Inorganic Chemistry Cite This: Inorg. Chem. XXXX, XXX, XXX-XXX

Reactions of Low-Coordinate Cobalt(0)–N-Heterocyclic Carbene **Complexes with Primary Aryl Phosphines**

Dongyang Wang, Qi Chen, Xuebing Leng, and Liang Deng*®

State Key Laboratory of Organometallic Chemistry, Center for Excellence in Molecular Synthesis, Shanghai Institute of Organic Chemistry, University of Chinese Academy of Sciences, Chinese Academy of Sciences, 345 Lingling Road, Shanghai 200032, P. R. China

S Supporting Information

ABSTRACT: Aiming to get knowledge on the reactivity of low-coordinate cobalt(0) species toward primary phosphines, the reactions of [(IPr)Co- $(vtms)_2$ and $[(ICy)_2Co(vtms)]$ (IPr = 1,3-bis(2',6'-diisopropylphenyl)imidazol-2-ylidene, ICy = 1,3-dicyclohexylimidazol-2-ylidene, and vtms = vinyltrimethylsilane) with several primary aryl phosphines have been examined. The reactions of $[(IPr)Co(vtms)_2]$ and $[(ICy)_2Co(vtms)]$ with H₂PDmp (Dmp = 2,6-dimesitylphenyl) at 80 °C furnish the diamagnetic cobalt(I) phosphido complexes [(NHC)Co(PHDmp)] (NHC = IPr, 1; ICy, 2) that feature the Co-(η^6 -mesityl) interaction. Complex 1 can coordinate CO to generate the terminal phosphido complex [(IPr)Co(CO)₃(PHDmp)] (3) and can be oxidized by $[Cp_2Fe][BAr_4]$ to yield the cobalt(II) phosphido complex $[(IPr)Co(PHDmp)][BAr_4]$ (4, $BAr_4^F = tetrakis(3,5-di(trifluoromethyl)$ phenyl)borate). For the reactions with sterically less-hindered primary phosphines, [(IPr)Co(vtms)₂] is inert toward H₂PC₆H₂-2,4,6-Me₃ (H₂PMes)



at room temperature, whereas $[(ICy)_2Co(vtms)]$ can react with H₂PMes at room temperature to produce the cobalt(II) phosphido alkyl complex trans-[(ICy)2Co(CH2CH2SiMe3)(PHMes)] (5). At 80 °C, the cobalt(0) alkene complexes $[(IPr)Co(vtms)_2]$ and $[(ICy)_2Co(vtms)]$ and also the cobalt phosphido complexes, 1, 2, and 5 can serve as precatalysts for the dehydrocoupling reaction of H_2 PMes to afford MesHPPHMes. NHC-Co(I)-phosphido species are proposed as the in-cycle intermediates for these cobalt-catalyzed dehydrocoupling reactions.

INTRODUCTION

Primary phosphines H₂PR are useful precursors in the synthesis of phosphorous compounds, and there is great interest in metal-mediated reactions of primary phosphines.^{1,2} Similar to secondary and tertiary phosphines, primary phosphines can coordinate to metal to form phosphine complexes. However, primary phosphines are sterically less demanding as compared to their secondary and tertiary congeners and thus can more readily form metal complexes with coordination saturation.³⁻⁵ The P–H bonds of primary phosphines can be activated by metal species to form phosphido and phosphinidene metal complexes that commonly exist in bi- and multinuclear forms with the phosphorous ligands behaving as bridging ligands.⁶⁻¹⁵ The bridging nature renders further transformation of the phosphorous ligands difficult. Probably related to these factors, while a series of metal-catalyzed transformations of primary phosphines have been developed,^{16–18} for example hydro-phosphination of alkenes and alkynes^{12,19–32} and phosphine dehydrocoupling;^{25,26,33-35} these known catalytic systems generally suffer from low catalytic efficiency. In terms of catalysts, the majority of them are the complexes of rare earth metals,¹⁹ the group 4 metals Ti and Zr,^{21,24,31,35–39} the group 9 metal Rh,^{33,34} and the group 10 metals Ni, Pd, and Pt.^{36,40} The

exploration on other transition-metal complexes is scarce.^{9,20,22,25,28,29,41,42} This status quo urges further exploration on reactions of primary phosphines with metal complexes.

Recently, we synthesized a series of three-coordinate NHCcobalt(0)-alkene complexes in the forms of (NHC)Co-(dvtms), (NHC)Co(vtms)₂, and (NHC)₂Co(vtms). $^{43-46}$ These cobalt(0) complexes can perform oxidative addition reactions with organic azides to form cobalt imido complexes.^{43,44,46} They can also react with hydrosilanes to produce cobalt silyl complexes.⁴⁵ The observed reactivity prompted our further exploration on their reactions toward hydrophosphines. Herein, we wish to report the reactions of two representative NHC-cobalt(0)-alkene complexes $[(IPr)Co(vtms)_2]^{44}$ and [(ICy)₂Co(vtms)]⁴⁵ with primary phosphines, bearing different aryl groups. The study revealed the capability of the lowcoordinate cobalt(0) species of performing oxidative addition with P-H bonds, leading to the preparation of NHC-bound cobalt(I) and cobalt(II) phosphido complexes. Moreover, the low-coordinate NHC-cobalt(0)-alkene complexes as well as the resultant cobalt phosphido complexes proved to be effective catalysts for the dehydrocoupling reaction of primary

Received: October 16, 2018

phosphines to form diphosphines, adding a rare example of an effective cobalt catalyst for the dehydrocoupling of hydro-phosphine.

RESULTS AND DISCUSSION

Reactions of NHC–Cobalt(0)-Alkene Complexes with 2,6-Dimesitylphenylphosphine. Only a handful of reports on the reaction of cobalt(0) complexes with hydrosphosphines are known in the literature. Geoffroy et al. showed that $Co_2(CO)_8$ can react with the secondary phosphine HPPh₂ to form di- and trinuclear cobalt complexes, bearing bridging diphenylphosphido ligand $[\mu$ -PPh₂]^{1-.47} Huttner et al. found that the cobalt(0) species generated in situ by the interaction of $(CH_3C(CH_2PPh_2)_3)Cocl_2$ with KC₈ (2 equiv) reacts with the primary phosphine H₂PPh to produce the diphosphene complex $[(CH_3C(CH_2PPh_2)_3)Co(\eta^2-PhPPh)].^{48}$ Noting the rarity, we started our exploration on the reactions of NHC– Co(0)-alkene complexes with the sterically hindered primary phosphine H₂PDmp⁴⁹ (Dmp = 2,6-dimesitylphenyl) with the aim to access terminal phosphido cobalt complexes.

 H_2PDmp is found inert toward the cobalt(0) complexes $[(IPr)Co(vtms)_2]$ and $[(ICy)_2Co(vtms)]$ at room temperature. Heating the 1:1 mixture of H_2PDmp with the cobalt(0) complexes at 80 °C, however, leads to the occurrence of reaction as evidenced by color change from green to brown. After workup, the cobalt(I) phosphido complexes [(NHC)-Co(PHDmp)] (NHC = IPr, 1; ICy, 2) were isolated in 46 and 62% yields, respectively, as red crystalline solids from the resultant mixtures (Scheme 1). Complexes 1 and 2 have been

Scheme 1. Reactions of NHC–Co(0)-Alkene Complexes with H_2PDmp



characterized by ¹H, ¹³C, and ³¹P NMR spectroscopies, infrared (IR) spectroscopy, absorption spectroscopy, and combustion analysis (C, H, and N). The molecular structure of **1** has been established by a single-crystal X-ray diffraction study.

Complexes 1 and 2 are air- and moisture-sensitive. They are diamagnetic. Their ¹H NMR spectra show characteristic doublets at 2.06 and 2.70 ppm, respectively, with the same H–P coupling constant of $J_{P-H} = 152$ Hz (Figures S7 and S11), assignable to the phosphorous-bound hydrogen atoms. Accordingly, the ³¹P NMR spectra of 1 and 2 exhibit doublets at -28.3 and -35.0 ppm, respectively, with the coupling constants J_{P-H} identical to those obtained from their ¹H NMR spectra. The ³¹P NMR chemical shifts are low-field shifted as compared to the free phosphine ligand H₂PDmp (-147 ppm). Being supportive to the presence of hydrogen atoms on their phosphorous atoms, the IR spectra of 1 and 2 measured on KBr pellets feature P–H stretchings at 2196 and 2164 cm⁻¹, respectively (Figures S43 and S44).

The solid-state structure of 1 established by X-ray crystallography revealed its structure as an NHC–cobalt(I)-phosphido complex, featuring the $\text{Co}-(\eta^6\text{-arene})$ interaction between the metal center and a flanking mesityl group (Figure 1). The displacement of the cobalt center toward the centroid



Figure 1. Molecular structure of 1 showing 30% probability ellipsoids. Except the hydrogen atom on phosphorous, all other hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co1-C1 1.892(3), Co1-P1 2.2254(9), P1-H1 1.16(4), C1-Co1-P1 90.16(9), and Co1-P1-H1 103.2(19).

of the flanking aryl ring is 1.586 Å, which is slightly shorter than the corresponding distance in the cobalt(II) thiolate complex $[Co(SC_6H_3-2,6-(C_6H_3-2,6-Pr_2)_2)_2]$ (1.621 Å),⁵⁰ indicating a strong Co– $(\eta^6$ -arene) interaction in the cobalt(I) complex. The high quality of the crystal structure data of 1 allows the location of hydrogen atoms on the Fourier diffraction map. The sum of the angles around the phosphorous atom is 300°. The phosphido ligand has a Co-P distance of 2.2254(9) Å that is comparable to those of the low-spin cobalt(I) phosphido complexes $[Co(\kappa_3-P-(CH_2CH_2PMe_2)_2)(\kappa_2-P(CH_2CH_2PMe_2)_3)]$ (2.297(1) Å)⁵¹ and Thomas' $[(PPP)Co(CO)_2]$ (2.2386(6) Å)⁵² and is apparently longer than those in the cobalt(III) phosphido complex $[K(THF)_4][Co(1,2-(PBu^t)_2C_2B_{10}H_{12})_2]$ (2.1437(5) Å),⁵³ the cobalt terminal phosphinidene complex [(Cp)Co-(PPh₃)(PMes*)] (2.1102(8) Å),⁵⁴ and the bridging phosphinidene complex $[(IMe_4)_2Co(PMes)]_2$ (2.163(1) Å).⁵⁵ These metric data indicate the single bond nature of the Co-P interaction in 1. The IPr ligand has the short Co-C bond of 1.892(3) Å that is comparable to its counterparts in the reported low-spin cobalt(I)-NHC complexes having twolegged piano stool geometry, for example CpCo(IPr)(CO) $(1.888(3) \text{ Å}),^{56} \text{ CpCo}(\text{IPr}_2\text{H}_2)(\text{PPh}_3) (1.880(2) \text{ Å}),^{56}$ and $Cp*Co(IPr)(CO) (1.902(5) Å).^{5}$

The attainment of the phosphido complexes 1 and 2 indicates the capability of the low-coordinate NHC-cobalt(0)alkene complexes in mediating P-H bond activation. The reactions might proceed via the sequential steps of oxidative addition of the cobalt(0) species with the primary phosphine to form cobalt(II) phosphido hydride species (NHC)Co-(PHDmp)(H) that undergo further Co-H bond homolytic cleavage to produce the cobalt(I) phosphido complexes. However, the high reaction temperature prevents the isolation of the cobalt hydride intermediate, we noted that the oxidative addition of cobalt(0) species with hydrophosphine was observed on $\text{Co}_2(\text{CO})_{8}$,⁴⁷ and homolytic cleavage of the Co–H bond is also a well-recognized reaction of cobalt(II) hydrides species.⁵⁹ Notably, NMR analysis indicated that, in addition to the cobalt(I) phosphido complexes, the preparation of 1 and 2 also gave vinyltrimethylsilane in high yields and without the alkene hydrogenation product ethyltrimethylsilane or the alkene hydrophosphination product Me₃SiCH₂CH₂PHDmp. This observation implies that the steric encumbrance of the Dmp group might render the proposed cobalt(II) phosphido hydride intermediate (NHC)-Co(PHDmp)(H) devoid of the coordination of vinyltrimethylsilane.

Reactivity of the Cobalt(I) Phosphido Complex [(IPr)Co(PHDmp)]. Complexes 1 and 2 are among the rare examples of transition-metal complexes, featuring terminal primary phosphido ligands.^{12,34,36,38,41} With them in hand, we further investigated their reactivity. Complex 1 is found inert toward vinyltrimethylsilane and styrene at room temperature. Heating the reaction mixtures of 1 with the alkenes (8 equiv) in C_6D_6 at 80 °C for 2 days led to the formation of trace amounts of new species that shows the ³¹P NMR signal at ca. -60 ppm with molecular mass equaling the alkene hydrophosphination products (Figure S42). However, the low yields of these new species render the attempts to isolate them unsuccessful. With the aim of converting the phosphido complex into a phosphinidene complex, the reactions of 1 with 2,4,6-tri(tert-butyl)phenoxyl radical, KH, and NaN(SiMe₃)₂ were examined. To our disappointment, the former reaction gave H₂PDmp and an intractable paramagnetic mixture, whereas no reaction occurred for the latter two trials. In contrast to these unsuccessful attempts, the reactions of 1 with CO (1 atm) or with $[Cp_2Fe]\overline{[BAr_4]}$ (Ar^F = 3,5-di-(trifluoromethyl)phenyl, 1 equiv) proceed cleanly, from which the new phosphido complexes [(IPr)Co- $(CO)_3(PHDmp)$] (3) and $[(IPr)Co(PHDmp)][BAr_4^F]$ (4) were isolated in 71 and 88% yields, respectively (Scheme 2).

Scheme 2. Reactions of 1 with CO and $[Cp_2Fe][BAr_4^F]$



Complex 3 is a cobalt(I) phosphido complex devoid of the π -interaction between its cobalt center and the flanking arene rings of the ligands (Figure 2). Its IPr and phosphido ligand [PHDmp]¹⁻ on the axial positions have the Co–P and Co–C(carbene) distances of 2.3701(7) and 1.970(2) Å, respectively, which are longer than the corresponding ones in 1 by 0.15 and 0.08 Å. The elongation should be related to the strong *trans*-influence of NHC and phosphido anions.^{36,60} The ³¹P NMR spectrum of 3 exhibits a doublet at -89.07 ppm with a J_{P-H} value of 187 Hz (Figure S18), supporting the



Figure 2. Molecular structure of 3 showing 30% probability ellipsoids. Except the hydrogen atom on phosphorous, all other hydrogen atoms were omitted for clarity. Selected bond lengths (Å) and angles (°): Co1-C1 1.970(2), Co1-P1 2.3701(7), P1-H1 1.25(4), C1-Co1-P1 170.66(6), and Co1-P1-H1 117.7(19).

presence of a hydrogen atom on the phosphorous atom. A P– H stretching resonance at 2329 cm⁻¹ is also observed in the IR spectrum of **3** (Figure S45).

Complex 4 is a low-spin cobalt(II) phosphido complex. It has a solution magnetic moment of 2.3(1) $\mu_{\rm B}$ that is slightly larger than the spin-only value of 1.73 $\mu_{\rm B}$ for 3d metal ions with an S = 1/2 spin state. Owing to its paramagnetism, no ³¹P NMR signal was observed in the range of -400 to +300 ppm in the spectrum of 4. The X-band electron paramagnetic resonance (EPR) spectrum of the solid sample of 4 measured at 5 K displays noticeable ⁵⁹Co (I = 7/2) nuclear hyperfine splitting (Figure 3) and can be simulated as an S = 1/2 system



Figure 3. EPR spectra (black) of 4 recorded in the solid at 5 K. Instrumental parameters: $\nu = 9.38$ GHz, modulation frequency = 100 kHz, modulation amplitude = 5 G, microwave power = 0.03991 mW, conversion time = 58.59 ms, time constant = 0 ms, and sweep time = 60 s. Simulation (red) provides $g_1 = 2.37$, $g_2 = 2.04$, and $g_3 = 2.02$; $A_Co_1 = 155$ MHz, $A_Co_2 = 73$ MHz, and $A_Co_3 = -39$ MHz.; line width = 4.43 G.

with $g_1 = 2.37$, $g_2 = 2.04$, and $g_3 = 2.02$; $A_Co_1 = 155$ MHz, $A_Co_2 = 73$ MHz, and $A_Co_3 = -39$ MHz. The crystal structure of 4 consists of well-separated cations [(IPr)Co-(PHDmp)]¹⁺ and anions [BAr^F₄]¹⁻. The cation [(IPr)Co-(PHDmp)]¹⁺ displays a two-legged piano stool geometry that is similar to 1 (Figure 4) and its Co–P distance is also

С



Figure 4. Structure of the cation in 4 showing 30% probability ellipsoids. Except the hydrogen atom on phosphorous, all other hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co1-C1 1.962(4), Co1-P1 2.2363(13), P1-H1 1.239, C1-Co1-P1 92.76(10), and Co1-P1-H1 105.56.

comparable to that in [(IPr)Co(PHDmp)] (1) (2.2254(9) and 2.2363(1) Å, respectively). These Co-P bonds are located on the long end of the Co-P bonds of cobalt phosphido complexes.⁵¹⁻⁵³ Orbital composition analysis on the frontier orbitals of [(IPr)Co(PHDmp)] and [(IPr)Co(PHDmp)]¹⁺ indicated that the Co-P interaction is essentially a σ -bond in nature (Figures S47 and S48). On the other hand, the Co-C(carbene) and Co-C(arene) distances in the cation $[(IPr)Co(PHDmp)]^{1+}$ of 4 is longer than the corresponding ones in 1 (Table 1). The long Co-C distances in 4 hint weakened metal-ligand interactions between the cobalt center and IPr and the η^6 -mesityl moiety, which might be because of decreased metal-to-ligand backdonation in cobalt(II) species over the cobalt(I) complex. The structure resemblance between the cation [(IPr)Co(PHDmp)]¹⁺ and 1 suggests the reversibility of the one-electron redox event [(IPr)Co- $(PHDmp)]^{1+/0}$. Indeed, a redox wave with the half-wave potential $E_{1/2} = -0.70$ V [vs saturated calomel electrode (SCE)] has been observed in the cyclic voltammogram of 1 (Figure S1).

Reactions of NHC–Cobalt(0)-Alkene Complexes with Sterically Less-Hindered Primary Aryl Phosphines. The successful preparation of the aforementioned terminal phosphido complexes prompted further study on the reactions of the NHC–Co(0)-alkene complexes with sterically lessdemanding primary aryl phosphines, which then revealed the ability of the cobalt(0) complexes in catalyzing the dehydrocoupling of primary aryl phosphines to afford diphosphines.

Heating the C_6D_6 solution of $H_2PC_6H_2$ -2,4,6-Me₃ (H_2PMes) with $[(IPr)Co(vtms)_2]$ (10 mol %) at 80 °C led to the slow formation of the diphosphine MesHPPHMes as a mixture of its meso- and racemic isomers as indicated by ³¹P NMR analysis. The reaction in 10 h can give the diphosphine in 61% yield along with partial retaining of the primary phosphine (36%) (entry 1, Table 2). Further extending the

Table 2. Cobalt–NHC Complex-Catalyzed Dehydrocoupling of Hydrophosphines^a

 $2 H_2 PAr \xrightarrow{10 \text{ mol } \% \text{ [Co]}} ArHPPHAr + H_2$

entry	Catalyst	H ₂ PAr	yield ^b	ratio of meso/rac ^c
1	[(IPr)Co(vtms) ₂]	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	61%	1.6:1
2 ^{<i>d</i>}	[(IPr)Co(vtms) ₂]	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	53%	1.7:1
3	[(ICy) ₂ Co(vtms)]	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	55%	1.5:1
4	CoCl ₂	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	trace	
5	[(PPh ₃) ₃ CoCl]	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	trace	
6	$[(IPr)CoCl_2]_2$	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	14%	1.7:1
7	IPr	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	17%	1.7:1
8 ^d	$[Co_2(CO)_8]$	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	6%	1.4:1
9	[(IPr)Co(vtms) ₂]	H ₂ PC ₆ H ₂ -2,4,6-Pr ⁱ ₃	73%	1.2:1
10	[(IPr)Co(vtms) ₂]	H_2PPh	47%	1.1:1
11	[(IPr)Co(vtms) ₂]	HPPh ₂	7%	
12	[(IPr)Co(vtms) ₂]	H_2PBu^t	8%	0.6:1
13	[(IPr)Co(PHDmp)] (1)	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	67%	1.7:1
14	[(ICy)Co(PHDmp)] (2)	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	63%	1.7:1
15	$[(ICy)_2Co(PHMes) (CH_2CH_2SiMe_3)] (5)$	H ₂ PC ₆ H ₂ -2,4,6-Me ₃	47%	1.7:1

^{*a*}Conditions: hydrophosphine (0.05 mmol) and cobalt complex (10 mol %) in C₆D₆ (0.35 mL) at 80 °C for 10 h. ^{*b*}NMR yields determined by ³¹P NMR using P(OPh)₃ as an internal standard. ^{*c*}The assignment of the ³¹P NMR signals to the rac- or mesoisomer has not been made. ^{*d*}5 mol % metal complex was used.

Table 1. Selected Bond Distance (Å) and Angles (deg) of [(IPr)Co(PHDmp)] (1), $[(IPr)Co(CO)_3(PHDmp)]$ (3), and $[(IPr)Co(PHDmp)][BAr^F_4]$ (4)

	1	3	4
Co-C(carbene)	1.892(3)	1.970(2)	1.962(4)
$Co-C(arene)^a$	2.044(3) - 2.184(3)		2.069(4) - 2.263(3)
Co-C(arene) in average	2.123(3)		2.172(4)
Co-X ^b	1.586		1.661
$C(arene) - C(arene)^{c}$	1.413(4)		1.403(6)
Co-P	2.2254(9)	2.3701(7)	2.2363(1)
P-H	1.16(4)	1.25(4)	1.23(9)
ΣP^{cl}	299.92	354.34	311.11
C(carbene)-Co-P	90.16(9)	170.66(6)	92.76(10)

^{*a*}Distances between the cobalt center and the carbon atoms on the flanking arene ring. ^{*b*}Distances between the cobalt center and the centroid of the flanking arene ring. ^{*c*}C(arene)–C(arene) distances of the flanking arene ring. ^{*d*}The sum of angles around the phosphorous atom.

reaction time to 24 h or adding one more equivalent of H₂PMes to the mixture for further reaction did not lead to further production of the dehydrocoupling product. The reaction employing a 5 mol % catalyst can still afford the diphosphine in 53% yield (entry 2). Similar to [(IPr)Co- $(vtms)_2$, the bis(NHC)cobalt(0) complex [(ICy)_2Co(vtms)] can also catalyze the dehydrocoupling reaction and exhibits comparable catalytic activity as that of $[(IPr)Co(vtms)_2]$ (entry 3). In contrast, the reactions using $[(IPr)CoCl_2]_2$, IPr, and $Co_2(CO)_8$ gave MesHPPHMes in poor yields (14, 17, and 6% yields, respectively), and CoCl₂ and (PPh₃)₃CoCl are found ineffective in promoting the dehydrocoupling reaction (entries 4-8). In addition to the dehydrocoupling reaction of H_2PMes , the cobalt(0) complex [(IPr)Co(vtms)₂] can also catalyze the conversion of H₂PC₆H₂-2,4,6-Prⁱ₃ and H₂PPh to the corresponding diphosphines in 73 and 47% yields, respectively, (entries 9 and 10). The catalytic system is sensitive to the steric nature, and the cobalt(0) complex-catalyzed dehydrocoupling reaction of HPPh₂ and H₂PBu^t only afford the diphosphines in 7 and 8% yield, respectively, (entries 11 and 12).

As aforementioned, effective late transition-metal catalysts for the dehydrocoupling of hydrophosphine are rare. Hence, the NHC–cobalt complexes showed above add new examples to the category after the rhodium(I) complexes $[Cp*Rh-(CH_2CHSiMe_3)_2]^{33}$ and $[(Pr_2PCH_2CH_2PPr_2)Rh(CH_2Ph)]^{34}$ and the iron(II) complexes $[(DippNCMeCHCMeNDipp)Fe-(CH_2SiMe_3)]$ and $[((xy1)NCMeCHCMeN(xy1))Fe-(CH_2SiMe_3)(THF)]^{.25}$ Considering the different steric nature of H₂PMes versus H₂PDmp, it can be proposed that the interaction of $[(IPr)Co(vtms)_2]$ with H₂PMes might allow the formation of the cobalt(0)-alkene-phosphine intermediate (IPr)Co(PH_2Mes) (CH_2CHSiMe_3) (A in Scheme 3). Intermediate A could convert to the cobalt(II) phosphido alkyl species (IPr)Co(CH_2CH_2SiMe_3)(PHMes) (B) via,





possibly, the sequential steps of α -H elimination and migratory insertion. The further reaction of **B** with H₂PMes might give the cobalt(II) phosphido hydrido species (IPr)Co(H)-(PHMes) (**C**) and Me₃SiCH₂CH₂PHMes via either oxidative addition and reductive elimination or σ -bond metathesis mechanism. Species **C** could then undergo Co–H bond cleavage to convert into the cobalt(I) phosphido intermediate (IPr)Co(PHMes) (**D**) that could be the in-cycle species for the cobalt-catalyzed dehydrocoupling reaction. Scheme 3 illustrates an oxidative addition-reductive elimination pathway³³ for the catalytic dehydrocoupling reaction of H₂PMes. However, other mechanisms with σ -bond metathesis¹⁹ or the nucleophilic attack of hydrophosphine toward cobalt phosphinidene species as the step of P–P bond formation³⁷ cannot be excluded.

Being supportive to the proposed mechanism (Scheme 3), a cobalt(II) phosphido alkyl complex trans-[(ICy)₂Co-(CH₂CH₂SiMe₃)(PHMes)] (5), as an analog of intermediate **B**, has been isolated in 67% yield from the equimolar reaction of [(ICy)₂Co(vtms)] with H₂PMes at room temperature (Scheme 4). Complex 5 has been characterized by solution





magnetic susceptibility measurement (2.6(1) μ B), singlecrystal X-ray diffraction study (Figure 5), and elemental



Figure 5. Structure of 5 showing 30% probability ellipsoids. Except the hydrogen atom on phosphorous, all other hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (°): Co1–C1 1.912(5), Co1–C2 1.907(5), Co1–C3 2.046(5), Co1–P1 2.2766(16), C1–Co1–P1 85.26(16), C1–Co1–C2 178.0(2), and C3–Co1–P1 174.24(14).

analysis. In addition, the cobalt(I) phosphido complexes [(NHC)Co(PHDmp)] (NHC = IPr, 1; ICy, 2) obtained from the reactions of the NHC-Co(0)-alkene complexes with H₂PDmp also give credence to the formation of cobalt(I) phosphido species **D** in the proposed mechanism. Moreover, a secondary phosphine species that shows the ³¹P NMR doublet at -74 ppm and has the mass of 252 as indicated by GC-MS analysis, presumably Me₃SiCH₂CH₂PHMes, has been observed as a byproduct in the catalytic dehydrocoupling reactions of H₂PMes using [(IPr)Co(vtms)₂] as catalysts (Figure S21). Intriguingly, all the cobalt phosphido complexes **1**, **2**, and **5** proved to be competent catalysts for the dehydrocoupling reaction of H₂PMes (entries 13-15 in Table 2). It should be mentioned that a close examination on the ³¹P NMR spectra of the reaction mixtures revealed the formation of H₂PDmp, rather than DmpHPPHMes, in the catalytic reactions using 1 and 2 as catalysts (Figures S39 and S40), suggesting that the interaction of H₂PMes with 1 and 2 might proceed in an σ -bond metathesis pathway to form (NHC)Co(PHMes) (**D**) and H₂PDmp. This reaction mode is different from the P–P bond formation reaction of (NHC)-Co(PHMes) with H₂PMes (Scheme 3) and might be caused by the existence of the Co–(η^6 -arene) interaction in the terphenyl-substituted phosphido complexes.

CONCLUSIONS

In this study, we examined the reactions of low-coordinate NHC-Co(0)-alkene complexes with primary aryl phosphines and found that the reactions can lead to either the formation of cobalt phosphido complexes or catalytic dehydrocoupling reactions of primary aryl phosphines to form diphosphines. The study showed that the reactions of $[(IPr)Co(vtms)_2]$ and [(ICy)₂Co(vtms)] with H₂PDmp at 80 °C furnish low-spin cobalt(I) phosphido complexes [(IPr)Co(PHDmp)] (1) and [(ICy)Co(PHDmp)] (2), whereas catalytic dehydrocoupling of the primary phosphines to afford diphosphines in the form of ArHPPHAr takes place when the NHC-Co(0)-alkene complexes were treated with the sterically less-demanding hydrophosphines, H₂PMes, H₂PC₆H₂-2,4,6-Prⁱ₃, and H₂PPh, at 80 °C. In contrast to these reactions, a cobalt(II) phosphido alkyl complex trans- $[(ICy)_2Co(CH_2CH_2SiMe_3)(PHMes)]$ (5) has been isolated from the reaction of $[(ICy)_2Co(vtms)]$ with H₂PMes at room temperature. The distinct reaction outcomes should originate from the different steric nature of the aryl phosphines and also the NHCs. In addition to the reactions of cobalt(0) complexes, a preliminary reactivity study on the cobalt phosphido complexes has been performed, which led to the preparation of the cobalt(I) phosphido complex [(IPr)- $Co(PHDmp)(CO)_3$] (3) devoid of the $Co-(\eta^6-arene)$ interaction from the reaction of 1 with CO and the cobalt(II) phosphido complex $[(IPr)Co(PHDmp)][BAr_{4}^{F}]$ (4) from the one electron-oxidation of 1 by the ferrocenium cation. The cobalt phosphido complexes 1, 2, and 5 proved to be effective catalysts in promoting the dehydrocoupling reaction of H₂PMes. The accessibility of these cobalt phosphido complexes and their fine performance in catalyzing the dehydrocoupling reactions should benefit from the use of these strongly σ -donating and sterically demanding NHCs as ancillary ligands.

EXPERIMENTAL SECTION

General Considerations. All manipulations on air- and moisturesensitive materials were performed under an atmosphere of dry dinitrogen with the rigid exclusion of air and moisture using standard Schlenk or cannula techniques or in a glovebox. Solvents were dried with a solvent purification system (Innovative Technology) and degassed prior to use. $[(IPr)Co(vtms)_2]$,⁴⁴, $[(ICy)_2Co(vtms)]$,⁴⁵ H_2PDmp ,⁴⁹, $H_2PC_6H_2$ -2,4,6- Pr_i^3 ,⁶¹, H_2PMes ,⁶², $[Cp_2Fe][BAr^F_4]$,⁶³ and 2,4,6-tris-*tert*-butylphenoxyl radical⁶⁴ were synthesized according to literature procedures. All other chemicals were purchased from chemical vendors and used as received unless otherwise noted. ¹H, ¹³C, and ³¹P spectra were recorded with a Varian 400 MHz, Agilent 400 MHz, or Bruker 400 MHz spectrometer at 400, 100, and 162 MHz, respectively. Chemical shifts were reported in units of ppm with references to the residual protons of the deuterated solvents for proton chemical shifts, the ¹³C of deuterated solvents for carbon chemical shifts, and the ³¹P of 85% phosphorous acid (external standard) for phosphine chemical shifts. Elemental analysis was

performed by the Analytical Laboratory of Shanghai Institute of Organic Chemistry (CAS). Solution magnetic moments were measured at room temperature by the method originally described by Evans with stock and experimental solutions containing a known amount of a (CH₃)₃SiOSi(CH₃)₃ standard.^{65,66} Absorption spectra were recorded with a Shimadzu UV-3600 UV-vis-NIR spectrophotometer. IR spectra were recorded with a Nicolet Avatar 330 FT-IR spectrophotometer or Bruker TENSOR 27 ATR-FTIR spectrophotometer. The X-band EPR experiments were performed in sealed quartz tubes on a Bruker EMX plus spectrometer (microwave frequency ca. 9.38 GHz) equipped with a He temperature control cryostat system. Electrochemical measurements were carried out in a glovebox under an argon atmosphere with a CHI 600D potentiostation. A glassy carbon was used as the working electrode, a platinum wire was used as the auxillary electrode, and a SCE was used as the reference electrode. 0.1 M [Buⁿ₄N][PF₆] in tetrahydrofuran (THF) was used as the supporting electrolyte and was prepared in the glovebox. Under these conditions, $E_{1/2} = 0.55$ V for the [Cp₂Fe]^{0,+} couple.

X-ray Structure Determination. Crystals were coated with Paratone-N oil and mounted on a Bruker APEX CCD-based diffractometer equipped with an Oxford low-temperature apparatus. Cell parameters were retrieved with SMART software and refined using SAINT software on all reflections. Data integration was performed with SAINT, which corrects for Lorentz-polarization and decay. Absorption corrections were applied using SADABS.⁶⁷ Space groups were assigned unambiguously by analysis of the symmetry and systematic absences determined by XPREP.⁶⁸ All structures were solved and refined using SHELXTL. The metal and first coordination sphere atoms were located from direct-method E maps. Nonhydrogen atoms were found in alternating difference Fourier synthesis and leastsquares refinement cycles and during the final cycles were refined anisotropically. Hydrogen atoms on the coordination sphere of phosphorous were located from the difference maps and refined. Other hydrogen atoms were placed in calculated positions employing a riding model. CCDC 1871977-1871980 contains the supplementary crystallographic data for complexes 1, 3, 4, and 5. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data request/cif.

Computational Details. To have a better understanding of the electronic structure of [(IPr)Co(PHDmp)] (1) and the cation $[(IPr)Co(PHDmp)]^+$ in 4, density functional theory^{69,70} study has been performed with the ORCA 3.03 program⁷¹ using the B3LYP^{72,73} method. Coordinates of the calculated structures are based on the crystal structure data without geometry optimization. The SVP basis set^{74,75} was used for the C, N, and H atoms, and the TZVP basis set⁷⁶ was used for the Co and P atoms. The RIJCOSX approximation⁷⁷ with matching auxiliary basis sets^{74,75} was employed to accelerate the calculations. The Mulliken spin population and Mayer bond orders of selected bonds of 1 and the cation $[(IPr)Co(PHDmp)]^+$ in 4 are shown in the Supporting Information (Figures S47–S50).

Preparation of [(IPr)Co(PHDmp)] (1). To the solution of $[(IPr)Co(vtms)_2]$ (130 mg, 0.20 mmol) in toluene (15 mL) was added H₂PDmp (70 mg, 0.20 mmol). After stirring for 10 h at 80 °C, the color of the solution changed from green to brown red. After removal of the solvent under vacuum, the brown red solid was washed by n-hexane (3 mL) quickly, extracted by diethyl ether (5 mL), and filtered to give a brown red solution. Removal of the solvent by vacuum afforded 1 as a brown red solid (73 mg, 46%). Red crystals of 1 were obtained by standing its diethyl ether solution at room temperature after evaporation of the solvent. ¹H NMR (400 MHz, $C_6 D_{61}$ 293 K): δ (ppm) 7.29 (t, 2H), 7.19 (d, 4H), 7.10–7.02 (m, 2H), 6.51 (s, 2H), 6.96 (s, 2H), 6.84 (d, 1H), 5.60 (s, 2H), 3.43 (br, 2H), 3.08 (br, 2H), 2.36 (s, 3H), 2.15 (s, 6H), 2.06 (d, J = 152 Hz, 1H), 1.74 (s, 6H), 1.64 (s, 3H), 1.44 (br, 6H), 1.15 (br, 6H), 0.95 (br, 12H). ¹³C NMR (101 MHz, C₆D₆, 292 K): δ (ppm) 195.26 (d, J = 5 Hz), 155.8 (d, J = 35 Hz), 148.36 (d, J = 8 Hz), 146.18 (d, J = 9 Hz), 145.08 (d, J = 13 Hz), 140.11, 138.96, 136.00, 135.36, 129.32, 128.35, 128.24, 126.28, 125.14, 124.83, 124.30, 96.61, 94.85, 94.07, 90.57, 28.84, 26.68, 26.20, 23.27, 21.35, 21.18, 20.41, 19.51. ³¹P{¹H}

NMR (162 MHz, $C_6 D_6$, 292 K): δ (ppm) –28.30. ³¹P NMR (162 MHz, $C_6 D_6$, 292 K): δ (ppm) –28.28 (d, J = 152 Hz). Anal. Calcd for $C_{51}H_{62}CoN_2P$: C, 77.25; N, 3.53; H, 7.88. Found: C, 76.89; N, 3.47; H, 7.96. Absorption spectrum (THF, 295 K): λ_{max} nm (ε , M⁻¹ cm⁻¹): 283 (11 000), 334 (9190), 443 (4600), 583 (1690) nm. IR spectrum (KBr, cm⁻¹): ν_{P-H} 2196.

Preparation of [(ICy)Co(PHDmp)] (2). To the solution of [(ICy)₂Co(vtms)] (125 mg, 0.20 mmol) in toluene (15 mL) was added H₂PDmp (70 mg, 0.20 mmol). After stirring for 10 h at 80 °C, the color of the solution changed to brown red. After removal of the solvent under vacuum, the brown red solid was washed by n-hexane (3 mL), extracted by diethyl ether (5 mL), and filtered to give a brown red solution. Removal of the solvent by vacuum afforded 2 as a brown red solid (79 mg, 62%). Brown red crystals of 2 were obtained by standing its diethyl ether solution at room temperature after evaporation of the solvent. ¹H NMR (400 MHz, C_6D_6 , 293 K): δ (ppm) 7.37 (d, 1H), 7.22 (t, 1H), 6.93 (d, 1H), 6.88 (s, 2H), 6.28 (s, 2H), 5.92 (br, 4H), 2.70 (d, J = 152 Hz, 1H), 2.31 (s, 6H), 2.26 (s, 6H), 2.18 (s, 3H), 2.07 (br, 2H), 1.76 (br, 4H), 1.58-1.34 (br, 8H), 1.17 (br, 5H), 0.97 (br, 4H). 13 C NMR (101 MHz, C₆D₆, 292 K): δ (ppm) 187.46 (d, J = 19 Hz), 156.18 (d, J = 35 Hz), 145.80 (d, J = 11 Hz), 145.30 (d, J = 9 Hz), 139.99, 135.48, 135.16, 128.03, 125.69, 125.29, 124.96, 116.57, 94.50, 92.76, 84.31, 59.70, 34.21, 33.76, 33.73, 26.22, 25.82, 25.55, 21.00, 20.48, 20.43, 19.61. ³¹P{¹H} NMR (162 MHz, C₆D₆, 298 K): δ (ppm) -34.99. ³¹P NMR (162 MHz, C₆D₆, 298 K): δ (ppm) -34.99 (J = 152 Hz). Anal. Calcd for C39H50CoN2P: C, 73.57; N, 4.40; H, 7.92. Found: C, 72.78; N, 4.38; H, 7.72. Absorption spectrum (THF, 295 K): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 275 (11 000), 321 (6590), 384 (3000), 463 (1540), 561 (690) nm. IR spectrum (KBr, cm⁻¹): ν_{P-H} 2164.

Preparation of [(IPr)Co(CO)₃(PHDmp)] (3). The toluene (5 mL) solution of [(IPr)Co(PHDmp)] (1, 160 mg, 0.20 mmol) in a 25 mL flask was quickly frozen with liquid N2 and subjected to vacuum to remove the N₂ atmosphere in the flask. Then, CO was introduced to the mixture via a CO balloon (1 atm). The reaction mixture was allowed to warm to room temperature. The color of the solution changed from brown red to yellow immediately. After 10 min, the volatiles were removed under vacuum to yield yellow solid that was then extracted with diethyl ether and filtered. Yellow crystals of 3 (125 mg, 71%) were obtained by standing its diethyl ether solution at room temperature after evaporation of the solvent. ¹H NMR (400 MHz, C₆D₆, 294 K): δ (ppm) 7.22 (t, 2H), 7.12 (d, 2H), 7.07 (t, 1H), 6.99 (d, 2H), 6.93 (d, 4H), 6.87 (s, 2H), 6.44 (s, 2H), 3.80 (d, J = 187 Hz, 1H), 2.55 (m, 4H), 2.28 (br, 18H), 1.37 (d, J = 7 Hz, 6H), 1.24 (d, J = 7 Hz, 6H), 0.99 (d, J = 7 Hz, 6H), 0.91 (d, J = 7 Hz, 6H). ¹³C NMR (101 MHz, C₆D₆, 294 K): δ (ppm) 200.82, 187.38 (d, J = 3Hz), 147.64, 147.52, 146.44, (d, J = 7 Hz), 145.52, 144.94, 140.62, 136.74, 135.90, 130.70, 129.20, 128.76, 128.37, 126.98, 125.46, 124.59, 124.44, 28.88, 28.83, 25.83, 23.18, 22.74, 21.61, 21.53, 21.49, 21.26. ³¹P{¹H} NMR (162 MHz, C₆D₆, 292 K): δ (ppm) -89.07. ³¹P NMR (162 MHz, C₆D₆, 292 K): δ (ppm) -89.84 (J = 187 Hz). Anal. Calcd for C54H62CoN2O3P: C, 73.96; N, 3.19; H, 7.13. Found: C, 73.96; N, 3.22; H, 7.21. Absorption spectrum (THF, 295 K): λ_{max} , nm (e, M⁻¹ cm⁻¹): 287 (1330), 326 (840), 419 (570) nm. IR spectrum (KBr, cm⁻¹): ν_{P-H} 2329, ν_{CO} 2028, 1962, 1943.

Preparation of [(**IPr)Co(PHDmp)**][**BAr^F**₄] (4). To a diethyl ether (10 mL) solution of [(**IPr)Co(PHDmp)**] (1, 160 mg, 0.20 mmol) was added [Cp₂Fe][**BAr**^F₄] (210 mg, 0.20 mmol) slowly. The color of the solution changed to dark green immediately. The reaction mixture was stirred for 10 min at room temperature and then subjected to vacuum to remove all the volatiles. The resulting dark green solid was washed with *n*-hexane (3 mL × 3) first, then extracted with diethyl ether (5 mL) and filtered. The dark green crystalline solid of 4 (290 mg, 88%) was obtained by slow evaporation of its diethyl ether solution at room temperature. ¹H NMR (400 MHz, C₆D₆ and THFd₈, 293 K): δ (ppm) 8.25 ($\nu_{1/2}$ = 20 Hz), 7.60 ($\nu_{1/2}$ = 22 Hz), 6.80 ($\nu_{1/2}$ = 42 Hz), 5.88 ($\nu_{1/2}$ = 104 Hz), 4.03 ($\nu_{1/2}$ = 179 Hz), 2.04, 1.28, -0.96 ($\nu_{1/2}$ = 246 Hz). Anal. Calcd for C₈₃H₇₄BCoF₂₄N₂P: C, 60.19; N, 1.69; H, 4.50. Found: C, 59.88; N, 1.47; H, 4.51. Magnetic Susceptibility (C₆D₆, 293 K): μ_{eff} 2.3(1) μB. Absorption spectrum (THF, 295 K): λ_{max} nm (ϵ , M⁻¹ cm⁻¹): 438 (2030), 578 (1370), 1216 (210) nm.

Preparation of [(ICy)₂Co(CH₂CH₂SiMe₃)(PHMes)] (5). To the solution of $[(ICy)_2Co(vtms)]$ (125 mg, 0.20 mmol) in *n*-hexane (15 mL) was added H₂PMes (31 mg, 0.20 mmol). After stirring for 10 h at room temperature, the color of the solution changed to green. After removal of the solvent under vacuum, the green solid was washed by n-hexane (5 mL) quickly, extracted by diethyl ether (8 mL), and filtered to give a green solution. Removal of the solvent by vacuum afforded 5 as a green solid (104 mg, 67%). Green crystals of 5 were obtained by standing its diethyl ether solution at room temperature after evaporation of the solvent. ¹H NMR (400 MHz, C_6D_{61} 293 K): δ (ppm) 42.75 ($\nu_{1/2}$ = 161 Hz), 20.37 ($\nu_{1/2}$ = 116 Hz), 17.53 ($\nu_{1/2}$ = 113 Hz), 4.84 ($\nu_{1/2}$ = 24 Hz), 0.26 ($\nu_{1/2}$ = 6 Hz), 0.07 ($\nu_{1/2}$ = 35 Hz), -0.76 ($\nu_{1/2}$ = 10 Hz), -4.11 ($\nu_{1/2}$ = 31 Hz), -5.70 ($\nu_{1/2}$ = 25 Hz), $-7.52 (\nu_{1/2} = 34 \text{ Hz}), -10.36 (\nu_{1/2} = 184 \text{ Hz}), -10.99 (\nu_{1/2} = 31$ Hz), -19.68 ($\nu_{1/2}$ = 77 Hz), -24.03 ($\nu_{1/2}$ = 87 Hz). Anal. Calcd for C44H73CoN4PSi: C, 68.10; N, 7.22; H, 9.48. Found: C, 68.12; N, 7.23; H, 9.88. Magnetic susceptibility (C₆D₆, 293 K): μ_{eff} 2.6(1) μB. Absorption spectrum (THF, 295 K): λ_{max} , nm (ϵ , M⁻¹ cm⁻¹): 324 (14 010), 351 (11 860), 408 (3910), 598 (910) nm. IR spectrum (KBr, cm⁻¹): $\nu_{\rm P-H}$ 2315.

General Procedure for the Cobalt-Catalyzed Dehydrocoupling Reactions of Hydrophosphines. A J-Young NMR tube was charged with a hydrophosphine (0.05 mmol), a cobalt catalyst (10 or 5 mol %), and C_6D_6 (0.35 mL). The mixture was heated at 80 °C and followed by ³¹P NMR, which indicated the slow formation of diphosphine. After 10 h, the yield of diphosphine did not show apparent increase. Then, the mixture was cooled to room temperature, and OPPh₃ (5.5 mg, 0.02 mol) was added to the mixture as an internal standard to quantify the yield of diphosphine by ³¹P NMR. The diphosphines, MesHPPHMes,⁷⁸ 2,4,6-Prⁱ₃H₂C₆-HPPHC₆H₂-2,4,6-Prⁱ₃,⁷⁹ PhHPPHPh,⁸⁰ Ph₂PPPh₂,²⁹ Bu'HPPHBu'⁸¹ show identical ³¹P NMR chemical shifts as those reported in the literature. The performance of different cobalt catalysts is compiled in Table 2. Figures S21–S42 depict the ³¹P NMR spectra of the resultant mixtures.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.8b02937.

Crystallographic data, table for crystal data, absorption spectra, IR spectra, NMR spectra, cyclic voltammogram, MO diagrams, Mulliken spin populations, and bond orders of the calculated structure (PDF)

Accession Codes

CCDC 1871977–1871980 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

AUTHOR INFORMATION

Corresponding Author

*E-mail: deng@sioc.ac.cn.

ORCID 💿

Liang Deng: 0000-0002-0964-9426

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The work was supported by the National Key Research and Development Program (2016YFA0202900), the National Natural Science Foundation of China (nos. 21725104, 21690062, 21432001, and 21821002), and the Strategic Priority Research Program of the Chinese Academy of Sciences (no. XDB20000000).

REFERENCES

(1) Brynda, M. Towards "user-friendly" Heavier Primary Pnictanes: Recent Developments in the Chemistry of Primary Phosphines, Arsines and Stibines. *Coord. Chem. Rev.* **2005**, *249*, 2013–2034.

(2) Fleming, J. T.; Higham, L. J. Primary Phosphine Chemistry. Coord. Chem. Rev. 2015, 297-298, 127-145.

(3) Huang, J.-S.; Yu, G.-A.; Xie, J.; Wong, K.-M.; Zhu, N.; Che, C.-M. Primary and Secondary Phosphine Complexes of Iron Porphyrins and Ruthenium Phthalocyanine: Synthesis, Structure, and P-H Bond Functionalization. *Inorg. Chem.* **2008**, *47*, 9166–9181.

(4) Goodwin, N. J.; Henderson, W.; Nicholson, B. K.; Fawcett, J.; Russell, D. R. (Ferrocenylmethyl)phosphine, an Air-Stable Primary Phosphine. J. Chem. Soc., Dalton Trans. **1999**, 1785–1794.

(5) Russell, S. K.; Bowman, A. C.; Lobkovsky, E.; Wieghardt, K.; Chirik, P. J. Synthesis and Electronic Structure of Reduced Bis(imino)pyridine Manganese Compounds. *Eur. J. Inorg. Chem.* **2012**, 535–545.

(6) Collman, J. P.; Rothrock, R. K.; Finke, R. G.; Moore, E. J.; Rose-Munch, F. Role of the Metal-Metal Bond in Transition-Metal Clusters. Phosphido-Bridged Diiron Carbonyl Complexes. *Inorg. Chem.* **1982**, *21*, 146–156.

(7) King, R. B.; Fu, W.-K.; Holt, E. M. Bis(di-isopropylamino)phosphido and Di-isopropylaminophosphinidene Metal-Carbonyl-Complexes from Reactions of Manganese and Cobalt Carbonyls with Bis(di-isopropylamino)Phosphine: X-Ray Crystal-Structures of $(Pr_2N)_2PMn_2(CO)_8H$ and $Pr_2NPCo_3(CO)_9$. J. Chem. Soc., Chem. Commun. **1984**, 1439–1440.

(8) Baker, R. T.; Fultz, W. C.; Marder, T. B.; Williams, I. D. Synthetic, Structural, and Bonding Studies of Phosphido-Bridged Early-Late Transition-Metal Heterobimetallic Complexes. *Organometallics* **1990**, *9*, 2357–2367.

(9) Derrah, E. J.; Pantazis, D. A.; McDonald, R.; Rosenberg, L. A Highly Reactive Ruthenium Phosphido Complex Exhibiting Ru–P π -Bonding. *Organometallics* **2007**, *26*, 1473–1482.

(10) Takemoto, S.; Kimura, Y.; Kamikawa, K.; Matsuzaka, H. P–H Bond Addition to a Dinuclear Ruthenium Imido Complex: Synthesis and Reactivity of an Amido Phosphido Complex. *Organometallics* **2008**, *27*, 1780–1785.

(11) Rookes, T. M.; Gardner, B. M.; Balázs, G.; Gregson, M.; Tuna, F.; Wooles, A. J.; Scheer, M.; Liddle, S. T. Crystalline Diuranium Phosphinidiide and μ -Phosphido Complexes with Symmetric and Asymmetric UPU Cores. *Angew. Chem., Int. Ed.* **2017**, *56*, 10495–10500.

(12) Rosenberg, L. Mechanisms of Metal-Catalyzed Hydrophosphination of Alkenes and Alkynes. ACS Catal. 2013, 3, 2845–2855.

(13) Pugh, T.; Tuna, F.; Ungur, L.; Collison, D.; McInnes, E. J. L.; Chibotaru, L. F.; Layfield, R. A. Influencing the Properties of Dysprosium Single-Molecule Magnets with Phosphorus Donor Ligands. *Nat. Commun.* **2015**, *6*, 7492–7499.

(14) Zhang, C.; Hou, G.; Zi, G.; Ding, W.; Walter, M. D. A Base-Free Terminal Actinide Phosphinidene Metallocene: Synthesis, Structure, Reactivity, and Computational Studies. *J. Am. Chem. Soc.* **2018**, *140*, 14511–14525.

(15) Danopoulos, A. A.; Braunstein, P.; Monakhov, K. Y.; van Leusen, J.; Kögerler, P.; Clémancey, M.; Latour, J.-M.; Benayad, A.; Tromp, M.; Rezabal, E.; Frison, G. Heteroleptic, Two-Coordinate $[M(NHC){N(SiMe_3)_2}]$ (M = Co, Fe) Complexes: Synthesis, Reactivity and Magnetism Rationalized by an Unexpected Metal Oxidation State. *Dalton Trans.* **2017**, *46*, 1163–1171. (16) Waterman, R. Dehydrogenative Bond-Forming Catalysis Involving Phosphines. *Curr. Org. Chem.* **2008**, *12*, 1322–1339.

(17) Waterman, R. Dehydrogenative Bond-Forming Catalysis Involving Phosphines: Updated Through 2010. *Curr. Org. Chem.* **2012**, *16*, 1313–1331.

(18) Zhu, Y.; Chen, T.; Li, S.; Shimada, S.; Han, L.-B. Efficient Pd-Catalyzed Dehydrogenative Coupling of P(O)H with RSH: A Precise Construction of P(O)-S Bonds. *J. Am. Chem. Soc.* **2016**, *138*, 5825–5828.

(19) Douglass, M. R.; Marks, T. J. Organolanthanide-Catalyzed Intramolecular Hydrophosphination/Cyclization of Phosphinoalkenes and Phosphinoalkynes. J. Am. Chem. Soc. 2000, 122, 1824–1825.

(20) Ohmiya, H.; Yorimitsu, H.; Oshima, K. Cobalt-Catalyzed syn Hydrophosphination of Alkynes. *Angew. Chem., Int. Ed.* **2005**, 44, 2368–2370.

(21) Roering, A. J.; Leshinski, S. E.; Chan, S. M.; Shalumova, T.; MacMillan, S. N.; Tanski, J. M.; Waterman, R. Insertion Reactions and Catalytic Hydrophosphination by Triamidoamine-Supported Zirconium Complexes. *Organometallics* **2010**, *29*, 2557–2565.

(22) Pullarkat, S. A.; Leung, P.-H. Chiral Metal Complex-Promoted Asymmetric Hydrophosphinations. *Top. Organomet. Chem.* **2011**, *43*, 145–166.

(23) Wauters, I.; Debrouwer, W.; Stevens, C. V. Preparation of Phosphines through C-P Bond Formation. *Beilstein J. Org. Chem.* **2014**, *10*, 1064–1096.

(24) Ghebreab, M. B.; Bange, C. A.; Waterman, R. Intermolecular Zirconium-Catalyzed Hydrophosphination of Alkenes and Dienes with Primary Phosphines. J. Am. Chem. Soc. **2014**, 136, 9240–9243. (25) King, A. K.; Buchard, A.; Mahon, M. F.; Webster, R. L. Facile, Catalytic Dehydrocoupling of Phosphines Using β -Diketiminate Iron(II) Complexes. Chem.—Eur. J. **2015**, 21, 15960–15963.

(26) Geer, A. M.; Serrano, Á. L.; de Bruin, B.; Ciriano, M. A.; Tejel, C. Terminal Phosphanido Rhodium Complexes Mediating Catalytic P-P and P-C Bond Formation. *Angew. Chem., Int. Ed.* **2015**, *54*, 472–475.

(27) Bange, C. A.; Waterman, R. Challenges in Catalytic Hydrophosphination. *Chem.*—*Eur. J.* **2016**, *22*, 12598–12605.

(28) Espinal-Viguri, M.; King, A. K.; Lowe, J. P.; Mahon, M. F.; Webster, R. L. Hydrophosphination of Unactivated Alkenes and Alkynes Using Iron(II): Catalysis and Mechanistic Insight. *ACS Catal.* **2016**, *6*, 7892–7897.

(29) Di Giuseppe, A.; De Luca, R.; Castarlenas, R.; Pérez-Torrente, J. J.; Crucianelli, M.; Oro, L. A. Double Hydrophosphination of Alkynes Promoted by Rhodium: the Key Role of an N-Heterocyclic Carbene Ligand. *Chem. Commun.* **2016**, *52*, 5554–5557.

(30) Bezzenine-Lafollée, S.; Gil, R.; Prim, D.; Hannedouche, J. First-Row Late Transition Metals for Catalytic Alkene Hydrofunctionalisation: Recent Advances in C-N, C-O and C-P Bond Formation. *Molecules* **2017**, *22*, 1901.

(31) Bange, C. A.; Conger, M. A.; Novas, B. T.; Young, E. R.; Liptak, M. D.; Waterman, R. Light-Driven, Zirconium-Catalyzed Hydro-phosphination with Primary Phosphines. *ACS Catal.* **2018**, *8*, 6230–6238.

(32) Sharpe, H. R.; Geer, A. M.; Lewis, W.; Blake, A. J.; Kays, D. L. Iron(II)-Catalyzed Hydrophosphination of Isocyanates. *Angew. Chem., Int. Ed.* **2017**, *56*, 4845–4848.

(33) Böhm, V. P. W.; Brookhart, M. Dehydrocoupling of Phosphanes Catalyzed by a Rhodium(I) Complex. *Angew. Chem., Int. Ed.* **2001**, 40, 4694–4696.

(34) Han, L.-B.; Tilley, T. D. Selective Homo- and Heterodehydrocouplings of Phosphines Catalyzed by Rhodium Phosphido Complexes. J. Am. Chem. Soc. **2006**, *128*, 13698–13699.

(35) Waterman, R. Selective Dehydrocoupling of Phosphines by Triamidoamine Zirconium Catalysts. *Organometallics* **2007**, *26*, 2492–2494.

(36) Waterman, R. Metal-Phosphido and -Phosphinidene Complexes in P-E Bond-Forming Reactions. *Dalton Trans.* 2009, 18–26. (37) Hou, Z.; Stephan, D. W. Generation and Reactivity of the First Mononuclear Early Metal Phosphinidene Complex, $Cp_{2}^{*}Zr=P-(C_{6}H_{2}Me_{3}-2,4,6)$. J. Am. Chem. Soc. **1992**, 114, 10088–10089.

(38) Greenberg, S.; Stephan, D. W. Stoichiometric and Catalytic Activation of P-H and P-P bonds. *Chem. Soc. Rev.* 2008, 37, 1482–1489.

(39) Alhomaidan, O.; Welch, G. C.; Bai, G.; Stephan, D. W. Hafnium–Phosphinimide Complexes. *Can. J. Chem.* **2009**, *87*, 1163–1172.

(40) Wicht, D. K.; Kovacik, I.; Glueck, D. S.; Liable-Sands, L. M.; Incarvito, C. D.; Rheingold, A. L. Chiral Terminal Platinum(II) Phosphido Complexes: Synthesis, Phosphorus Inversion, and Acrylonitrile Insertion. *Organometallics* **1999**, *18*, 5141–5151.

(41) Melenkivitz, R.; Mindiola, D. J.; Hillhouse, G. L. Monomeric Phosphido and Phosphinidene Complexes of Nickel. *J. Am. Chem. Soc.* **2002**, *124*, 3846–3847.

(42) Malisch, W.; Klüpfel, B.; Schumacher, D.; Nieger, M. Hydrophosphination with Cationic Primary Phosphine Iron Complexes: Synthesis of P-chiral Functionalized Phosphines. *J. Organomet. Chem.* **2002**, *661*, 95–110.

(43) Zhang, L.; Liu, Y.; Deng, L. Three-Coordinate Cobalt(IV) and Cobalt(V) Imido Complexes with N-heterocyclic Carbene Ligation: Synthesis, Structure, and Their Distinct Reactivity in C-H Bond Amination. J. Am. Chem. Soc. **2014**, *136*, 15525–15528.

(44) Du, J.; Wang, L.; Xie, M.; Deng, L. A Two-Coordinate Cobalt(II) Imido Complex with NHC Ligation: Synthesis, Structure, and Reactivity. *Angew. Chem., Int. Ed.* **2015**, *54*, 12640–12644.

(45) Sun, J.; Gao, Y.; Deng, L. Low-Coordinate NHC-Cobalt(0)-Olefin Complexes: Synthesis, Structure, and Their Reactions with Hydrosilanes. *Inorg. Chem.* **2017**, *56*, 10775–10784.

(46) Yao, X.-N.; Du, J.-Z.; Zhang, Y.-Q.; Leng, X.-B.; Yang, M.-W.; Jiang, S.-D.; Wang, Z.-X.; Ouyang, Z.-W.; Deng, L.; Wang, B.-W.; Gao, S. Two-Coordinate Co(II) Imido Complexes as Outstanding Single-Molecule Magnets. J. Am. Chem. Soc. **201**7, 139, 373–380.

(47) Harley, A. D.; Guskey, G. J.; Geoffroy, G. L. Interconversion of Phosphido-Bridged Polynuclear Cobalt Carbonyl Complexes. Cleavage of the Phosphido Bridge during Hydroformylation Catalysis. *Organometallics* **1983**, *2*, 53–59.

(48) Winterhalter, U.; Zsolnai, L.; Kircher, P.; Heinze, K.; Huttner, G. Reductive Activation of Tripod Cobalt Compounds: Oxidative Addition of H–H, P–H, and Sn–H Functions. *Eur. J. Inorg. Chem.* **2001**, 89–103.

(49) Buster, B.; Diaz, A. A.; Graham, T.; Khan, R.; Khan, M. A.; Powell, D. R.; Wehmschulte, R. J. m-Terphenylphosphines: Synthesis, Structures and Coordination Properties. *Inorg. Chim. Acta* **2009**, *362*, 3465–3474.

(50) Nguyen, T.; Panda, A.; Olmstead, M. M.; Richards, A. F.; Stender, M.; Brynda, M.; Power, P. P. Synthesis and Characterization of Quasi-Two-Coordinate Transition Metal Dithiolates $M(SAr^*)_2$ (M = Cr, Mn, Fe, Co, Ni, Zn; Ar* = C₆H₃-2,6(C₆H₂-2,4,6-Prⁱ₃)₂. J. Am. Chem. Soc. **2005**, 127, 8545–8552.

(51) Edwards, P. G.; Read, P. W.; Hursthouse, M. B.; Malik, K. M. A. Synthesis and Structure of a Series of Unique Cobalt Phosphides. *J. Chem. Soc., Dalton Trans.* **1994**, 971–975.

(52) Pan, B.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Coordination of an N-Heterocyclic Phosphenium Containing Pincer Ligand to a $Co(CO)_2$ Fragment Allows Oxidation To Form an Unusual N-Heterocyclic Phosphinito Species. *Organometallics* **2011**, *30*, 5560–5563.

(53) Coburger, P.; Demeshko, S.; Rödl, C.; Hey-Hawkins, E.; Wolf, R. Oxidative P-P Bond Addition to Cobalt(-I): Formation of a Low-Spin Cobalt(III) Phosphanido Complex. *Angew. Chem., Int. Ed.* **2017**, *56*, 15871–15875.

(54) Termaten, A. T.; Aktas, H.; Schakel, M.; Ehlers, A. W.; Lutz, M.; Spek, A. L.; Lammertsma, K. Terminal Phosphinidene Complexes $Cp^{R}(L)M=PAr$ of the Group 9 Transition Metals Cobalt, Rhodium, and Iridium. Synthesis, Structures, and Properties. *Organometallics* **2003**, *22*, 1827–1834.

Article

(56) Simms, R. W.; Drewitt, M. J.; Baird, M. C. Equilibration between a Phosphine-Cobalt Complex and an Analogous Complex Containing an N-Heterocyclic Carbene: The Thermodynamics of a Phosphine-Carbene Exchange Reaction. *Organometallics* **2002**, *21*, 2958–2963.

(57) Vélez, C. L.; Markwick, P. R. L.; Holland, R. L.; Dipasquale, A. G.; Rheingold, A. L.; O'Connor, J. M. Cobalt 1,3-Diisopropyl-1Himidazol-2-ylidene Complexes: Synthesis, Solid-State Structures, and Quantum Chemistry Calculations. *Organometallics* **2010**, *29*, 6695– 6702.

(58) Dürr, S.; Zarzycki, B.; Ertler, D.; Ivanović-Burmazović, I.; Radius, U. Aerobic CO Oxidation of a Metal-Bound Carbonyl in a NHC-Stabilized Cobalt Half-Sandwich Complex. *Organometallics* **2012**, *31*, 1730–1742.

(59) Liu, Y.; Deng, L. Mode of Activation of Cobalt(II) Amides for Catalytic Hydrosilylation of Alkenes with Tertiary Silanes. J. Am. Chem. Soc. 2017, 139, 1798–1801.

(60) Tonner, R.; Heydenrych, G.; Frenking, G. Bonding Analysis of N-Heterocyclic Carbene Tautomers and Phosphine Ligands in Transition-Metal Complexes: A Theoretical Study. *Chem.*—*Asian J.* **2007**, *2*, 1555–1567.

(61) Kölle, P.; Linti, G.; Nöth, H.; Wood, G. L.; Narula, C. K.; Paine, R. T. Contributions to the chemistry of boron, 188. Synthesis and Structures of New 1,3,2,4-Diphosphadiboretanes. *Chem. Ber.* **1988**, 121, 871–879.

(62) Takeda, Y.; Nishida, T.; Minakata, S. 2,6-Diphospha-sindacene-1,3,5,7(2 H,6 H)-tetraone: A Phosphorus Analogue of Aromatic Diimides with the Minimal Core Exhibiting High Electron-Accepting Ability. *Chem.—Eur. J.* **2014**, *20*, 10266–10270.

(63) Chávez, I.; Alvarez-Carena, A.; Molins, E.; Roig, A.; Maniukiewicz, W.; Arancibia, A.; Arancibia, V.; Brand, H.; Manríquez, J. M. Selective Oxidants for Organometallic Compounds Containing a Stabilising Anion of Highly Reactive Cations: $(3,5-(CF_3)_2C_6H_3)_4B^-)Cp_2Fe^+$ and $(3,5(CF_3)_2C_6H_3)_4B^-)Cp^*_2Fe^+$. J. Organomet. Chem. **2000**, 601, 126–132.

(64) Manner, V. W.; Markle, T. F.; Freudenthal, J. H.; Roth, J. P.; Mayer, J. M. The first Crystal Structure of a Monomeric Phenoxyl Radical: 2,4,6-tri-tert-butylphenoxyl radical. *Chem. Commun.* **2008**, 256–258.

(65) Evans, D. F. The Determination of the Paramagnetic Susceptibility of Substances in Solution by Nuclear Magnetic Resonance. J. Chem. Soc. **1959**, 2003–2005.

(66) Sur, S. K. Measurement of Magnetic Susceptibility and Magnetic Moment of Paramagnetic Molecules in Solution by High-field Fourier Transform NMR Spectroscopy. *J. Magn. Reson.* **1989**, *82*, 169–173.

(67) Sheldrick, G. M. SADABS, Program for Empirical Absorption Correction of Area Detector Data; University of Göttingen: Germany, 1996.

(68) Sheldrick, G. M. SHELXTL 5.10 for Windows NT: Structure Determination Software Programs; Bruker Analytical X-ray systems, Inc.: Madison, WI, 1997.

(69) Hohenberg, P.; Kohn, W. Inhomogeneous Electron Gas. *Phys. Rev.* [*Sect.*] B **1964**, *136*, B864–B871.

(70) Kohn, W.; Sham, L. J. Self-Consistent Equations Including Exchange and Correlation Effects. *Phys. Rev.* [Sect.] A **1965**, 140, A1133–A1138.

(71) Neese, F. ORCA-An Ab Initio, Density Functional and Semiempirical Program Package, version 3.0.3; Max-Planck Institute for Bioinorganic Chemistry: Mülheim an der Ruhr: Germany, 2015.

(72) Becke, A. D. Density-Functional Thermochemistry. III. The Role of Exact Exchange. J. Chem. Phys. **1993**, 98, 5648–5652.

(73) Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti Correlation-Energy Formula into a Functional of the Electron Density. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785–789.

(74) Schäfer, A.; Horn, H.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets for Atoms Li to Kr. *J. Chem. Phys.* **1992**, *97*, 2571–2577.

(75) Schäfer, A.; Huber, C.; Ahlrichs, R. Fully Optimized Contracted Gaussian Basis Sets of Triple zeta Valance Quality for Atoms Li to Kr. *J. Chem. Phys.* **1994**, *100*, 5829–5835.

(76) Pantazis, D. A.; Chen, X.-Y.; Landis, C. R.; Neese, F. All-Electron Scalar Relativistic Basis Sets for Third-Row Transition Metal Atoms. J. Chem. Theory Comput. **2008**, *4*, 908–919.

(77) Neese, F.; Wennmohs, F.; Hansen, A.; Becker, U. Efficient, Approximate and Parallel Hartree-Fock and Hybrid DFT Calculation. A "chain-of-spheres" Algorithm for the Hartree-Fock Exchange. *Chem. Phys.* **2009**, 356, 98–109.

(78) Garner, M. E.; Arnold, J. Reductive Elimination of Diphosphine from a Thorium-NHC-Bis(phosphido) Complex. *Organomettlics* **2017**, *36*, 4511–4514.

(79) Zou, J.; Berg, D. J.; Oliver, A.; Twamley, B. Unusual Redox Chemistry of Ytterbium Carbazole-Bis(oxazoline) Compounds: Oxidative Coupling of Primary Phosphines by an Ytterbium Carbazole-Bis(oxazoline) Dialkyl. *Organometallics* **2013**, *32*, 6532– 6540.

(80) Erickson, K. A.; Dixon, L. S. H.; Wright, D. S.; Waterman, R. Exploration of Tin-Catalyzed Phosphine Dehydrocoupling: Catalyst Effects and Observation of Tin-Catalyzed Hydrophosphination. *Inorg. Chim. Acta* **2014**, *422*, 141–145.

(81) Baudler, M.; Gruner, C.; Tschäbunin, H.; Hahn, J. Beiträge zur Chemie des Phosphors, 110. 1,2-Di-tert-butyldiphosphan und tert-Butyldiphosphan. *Chem. Ber.* **1982**, *115*, 1739–1745.