bis*(*N*-aryliminoethyl-κ*N,N'*)pyridine-κ*N*]Co^{I}Cl (**22**), is readily prepared from the corresponding $CoCl_2$-complex. Analogs of this complex, which has a distorted square planar geometry around the central Co^{I}, was first made by Gal,[30] who prepared a sample for X-ray crystallography by reduction of the (PDI)$CoCl_2$-complex with "butadiene-Mg". The structure of our complex was confirmed by X-ray crystallography.



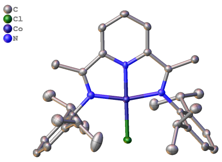


Figure 9: Solid-State structure of **22** at 50% probability ellipsoid with hydrogens omitted for clarity. Geometry around Co- square planer, N^{1}-Co-N^{2} = 81.63°, N^{2}-Co-N^{3} = 81.42°, Co-

N^1=1.91Å, Co-N^2=1.81Å, Co-N^3 =1.90Å, Co-Cl = 2.18 Å, Cl-Co-N^1 = 97.89°, Cl-Co-N^3 = 99.05°

Among the complexes we prepared, the QuinoxP*-complex **18** and the [Ph-BPE]-complex **19** are new. A chloride analog of [Ph-BPE] complex **19** and the [(^{i}Pr-Duphos)CoCl]$_2$-complex **20** were described in the literature while our studies were in progress.[11b] For use in catalytic reactions, these can be prepared in good yields by reduction of the corresponding CoX_2 complex with Zn. The previously reported preparations of the Zn-free complexes suitable for X-ray crystallography involved a stoichiometric reaction between of (**P~P**)$CoCl_2$ and (**P~P**)$Co(CH_2TMS)_2$ in THF at one atmosphere of hydrogen.[11b]

The structures of the Co(I) complexes are unexceptional except that the DPPE, DPP and BDPP ligands form ligand-bridged high-spin complexes with tetrahedral geometry around the metal, whereas the chiral ligands *i*-PrDuPhos, PhBenzP and QuinoxP* form halide bridged complexes. This could be related the steric effects imposed by the larger-bite angles of the former group, which do not allow for the formation of a more compact halide bridges.

Selectivity in the formation of the Co(I) versus Co(0) complex. One of the complications of the metal (Zn, Mn) reduction of the (P~P)CoX_2 complexes is the possibility of over-reduction to form Co(0)-complexes. Experiments were also carried (Figure 10) out using the [*(R,R)*-^{i}Pr-DuPhos]$CoBr_2$ to examine the selectivity of the *bis*-TMS-pyrazine reagent **11a**, for the selective preparation of the Co(I) complex (**20-Br**), thus avoiding over reduction to a Co(0)-complex, [*(R,R)*-^{i}Pr-DuPhos]Co^0[**L**] (**L** = solvent or an added diene).[11b] Treatment of the (Duphos)cobalt(II) bromide complex with large excess (5 equivalents) of **11a** and 10 equivalents of COD for 24 h at room temperature and isolation of the product only gave the Co^I -complex, **20-Br** (as identified by its distinct ^{1}H NMR, see p. S77 in the Supporting Information), thus confirming that the organic reductant **11a** resists over reduction of Co^{II} (see Supporting Information for details, p. S16 and S77).

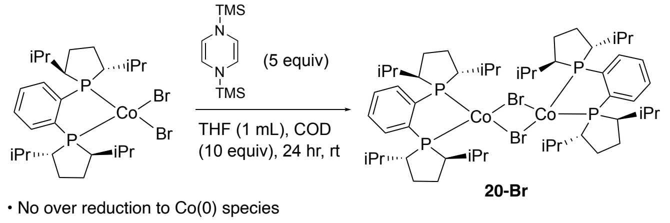


Figure 10. (Duphos)$CoBr_2$ reduction with excess bis-TMS-pyrazine (no over reduction)

UV Spectroscopy for monitoring the Co(II) to Co(I) reduction. Previously, we have used UV-Vis spectroscopy to monitor the reaction between (dppp)$CoBr_2$ and Zn, and, in that connection, reported the UV spectra of the ligand bridged Co(I) complexes **10** and **12**.[10] The UV spectra of each of the halide-bridged complexes **18, 19** and **20** is distinctly different (see Figure SI in Supporting Information, p. S20-21), providing no discernable information. Yet, they provide a way of monitoring the relative efficiency of the Co(II) to Co(I) reduction by the reducing agents. For example, the reduction of the (QuinoxP*)$CoBr_2$ complex to **18** can be monitored by a peak appearing at 850 nm, or, in the case of reduction of [(*SS*)-BDPP]$CoCl_2$ with the formation of **14,** the disappearance of peaks at 575, 625 and 725 nm (see Figure S2 in Supporting Information, p. S19). In each case the reduction using the *bis*-TMS-pyrazine reagent **11a** is significantly faster (at near stoichiometric amounts) than with excess metallic Zn, with the former effecting quantitative reduction in less than 30 min (Figure S2, a and b, P. S21 in the Supporting Information).

Synthesis of well-defined cationic Co(I) complexes and their uses as single-component catalysts.
{[(R,R)-QuinoxP]$Co^{(I)}(\eta^6$-$C_6D_6)$}$^+$ [BARF]$^-$ (**23**). A single component catalyst for regio- and enantioselective heterodimerization of a 1,3-diene and methyl acrylate.* This complex was prepared by the reaction of **18** with 2 equivalents of NaBARF in C_6D_6 (eq 11) and isolated as a purple crystalline solid. The compound was identified by NMR and X-ray crystallography of a solid sample. In the X-ray representation hydrogens/deuteriums and the counter anion [BARF]$^-$ are omitted for clarity (at 50% probability ellipsoid with H/D omitted for clarity). Complex **23** is similar to the Chirik's benzene complexes[15a] with Co-Benz distances (centroid of ring) all around 1.6 Å. However, Co-P distances in **23** were longer (2.165-2.173 Å) than those of Chirik's structures (2.142-2.157 Å).

We have alluded to the inability of isolated neutral Co(I) complexes (e.g., **5** or **10)**, to effect heterodimerization of 1,3-dienes with ethylene or methyl acrylate (Table 1, eq 3) in the absence of a halide sequestering agent [NaBARF or $(C_6F_5)_3B$],[3d] which suggested a key role for a cationic Co-species in these reactions. Isolation of [(**P~P**)Co^IL]$^+$ [BARF]$^-$ allows further confirmation of the role of putative cationic Co^I-species in these reactions. Results of a series of key experiments are listed in Table 3.

Entry 1 shows that the single-component cationic Co-species **23** is an excellent catalyst giving high yield, regio- and enantioselectivity for the 4,1-adduct (**24**). The same catalyst can be generated in situ from the halide-bridged Co^I-bimetallic species **18** (Figure 8) by treatment with NaBARF (entry 2). The excellent reactivities of these cobalt sources notwithstanding, from a practical perspective the reaction is best accomplished by simply carrying out the reduction and the activation of the (QuinoxP*)$Co^{II}Br_2$ complex in same pot using either Zn or 1,4-bis-TMS-pyrazine (entries 3 and 4). No loss of yield or enantioselectivity was noticed under these conditions. Most pleasingly, the organic reductant could be used in near stoichiometric amount with respect to the cobalt source whereas Zn is often needed in excess.

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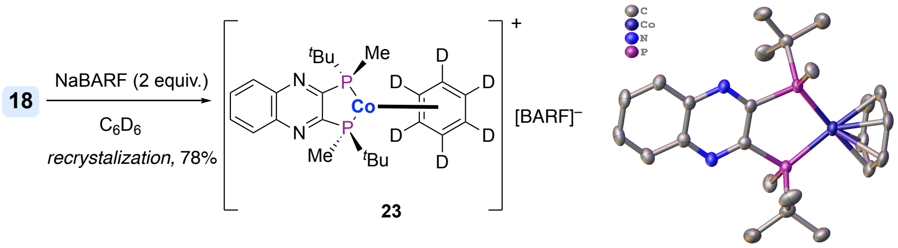

(11)

Figure 11. Solid-State structure of **23** at 50% probability ellipsoid with hydrogens omitted for clarity. [P-Co-P = 89.10^o, Co-P = 2.17Å, Co-C = 2.12Å, 2.15Å]

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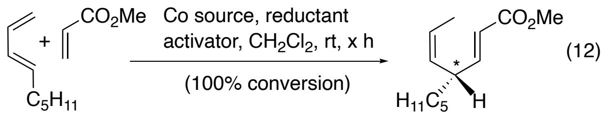
Table 3. Activator-free, single-component (entry 1) and in situ generated [Co^I]$^+$-catalysts for heterodimerization of a 1,3-diene and methyl acrylate[a]



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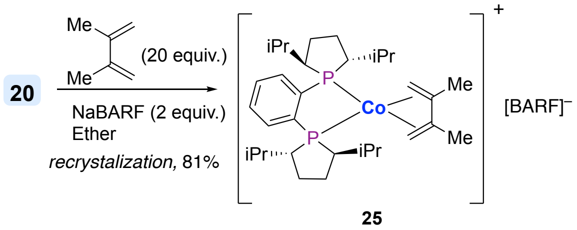
no.	Co^I-source (equiv)	reductant (equiv)	activator (equiv)	time (h)	Yield (%ee)[c]
1.[b]	{[(*R*)QuinoxP*]Co^I(C$_6$D$_6$)}$^+$[BARF]$^-$ (**23**, 0.01)	0	0	10	93 (94, *R*)
2.	{[(*R*)-QuinoxP*]Co^{I}Br}$_2$ (**18**, 0.02)	0	NaBARF (0.1)	6	94 (92, *R*)
3.	[(*R*)-QuinoxP*]Co^{II}Br$_2$ (0.05)	Zn (1)	NaBARF (0.1)	3	96 (93, *R*)
4.	[(*R*)-QuinoxP*]Co^{II}Br$_2$ (0.05)	**11a**[d] (0.05)	NaBARF (0.1)	4	92 (93, *R*)

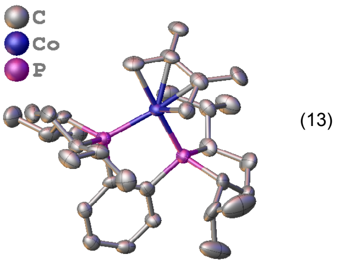
a. See Supporting Information for details. b. Single-component catalyst (shaded entry). c. Configuration confirmed as (*R*).[3d] d. **11a**: 1,4-*bis* TMS-1,4-dihydropyrazine.

*{[(R,R)-^{i}Pr-DuPhos]Co$^{(I)}$-η^4-(2,3-dimethylbutadiene)]}$^+$ [BARF]$^-$ (**25**). An activator-free, single component catalyst for regio- and enantioselective hydroacylation of isoprene.* We recently reported[5e] the synthesis of the cationic complex **25** (CCDC # 2016106) from **20** and an excess of 2,3-dimethylbutadiene (Eq 13) in connection with our work in the Co-catalyzed hydroacylation of 1,3-dienes. This compound is included here for the sake of completion.

This complex (**25**) was tested as a single-component catalyst for hydroacylation (Table 4, eq 14) of isoprene (entry1) and 2-trimethylsilyloxy-1,3-butadiene (entry 4). For comparison, the same catalyst was also generated in situ under the reaction conditions from the corresponding Co^I-bimetallic complex **20** by treatment with NaBARF (Table 4, entry 2). Both reactions gave the chiral 1,2-adduct as the major product in excellent enantioselectivity. Note that in the absence of NaBARF no reaction ensued (entry 3). These reactions strongly support the intermediacy of the cationic Co(I) intermediate in the more practical protocol for conducting this reaction which involves the in situ reduction of the complex **[**[(*R,R*)-*i*-Pr-DUPHOS]Co^{II}Br$_2$ by Zn reduction (to the Co(I) complex), and, subsequent removal of bromide by NaBARF in the same flask (Table 4, entry 4). The yield and selectivities remain unaffected.

*Single-component catalyst **25** in a cobalt-catalyzed hydroboration reaction.* Finally, the complex **25** was tested for a hydroboration reaction as shown in eq 14 and Table 4. Thus, comparison of the single-component catalyst (entry 1) with the in situ generated complex (entry 2) reveals that the former is more reactive (100% conversion with 2 mol% catalyst vs 80% conversion at 5 mol% for the in situ generated catalyst) and gives higher overall regio- and enantioselectivities.



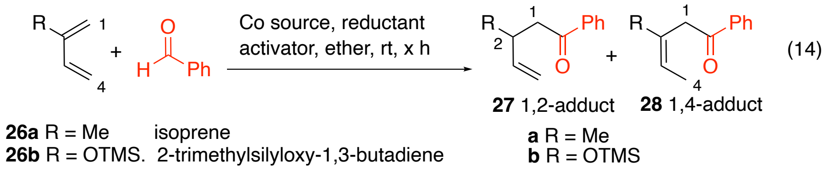


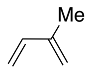
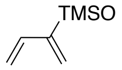
(13)

Figure 12. Solid-State structure of **25** at 50% probability ellipsoid with hydrogens omitted for clarity [Geometry around Co-tetrahedral, P-Co-P = 89.25°, P-Co-C = 92.97°, 96.85°, Co-P = 2.18Å, 2.20Å, Co-C = 2.01Å, 2.07Å]

]

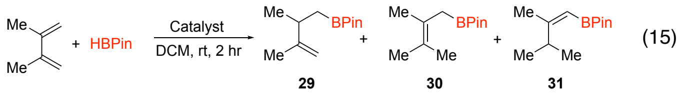
Table 4. Activator-free, single-component (entries 1 and 5) and in situ generated $[Co^{I}]^{+}$-catalysts for hydroacylation of isoprene and 2-trimethylsilyloxy-1,3-butadiene[a]



no	Co^{I}-source (equiv.)	reductant (equiv.)	activator (equiv.)	1,2:1,4 adduct	time (h)	conversion[c] (%ee)[d]
			(isoprene)			
1.[b]	{[(*R*,*R*)-*i*-Pr-DUPHOS]Co^{I}[2,3-DMBD]}$^{+}$[BARF]$^{-}$ (**25**, 0.01)	0	0	60:40	40	60 (96, *S*)
2.	{[(*R*,*R*)-*i*-Pr-DUPHOS]Co^{I}Cl}$_2$ (**20**, 0.025)	0	NaBARF (0.075)	60:40	24	100 (96, *S*)
3.	{[(*R*,*R*)-*i*-Pr-DUPHOS]Co^{I}Cl}$_2$ (**20**, 0.025)	0	0	N/A	24	N/A
4.	[(*R*,*R*)-*i*-Pr-DUPHOS]$Co^{II}Br_2$ (0.05)	Zn (0.5)	NaBARF (0.075)	60:40	24	93 (96, *S*)
			(2-trimethylsilyloxy-1,3-butadiene)			
5.[b]	{[(*R*,*R*)-*i*-Pr-DUPHOS]Co^{I}[2,3-DMBD]}$^{+}$[BARF]$^{-}$ (**25**, 0.05)	0	0	35:65	30	90 (98, *R*)
6.	[(*R*,*R*)-*i*-Pr-DUPHOS]$Co^{II}Br_2$ **20** (0.05)	Zn (0.5)	NaBARF (0.075)	35:65	30	87 (98, *R*)

a. See Supporting Information for details. b. Single-component catalyst (shaded entries). DMBD: 2,3-Dimethyl-1,3-butadiene. c. Conversion is based on the consumption of benzaldehyde. Regioselectivities and enantioselectivities were determined by GC and CSP-GC respectively. d. For the 1,2-adduct

Table 5. Single-component catalyst in an asymmetric hydroboration reaction[a]



no.	catalyst/additives (mol%)	conv.	**29** (% ee)	**30** (%)	**31** (%)
1[b]	**25** (2), no additives	100	53 (79)	33	14
2	**20** (5), Zn (50), NaBARF (10)	80	43 (70)	29	28

a. See Supporting Information for experimental details. Relative ratios of **29**, **30** and **31** determined by GC. b. Single-component catalyst.

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Conclusions

Even though cobalt(I) *bis*-phosphine complexes have been implicated in many highly efficient and selective carbon-carbon bond-forming reactions, until very recently a few of them have been fully characterized or demonstrated to be key intermediates in these reactions. Here we report a new practical method for the synthesis and isolation of a number of cobalt(I)-*bis*-phosphine complexes. We find that easily prepared *bis*-phosphine Co(II) halide complexes are readily reduced by 1,4-*bis*-trimethylsilyl-1,4-dihydropyrazine, leaving behind only innocuous volatile products which are easily removed under high vacuum. Further simplifying the process, we find that the starting cobalt(II) complexes could be prepared in situ from stoichiometric amounts of CoX$_2$ and the corresponding *bis*-phosphine, followed by treatment of the product with the organic reducing agent. Commercially available lithium nitride also reduces (*bis*-phosphine)CoX$_2$ complexes giving the corresponding Co(I) complexes. Depending on the structure of the phosphine, the cobalt(I) complexes crystallize as a *bis*-phosphine-bridged species [(**P~P**)(X)Co[μ–(**P~P**)]Co(X)(**P~P**)] or a halide-bridged species [(**P~P**)Co[μ–(2X)]Co(**P~P**)]. These methods can be used for the in situ generation of catalytically competent pre-catalysts for a variety of low-valent cobalt-catalyzed reactions. Included among these are the following regio- and enantioselective reactions of dienes: heterodimerizations with ethylene or methyl acrylate, hydroacylation and hydroboration. The neutral Co^I complexes are also useful for the synthesis of rare cationic cobalt(I)-alkene/arene complexes, and for the validation of involvement of these species as single-component catalysts in key reactions. Enantio- and regioselective heterodimerization of (*E*)-1,3-nonadiene and methyl acrylate, and hydroacylation of isoprene are illustrated. We believe that these cationic Co(I) complexes have broader utility in homogeneous catalysis. Further applications will be reported in due course.

Author Contributions

TVR conceived the research program and directed this research. The synthetic experiments including the preparation of the catalysts and their use in various reactions were carried out by MMP. CM carried out the X-ray crystallographic analysis. The manuscript was written by TVR in consultation with MMP.

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Conflicts of interest

The authors declare no competing financial interest.

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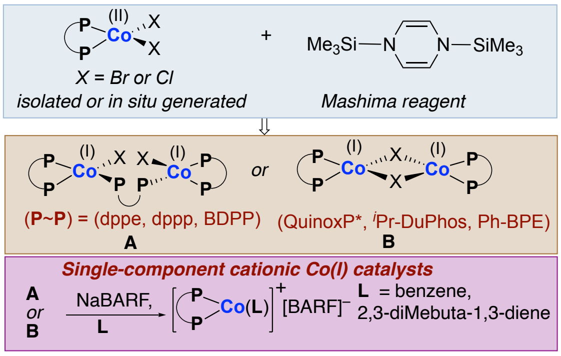

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