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Article

Activation of sp^3 Carbon−Hydrogen Bonds by Cobalt and Iron Complexes and Subsequent C−C Bond Formation

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The sp^3 C−H bond activation induced by $CoMe(PMe_3)_4$ and $FeMe_2(PMe_3)_4$ was investigated. C(sp^3)-cyclometalated complexes, based on diphosphinito PCP ligand $(Ph_2POCH_2)_2CH_2$, $Co\{(Ph_2POCH_2)_2CH\}(PMe_3)_2$ (**1**), and $Fe\{(Ph_2POCH_2)_2MeC\}(H)(PMe_3)_2$ (**2**), were obtained under mild conditions. Iodomethane is oxidatively added to **1**, affording $Co\{(Ph_2POCH_2)_2CH\}(PMe_3)(Me)(I)$ (**3**). Monocarbonylation of the hydrido-iron complex **2** occurs with substitution of a trimethylphosphine ligand *trans* to the hydrido ligand, affording $Fe\{(Ph_2POCH_2)_2MeC\}(H)(CO)(PMe_3)$ (**4**). The reaction of **2** with phenylacetylene delivered the demetalated new diphosphine ligand $(Ph_2POCH_2)_2CHCH_3$ (**6**) and bis(phenylethinyl)iron complex $Fe(PhCC)_2(PMe_3)_4$ (**5**). The new complexes **1**−**4** were characterized by spectroscopic methods and by X-ray diffraction analysis.

Introduction

The direct functionalization of hydrocarbons to various useful chemicals via transition-metal-mediated C−H bond activation has now become a major topic of research.[1] Until recently, the majority of the catalytic processes reported were applicable to only sp^2 C−H bonds. There is still no series of general, selective, efficient catalytic functionalization reactions of unactivated sp^3 C−H bonds owing to the strength of sp^3 C−H bonds and the weakly coordinating nature of aliphatic moieties.[2] The transition-metal-mediated activation of unreactive C−H bonds proceeds by several mechanisms, which include σ-bond metathesis, substitution by electrophilic metal complexes, and oxidative addition to low-valent metal centers, while most of the understanding of alkane activation has been obtained from studies of oxidative addition reactions. The precoordination of a substrate can facilitate the interaction between C−H bonds and metal centers and results in an easier and highly selective C−H bond cleavage. So, some transition metal species can cleave the sp^3 C−H bonds of their own ancillary ligands,[3] and some promising catalytic systems for the selective functionalization of sp^3 C−H bonds have been developed in the past few years.[4]

Transition metal complexes with PCP pincer ligands incorporating two phosphane arms and a central carbon atom as donor have attracted a substantial amount of interest.[5] The strong chelating nature of PCP pincer ligands makes them bond to a wide variety of transition metals and prevents the dissociation and ligand exchange process. However, research activity in this field has also mainly focused on sp^2-carbon- rather than sp^3-carbon-based compounds. Compared to the systems with a rigid phenyl ring backbone, ligands with an aliphatic backbone exhibit high flexibility as well as the higher electron-donating ability of the sp^3-metalated carbon atom in the corresponding metal complexes, which increase their reactivity.[6] A number of complexes with aliphatic backbones were recently described in nickel,[7] platinum,[8] iridium,[9] ruthenium,[10] and rhodium[11] chemistry.

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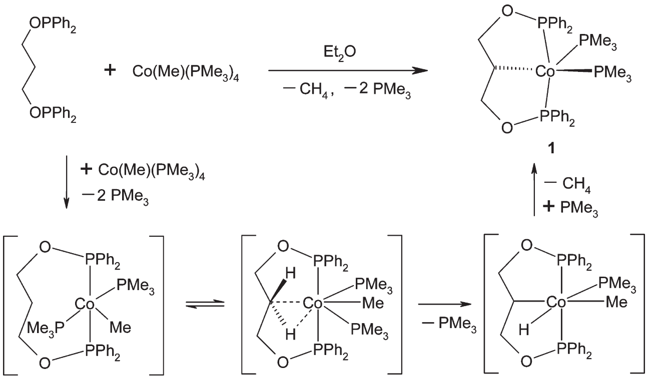
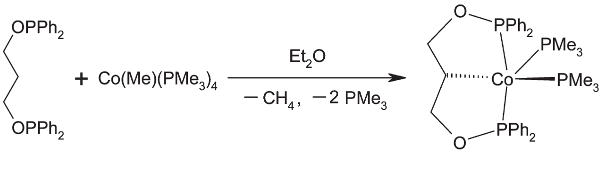
Scheme 1. Proposed Formation Mechanism of 1



Compared to the other platinum group metals (Ru, Os, Rh, Ir, Pd, Pt, Ni), iron- and cobalt-based catalysts are relatively underrepresented in the field of catalysis, although they have potentially lower cost and environmental impact. Our group has been investigating the use of first-row metals in the transformation of strong bonds.[12] The precoordination strategy in sp^3 C−H bond activation proves productive and results in the isolation and characterization of novel cobalt and iron complexes. We herein report our initial studies on the stoichiometric activation and functionalization of sp^3 C−H bonds under mild conditions by iron- and cobalt-based systems.

Results and Discussion

1. Reaction of $Co(Me)(PMe_3)_4$ with $(Ph_2POCH_2)_2CH_2$. When a solution of $(Ph_2POCH_2)_2CH_2$ was treated with $Co(Me)(PMe_3)_4$ in diethyl ether, compound **1** was isolated as a red solid in over 75% yield upon workup, which could be crystallized from diethyl ether at 0 °C (eq 1).



(1)

1

The reaction likely begins with the coordination of the cobalt to the phosphorus atom in ligand $(Ph_2POCH_2)_2CH_2$ by substituting two of the trimethylphosphines, which brings the metal closer to the central sp^3 C−H bond. This precoordination facilitates the interaction between C−H bonds and the metal center and results in an easier and highly selective C−H bond cleavage (Scheme 1). The methylmetal function here can utilize the new hydrido ligand, and reductive elimination of methane renders the reaction irreversible and affords a Co(I) complex **1** with two five-membered cobaltocycles in high yield.

The existence of the Co−C (sp^3) bond in **1** is initially indicated by NMR spectroscopic analysis. In the ^1H NMR spectrum the intensity ratio of the CH group (br, $\delta = 2.43$ ppm) and the CH_2 group ($\delta = 3.50$ and 3.73 ppm) is 1:4, which indicates that there is only one H left at the central carbon atom, while one C−H bond has been cleaved. **1** is stable in air for several hours. X-ray crystallography confirmed the molecular configuration of **1** (Figure 1) derived from solution data. Two five-membered cobaltocycles with considerable ring bending (sum of internal angles = 526.84° and 523.85°) are formed through two P atoms of the PPh_2 groups and a metalated sp^3-C atom. The cobalt atom is centered in a trigonal bipyramid. The Co1−C1 distance (2.081(4) Å) is within the range of Co−C (sp^3) bonds (2.03−2.15 Å),[3b] and the Co1−P4 distance (2.1693(13) Å) is substantially shorter than Co1−P5 (2.2170(13) Å), which is due to the electron-donating ability of the *trans*-C (sp^3) atom.

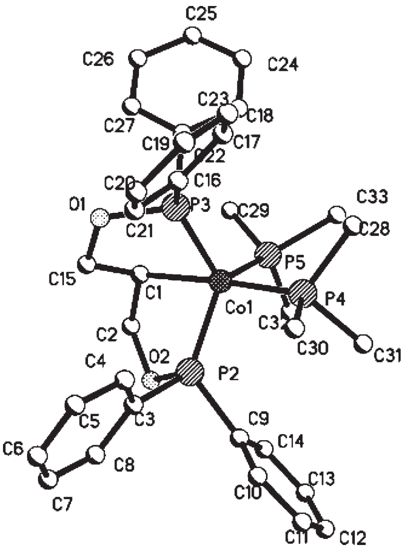
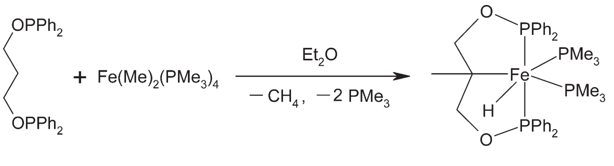


Figure 1. Molecular structure of **1** and selected bond distances (Å) and angles (deg): Co1−C1 2.081(4), Co1−P4 2.1693(13), Co1−P5 2.2170(13); C1−Co1−P4 172.88(14), P2−Co1−P3 124.35(5), P2−Co1−P4 97.43(5), P2−Co1−P5 115.01(5), P3−Co1−P5 114.59(5), C2−C1−C15 111.8(4).

2. Reaction of $Fe(Me)_2(PMe_3)_4$ with $(Ph_2POCH_2)_2CH_2$. Treating a diethyl ether solution of $(Ph_2POCH_2)_2CH_2$ with $Fe(CH_3)_2(PMe_3)_4$ gave rise to hydrido-iron(II) complex **2** (eq 2). Crystallization at 0 °C afforded a yellow crystalline solid in over 50% isolated yield. Complex **2** both in the solid state and in solution is stable at room temperature for 1 h at least.



(2)

2

Similar to the formation of cobalt complex **1**, the reaction may also start with the precoordination of the iron adduct, but the following double C−H activation process and C,C-coupling between two sp^3 carbons exhibit an unusual reaction pathway (Scheme 2). The substitution of two trimethylphosphines and elimination of methane afford **A**, then the C,C-coupling between the methyl group and the central carbon atom of $(Ph_2POCH_2)_2CH_2$ and the subsequent reductive elimination of iron species produce a new ligand backbone with a 3° sp^3 C−H bond, and then a C−H activation process once again in the new ligand backbone gives **2** as the final product. Klein and co-workers have reported similar results for the imine systems recently.[13]

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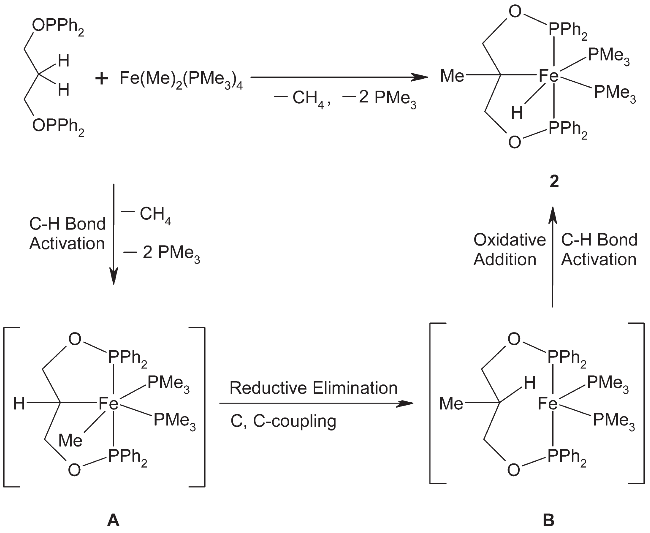
Scheme 2. Proposed Formation Mechanism of 2



For less sterically hindered C−H bonds and bonds with more s character, the activation is both kinetically and thermodynamically preferred. So, the 3° sp^3 C−H bond is the most difficult to cleave. In Klein's earlier research, when the monosubstituted triphenylphosphane substituents are changed from 2-methyl to 2-ethyl or 2-isopropyl, for steric strain reasons, the C−H activation can only happen to the *ortho*-sp^2 C−H bonds.[3b] Limited examples of transition-metal-mediated 3° sp^3 C−H bond activation have been reported.[14] However, in this whole process, **A** and **B**, with a new ligand backbone, have not been isolated. There should exist some interactions between the eliminated iron(0) fragment and the newly formed 3° sp^3-carbon; the second C−H activation could not be a pure 3° sp^3 C−H bond cleavage.

In contrast to the C−H activation, the alkane functionalization, which involves replacement of a C−H hydrogen by an organic functional group, has proved more difficult than the activation step, since alkyl hydride complexes tend to release alkane on attempted functionalization. Because formation of carbon−carbon bonds is the foundation of organic chemical synthesis, the activation of C−H bonds and the formation of C−C bonds in a single preparative step combine economy, efficiency, and elegance.

van Koten has also reported that, upon treatment of a Pt-NCN pincer complex with methyl iodide or higher alkyl halide reactants, a sp^2−sp^3 C−C coupling was induced between the *ipso*-C-donor atom of the ligand and the methyl or alkyl group, and the intermediate platinum-stabilized arenium complex [Pt(1-Me-NCN)](X′) was isolated and characterized,[15] while Milstein and co-workers have focused on C−C bond cleavage, which can be seen as the reverse process of C−C bond formation, by using alkylated pincer ligands.[16]

The IR spectrum gives evidence for hydrido-iron(II) **2**, with a typical ν(Fe−H) stretching band at 1919 cm^{-1}. The resonance of the hydrido hydrogen in the NMR spectrum is registered as a broad signal at −16.4 ppm. **2** shows CH_3 at 28.04 ppm and Fe−*C* (sp^3) at 64.48 ppm. This configuration of **2** is confirmed by X-ray structure analysis (Figure 2). The iron atom is centered in a slightly distorted octahedral geometry. The Fe1−C26 distance (2.185(2) Å) is within the range of Fe−C (sp^3) bonds.[3c] The most striking feature in the molecular structure of **2** is the methyl substituent attached to the metalated sp^3-carbon (C26).

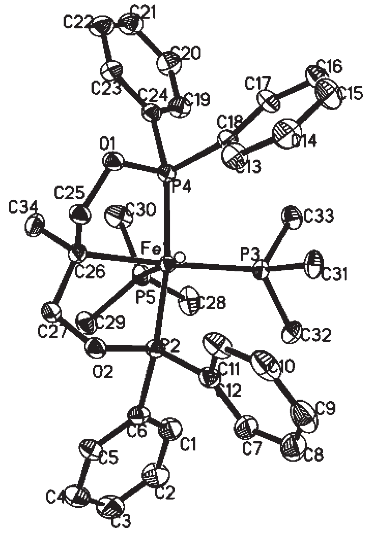
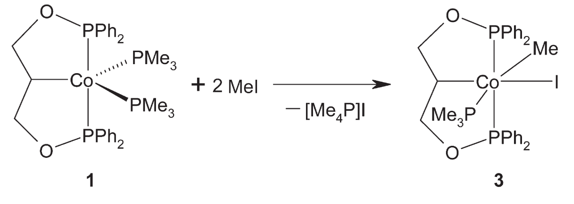


Figure 2. Molecular structure of **2** and selected bond distances (Å) and angles (deg): C26−Fe1 2.189(2), Fe1−P3 2.2301(7), Fe1−P5 2.2560(8); C26−Fe1−P3 170.02(7), P2−Fe1−P4 140.06(3), C26−Fe1−P5 93.34(7), C27−C26−C25 106.2(2), C27−C26−C34 108.3(2), C25−C26−C34 106.7(2), C34−C26−Fe1 119.71(18).

3. Reaction of 1 with Iodomethane. Motivated by our results of iron, we investigated the reaction of iodomethane with **1**. **1** reacted with excess iodomethane in diethyl ether by dissociation and quaternization of a trimethylphosphine (eq 3), undergoing an oxidative substitution reaction. Crystals of **3** were obtained from diethyl ether. An X-ray diffraction study of complex **3** revealed that the cobalt atom attains an octahedral coordination, with PMe_3 opposite CH_3, and the I atom opposite the metalated sp^3-carbon (Figure 3). The Co−C9 distance is 2.019(5) Å, which is slightly shorter than the Co−C (sp^3) bond length in complex **1**, reflecting the weaker *trans*-influence of the iodo ligand.



(3)

4. Study on Iron Hydride Complex 2. The insertion of small molecules such as CO, CO_2, olefins, and alkynes into the metal−hydride bond of mononuclear transition metal complexes represents a fundamental reaction in organometallic chemistry, which is also of great relevance for homogeneous catalysis, and the transition metal hydrides play a central role. Indeed, virtually all the major industrial processes in the petrochemical industry rely on the involvement of an M−H moiety in one or more key steps.[17] The chemistry of iron(II) classical and nonclassical hydride complexes has

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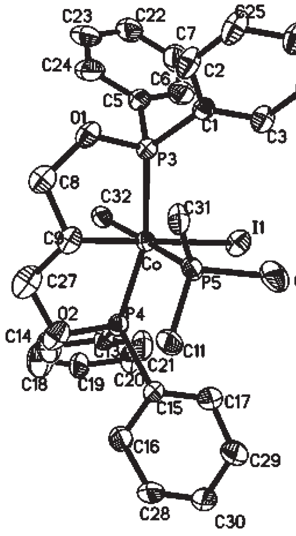
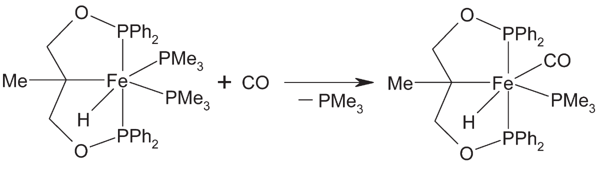


Figure 3. Molecular structure of **3** and selected bond distances (Å) and angles (deg): C9−Co 2.019(5), C32−Co 2.070(6), Co−P5 2.3040(16), I1−Co 2.6678(7); C9−Co−I1 178.6(2), C32−Co−P5 175.3(2), P4−Co−P3 162.72(6), C27−C9−C8 110.9(6).

considerably developed in the last 30 years, highlighting the syntheses of a number of complexes with interesting properties.[18] Our initial focus was on reactions involving insertion of unsaturated organic molecules into an iron hydride or iron alkyl.

4.1. Reaction of Complex 2 with Carbon Monoxide. For the catalytic C−H bond carbonylation by the $RhCl(CO)(PMe_3)_2$ system, the rhodium hydride complexes $Rh(C_6H_5)(H)Cl(PMe_3)_2$ and $Rh(C_6H_5)(H)Cl(CO)(PMe_3)_2$ were postulated as catalytic intermediates.[19]

The carbonyl hydride complex **4** is readily formed by placing a diethyl ether solution of **2** under an atmosphere of CO at 20 °C (eq 4). Yellow-orange crystals of **4** were obtained from pentane.



2 **4** (4)

The Fe−H bond remains unaffected in this transformation. Carbon monoxide substitutes one of the trimethylphosphines, selectively occupying the *trans*-position to the hydrido ligand. In the infrared spectra a strong (C≡O) absorption is registered at 1907 cm^{-1} and clearly indicates a terminal carbon monoxide ligand. The Fe−H band is found at 1861 cm^{-1}. In ^{1}H NMR spectrum, the proton resonance of the Fe−H is recorded at −10.01 ppm as a doublet of triplets due to the coupling of the hydrido nucleus with *trans*- and *cis*-diposed phosphorus atoms. In comparison with **2**, the downfield shifting of Fe−H resonance is caused by strong back-bonding and the *trans*-influence of CO ligand.

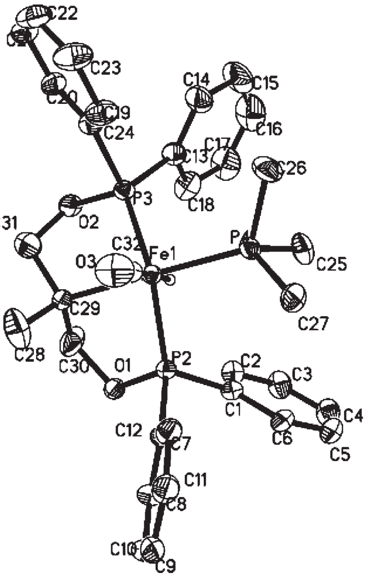
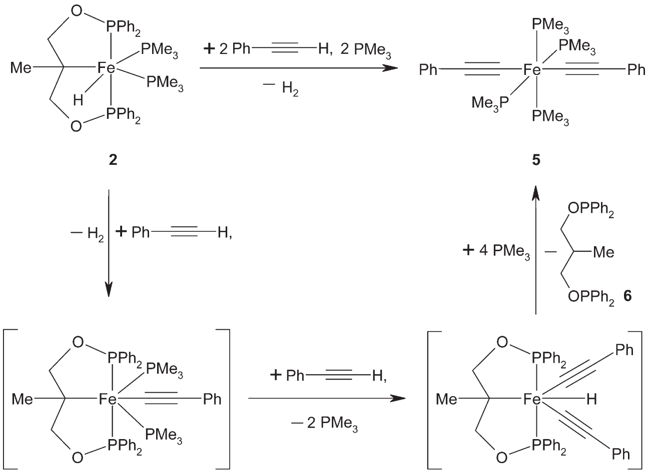


Figure 4. Molecular structure of **4** and selected bond distances (Å) and angles (deg): C29−Fe1 2.157(3), Fe1−P4 2.2231(10), C32−Fe1 1.749(4), O3−C32 1.167(4); C29−Fe1−P4 174.2(1), P3−Fe1−P2 144.0(1), C30−C29−C31 107.8(4), C28−C29−C31 105.2(4), O3−C32−Fe1 178.1(4), C32−Fe1−C29 93.4(2), C32−Fe1−P4 92.4(2).

Scheme 3. Proposed Formation Mechanism of 5



The expected configuration is confirmed by X-ray diffraction analysis (Figure 4). The iron atom is coordinated with two five-membered metallacycles, one trimethylphosphine, one carbonyl ligand, and one hydride ligand in a distorted octahedral geometry.

4.2. Reaction of Complex 2 with Phenylacetylene. We first investigated the reaction of **2** with phenylacetylene, but this attempt resulted in total dissociation of the diphosphinito PCP ligand to afford the bis(phenylethynyl)iron(II) **5** in over 39% yield (eq 5). **5** was identified by IR and NMR spectroscopy. In the IR spectrum, the typical Fe−H absorption at 1919 cm^{-1} of the hydrido iron complex **2** is absent, and the C≡C band is found at 2037 and 1986 cm^{-1}. The ^{1}H NMR spectrum in C_6D_6 reveals only PMe_3 and aromatic protons at 1.4 and 7.0−7.5 ppm, respectively, indicating that the

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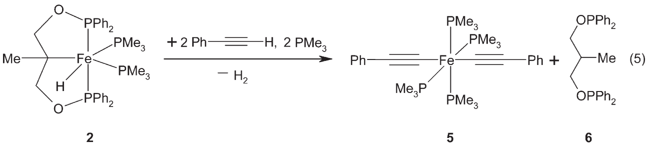
Table 1. Crystallographic Data for Complexes 1, 2, 3, and 4

	1	2	3	4
empirical formula	$C_{33}H_{43}CoO_2P_4$	$C_{34}H_{46}FeO_2P_4$	$C_{31}H_{37}CoIO_2P_3$	$C_{32}H_{37}FeO_3P_3$
fw	654.48	666.44	720.35	618.38
cryst syst	orthorhombic	monoclinic	trigonal	triclinic
space group	$P2(1)2(1)2(1)$	$P2(1)/n$	$R3c$	$P\bar{1}$
a, Å	9.352(3)	9.8543(11)	20.7214(10)	9.4228(8)
b, Å	17.919(6)	17.5207(19)	20.7214(10)	13.1829(11)
c, Å	20.276(6)	20.085(2)	39.396(4)	13.6974(12)
α, deg	90	90	90	81.630(2)
β, deg	90	102.574(2)	90	78.7680(10)
γ, deg	90	90	120	75.4550(10)
V, Å^3	3397.7(18)	3384.7(6)	14649.4(18)	1607.0(2)
Z	4	4	18	2
D_c, g cm^{-3}	1.279	1.308	1.470	1.278
no. of rflns collected	19 845	21 089	30 111	9884
no. of unique data	7885	9426	9906	8220
R_{int}	0.0459	0.0405	0.0265	0.0195
θ_{max}, deg	27.60	29.49	30.46	28.56
R_1 ($I > 2\sigma(I)$)	0.0496	0.0495	0.0443	0.0580
wR_2 (all data)	0.1208	0.1701	0.1464	0.1692

dissociation of the PCP ligand did occur. In the ^{31}P NMR spectrum, this conjecture is proved through only one singlet assigned to PMe_3 at 20.9 ppm. All of these spectroscopic data are consistent with the results we obtained from the reaction of thiophenoliron hydrides with alkynes.[20] The proposed mechanism is depicted in Scheme 3. The demetalated new diphosphine ligand, $(Ph_2POCH_2)_2CHCH_3$ (**6**), was confirmed with LC/MS. Compound **6** is no longer a pincer ligand and has weak coordination ability.



Conclusion

In conclusion, using a precoordination strategy, we have achieved the activation of sp^3 C−H bonds induced by electron-rich cobalt and iron species in reaction with aliphatic PCP ligand $(Ph_2POCH_2)_2CH_2$. The reaction of $Fe(Me)_2(PMe_3)_4$ with $(Ph_2POCH_2)_2CH_2$ afforded a noteworthy hydrido iron(II) complex with a double sp^3 C−H activation process and a subsequent C,C-coupling between the sp^3 carbon of the aliphatic backbone and the CH_3 fragment.

The reaction of **1** with CH_3I gave rise to iodomethylcobalt(III) complex **3**. Carbonylation reaction of hydrido iron **2** afforded a monocarbonyl substituent derivative, where possible insertion reactions of CO into the Fe−C or Fe−H bonds were not observed. The reaction of **2** with phenylacetylene delivered the demetalated new diphosphine ligand **6** and bis(phenylethinyl)iron complex **5**.

Experimental Section

General Procedures and Materials. Standard vacuum techniques were used in manipulations of volatile and air-sensitive materials. Solvents were dried by known procedures and distilled under nitrogen before use. Infrared spectra (4000−400 cm^{-1}), as obtained from Nujil mulls between KBr disks, were recorded on a Nicoler 5700. NMR spectra were recorded using a Bruker Avance 300 or 400 MHz spectrometer. X-ray crystallography was performed with a Bruker Smart 1000 diffractometer. LC/MS were carried out using an Agilent 6510 Accurate-Mass Q-TOF LC/MS system. Melting points were measured in capillaries sealed under argon and were uncorrected. Elemental analyses were carried out on an Elementar Vario EL III.

Synthesis of Co{$(Ph_2POCH_2)_2CH$}$(PMe_3)_2$, 1. $(Ph_2POCH_2)_2CH_2$ (2.0 g, 4.5 mmol) in 30 mL of diethyl ether was combined with $Co(CH_3)(PMe_3)_4$ (1.55 g, 4.1 mmol) in 40 mL of diethyl ether with stirring at 0 °C. The reaction mixture changed immediately from orange-red to deep red and was kept stirring at room temperature for 24 h. During this period, some red powder precipitated slowly from the diethyl ether solution. After filtration, the solvents were reduced to give a red solid, which crystallized from diethyl ether at 4 °C. Yield: 2.07 g, 77%; mp (dec) > 112 °C. Anal. Calcd for $C_{33}H_{43}CoO_2P_4$ (**1**, 654.48 g/mol): C, 60.56; H, 6.62. Found: C, 60.82; H, 6.28. ^{1}H NMR (300 MHz, C_6D_6, 294 K, ppm): δ 0.87 (d, ^2J(PH) = 6.9 Hz, 9H, PCH_3), 1.02 (d, ^2J(PH) = 4.8 Hz, 9H, PCH_3), 2.42 (br, 1H, CH), 3.47 (m, 2H, CH_2), 3.72 (m, 2H, CH_2), 6.92−8.10 (m, 20H, aromatic-H). ^{13}C NMR (75.5 MHz, C_6D_6, 294 K, ppm): δ 12.9 (s, PCH$_3$), 20.5 (d, ^3J(PC) = 16.6 Hz, PCH$_3$), 22.3 (s, Co-C), 71.5 (d, ^2J(PC) = 6.0 Hz, CH$_2$), 125.7−147.2 (m, aromatic-C). ^{31}P NMR (121.5 MHz, C_6D_6, 294 K): δ −12.5 (t, ^2J(PP) = 98.5 Hz, 1P, PCH$_3$), 12.3 (s, 1P, PCH$_3$), 155.9 (d, ^2J(PP) = 83.0 Hz, 2P, PPh$_2$).

Synthesis of Fe{$(Ph_2POCH_2)_2(CH_3)C$}(H)$(PMe_3)_2$, 2. $(Ph_2POCH_2)_2CH_2$ (2.0 g, 4.5 mmol) in 30 mL of diethyl ether was combined with $Fe(CH_3)_2(PMe_3)_4$ (1.61 g, 4.1 mmol) in 30 mL of diethyl ether with stirring at 0 °C. The mixture was kept stirring at room temperature for 24 h; at this time the color changed from brown to red, and some yellow-orange powder precipitated from the solution. After filtration, the solid residue was extracted with diethyl ether. Complex **2** suitable for X-ray diffraction as yellow crystals was obtained from diethyl ether. Yield: 1.46 g, 53%; mp (dec) > 131 °C. Anal. Calcd for $C_{34}H_{46}FeO_2P_4$ (**2**, 666.44 g/mol): C, 61.28; H, 6.96. Found: C, 60.87; H, 7.08. IR (Nujol, cm^{-1}): ν(Fe−H); 1919 s. ^{1}H NMR (300 MHz, C_6D_6, 294 K, ppm): δ −16.4 (br, 1H, Fe-H), 0.69 (br, 9H, PCH_3), 0.88 (br, 9H, PCH_3), 3.26−3.95 (br, 4H, CH_2), 7.15−8.15 (m, 20H, aromatic-H). ^{13}C NMR (75.5 MHz, C_6D_6, 294 K, ppm): δ 12.5 (s, PCH$_3$), 22.8 (d, ^3J(PC) = 15.1 Hz, PCH$_3$), 28.0 (s, CH$_3$), 64.5 (s, Fe-C), 78.9 (s, CH$_2$), 126.3−130.6 (m, aromatic-C). ^{31}P NMR (121.5 MHz, C_6D_6, 294 K): δ 5.7 (s, 1P, PCH$_3$), 16.2 (s, 1P, PCH$_3$), 176.3 (d, ^2J(PP) = 59.2 Hz, 2P, PPh$_2$).

Synthesis of Co{$(Ph_2POCH_2)_2CH$}$(PMe_3)(CH_3)$(I) 3. 1 (610 mg, 0.93 mmol) was combined with CH_3I (754 mg, 5.31 mmol) in diethyl ether with stirring at 0 °C. The reaction mixture was kept stirring at room temperature for 24 h. During this period, a

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[20] Zhen, T.; Li, M.; Sun, H.; Harms. K.; Li, X. *Polyhedron*, accepted **2009**.

white powder precipitated slowly from the diethyl ether solution. After filtration, the solid residue was extracted with diethyl ether four times, and then the diethyl ether was combined together to afford reddish-pink crystals of **3** at 4 °C. Yield: 460 mg, 69%; mp (dec) > 134 °C. Anal. Calcd for $C_{31}H_{37}CoIO_2P_3$ (**3**, 720.35 g/mol): C, 51.69; H, 5.18. Found: C, 52.03; H, 5.02. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 0.84 (d, ^2J(PH) = 5.2 Hz, 9H, PC*H*$_3$), 1.23 (m, 3H, Co-C*H*$_3$), 2.37 (br, 1H, C*H*), 3.22−3.82 (m, 4H, C*H*$_2$), 6.67−8.66 (m, 20H, aromatic-*H*). ^{13}C NMR (100.6 MHz, C_6D_6, 300 K, ppm): δ 15.8 (d, ^3J(PC) = 27.3 Hz, P*C*H$_3$), 25.6 (s, Co-*C*H$_3$), 29.9 (s, *C*H$_3$), 67.6 (s, Co-*C*), 71.7 (s, *C*H$_2$), 128.4−144.1 (m, aromatic-*C*). ^{31}P NMR (162.0 MHz, C_6D_6, 298 K): δ −20.6 (s, 1P, *P*CH$_3$), 148.7 (s, 2P, *P*Ph$_2$).

Synthesis of Fe{($Ph_2POCH_2)_2(CH_3$)C}(H)(CO)(PMe_3), 4. A sample of **2** (450 mg, 0.67 mmol) in diethyl ether was stirred under 1 bar of CO at 20 °C. After 12 h, all volatiles were removed in vacuo, and the residue was extracted with pentane, which gave yellow-pink crystals of **4** at −18 °C. Yield: 270 mg, 65%; mp (dec) > 140 °C. Anal. Calcd for $C_{32}H_{37}FeO_3P_3$ (**4**, 618.38 g/mol): C, 62.15; H, 6.03. Found: C, 62.40; H, 6.21. IR (Nujol, cm^{-1}): ν(C≡O), 1907 s; ν(Fe−H), 1861 s. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ −10.0 (td, ^2J(P_{PPh}H, 75.7° and 72.8°) = 56.9 Hz, ^2J(P_{PMe}H, 88.5°) = 33.1 Hz, 1H, Fe-*H*), 0.70 (d, ^2J(PH) = 7.7 Hz, 9H, PC*H*$_3$), 1.00 (t, ^4J(PH) = 7.2 Hz, 3H, C*H*$_3$), 3.55 (m, 2H, C*H*$_2$), 3.95 (m, 2H, C*H*$_2$), 7.05−8.41 (m, 20H, aromatic-*H*). ^{13}C NMR (100.6 MHz, C_6D_6, 300 K, ppm): δ 22.0 (d, ^3J(PC) = 24.2 Hz, P*C*H$_3$), 30.9 (s, *C*H$_3$), 58.1(d, ^2J(PC) = 12.5 Hz, Fe-*C*), 79.8 (t, ^2J(PC) = 10.4 Hz, *C*H$_2$), 127.3−146.0 (m, aromatic-*C*). ^{31}P NMR (162.0 MHz, C_6D_6, 298 K): δ 20.3 (br, 1P, *P*CH$_3$), 188.7 (d, ^2J(PP) = 56.8 Hz, 2P, *P*Ph$_2$).

Reaction of 2 with Phenylacetylene. Phenylacetylene (552 mg, 5.42 mmol) in 10 mL of diethyl ether was added to a sample of **2** (570 mg, 0.86 mmol) in 30 mL of diethyl ether at 0 °C. The mixture was kept stirring at 20 °C for 16 h, effecting a change of color from yellow to orange-red and precipitation of a yellow powder. The mixture was then filtered. The yellow solid residue was dissolved in 20 mL of THF and crystallized at 20 °C to give yellow crystals of **5**, $Fe(PhCC)_2(PMe_3)_4$, which were suitable for X-ray diffraction.[20] Yield: 188 mg, 39%. IR (Nujol, cm^{-1}): ν(C≡C), 2037 and 1986 cm^{-1}. ^{1}H NMR (400 MHz, C_6D_6, 298 K, ppm): δ 1.44 (br, 36H, PC*H*$_3$), 7.07−7.51 (m, 20H, aromatic-*H*). ^{31}P NMR (162.0 MHz, C_6D_6, 298 K): δ 20.9 (s, *P*CH$_3$). The demetalated new diphosphine ligand, $(Ph_2POCH_2)_2CHCH_3$ (**6**), was found in the mother solution with LC/MS.

X-ray Structure Determinations. Intensity data were collected on a Bruker SMART diffractometer with graphite-monochromated Mo Kα radiation (λ, 0.71073 Å). Crystallographic data for complexes **1**, **2**, **3**, and **4** are summarized in Table 1. The structures were solved by direct methods and refined with full-matrix least-squares on all F^2 (SHELXL-97) with non-hydrogen atoms anisotropic. CCDC-735322 (**1**), CCDC-735323 (**2**), CCDC-735320 (**3**), and CCDC-735321 (**4**) contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax:(+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Crystallographic data for **1**, **2**, **3**, and **4**. This material is available free of charge via the Internet at http://pubs.acs.org.