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Preparation of Cobalt-Containing Ligands with NHC- and/or P-Coordinating Sites and Their Application in Heck Reactions: The Formation of an Unexpected Cobalt-Containing Zwitterionic Complex

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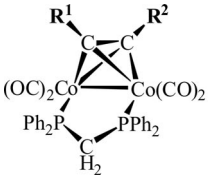
An unexpected cobalt-containing zwitterionic complex, [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-(R1)PC≡CCH_2(R2)}] (**8**; R1 = Ph_2Bz; R2 = 3-$CoBr_3$-1-benzimidazole), has been obtained during an attempt to modify the imidazole moiety in the alkyne-bridging dicobalt complex [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-Ph_2PC≡CCH_2(IM)}] (**5**; IM = benzimidazole) to a carbene-type substituent by reaction with benzyl bromide. As revealed in the crystal structure of **8**, it is clear that the benzyl bromide was nucleophilically attacked by the phosphane moiety of **5** with the result the addition of the benzyl moiety. This phosphane site in **8** is in a tetrahedral environment and presumably cationic in nature. In addition, an unusual anionic species $CoBr_3^-$ was found to have attached itself to the free nitrogen site of the imidazole moiety. Thus **8** can be regarded as an unusual metal-containing zwitterionic complex. When the phosphane site of **5** was replaced by a non-reactive substituent, for example, [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-RC≡CCH_2(IM)}] (**5′**: R = H; **5_O**: R = Ph_2(O)P), nucleophilic attack took place exclusively on the imidazole moiety and led to the formation of [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-RC≡CCH_2(IM′)}$^+$]Br^- [**9′**: R = H; **9_O**: R = Ph_2(O)P; IM′ = 3-benzyl-1*H*-benzimidazole]. Complex **9′** could act as a carbene precursor, which was demonstrated by the formation of the bis-**9′**-coordinated palladium complex [*trans*-({(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-HC≡CCH_2(IM′)})$_2PdBr_2$] (**11**) on treatment with [Pd(cod)Cl_2]. Fair-to-good efficiencies were observed in Heck reactions employing either isolated **11** or in situ **9′**/$PdCl_2$ (2:1) as the catalytic precursor.

Introduction

For the past few decades metal-catalysed cross-coupling reactions have probably been the most frequently employed method for the formation of C–X (X = C, N, O, S) bonds in modern synthetic chemistry.[1] Meanwhile, it has been demonstrated repeatedly that a well-chosen ligand is crucial to the success of palladium-catalysed Suzuki reactions.[2] Therefore considerable effort has been devoted to searching for more efficient ligands for these reactions. For many years, various types of organic phosphanes and phosphane derivatives have most frequently been employed as ligands.[1e,2,3] Nevertheless, relatively few transition-metal-containing phosphanes have been reported and examined.[3f,3g,4] In our previous work we demonstrated that a new category of metal-containing phosphanes [(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$(μ,η-R^1C≡CR^2)] [R^1,R^2 = P(*t*Bu)$_2$, P(*i*Pr)$_2$, PCy_2, PPh_2, Ph, py] could be easily prepared by synthetic procedures reported previously (Figure 1).[5] These complexes are essentially disubstituted alkyne-bridged dicobalt complexes coordinated by a bidentate ligand, bis(diphenylphosphanyl)methane (dppm). This new class of phosphane naturally leads to bulky ligands, which is clearly beneficial to the reductive elimination process of the catalytic cycle in the widely accepted Suzuki reaction mechanism. Their role as legitimate and active ligands in palladium-catalysed cross-coupling reactions has also been carefully evaluated.[5,6]



R^1, R^2: P(*t*Bu)$_2$, P(*i*Pr)$_2$, PCy_2, PPh_2, Ph, py, H

Figure 1. General structure of cobalt-containing mono- or bidentate phosphanes.

As is known, most phosphane ligands are electron-rich and are subject to ready oxidation in an oxygen-containing environment. This oxidation will naturally lead to a great reduction in its catalytic performance as a ligand. Recently, since the first report of Arduengo et al. in 1991, the versatile N-heterocyclic carbenes (NHCs) have emerged as potent alternatives.[7] NHCs have attracted much attention because of their superb stability towards oxidation, adjustable steric factor through the modification of substituents and strong σ-donating capacity towards low-valence transition metals.[8] Numerous applications of NHCs in catalysis have been developed.[8c–8g,9] The advantage of combining the merits of both phosphanes and NHCs by coupling these

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two distinct ligands in an organic or ferrocenyl moiety has been proposed and put into effect.[10] In contrast, the full power of uniting an NHC and a phosphane in a dicobalt framework has yet to be realized.[11] In this work, a new category of dicobalt-based NHCs has been explored and their role as authentic ligands has been examined.

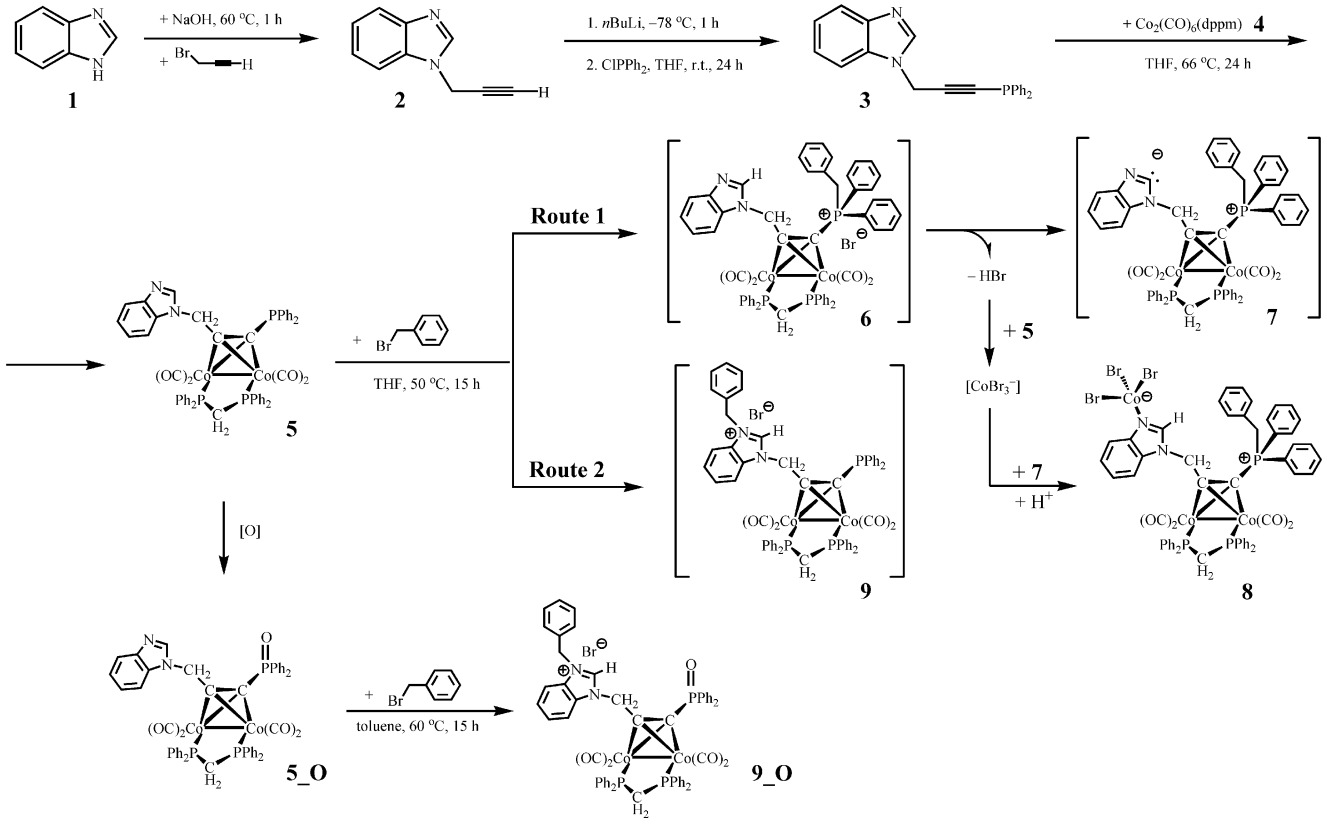
Results and Discussion

Preparation of Cobalt-Containing Mono- or Bidentate Ligands with NHC- and/or P-Coordinating Sites and Their Reactions with a Palladium Salt

A phosphanyl-benzimidazole-disubstituted alkyne-bridged dicobalt complex [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-$Ph_2PC{\equiv}CCH_2$(IM)}] (**5**; IM = 1*H*-benzimidazole) was prepared according to the procedure shown in Scheme 1. It was characterized by ^1H, ^{13}C and ^{31}P NMR spectroscopy. Unfortunately, the molecular structure of **5** could not be determined unambiguously by single-crystal X-ray diffraction methods due to disorder problems. However, the crystal structure of its oxidized form, [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-$Ph_2(O)PC{\equiv}CCH_2$(IM)}] (**5_O**; IM = 1*H*-benzimidazole), which was prepared by the oxidation of **5** with hydrogen peroxide, was determined unequivocally by this technique.

The ORTEP diagram of **5_O** depicted in Figure 2 shows the presence of a pseudo-tetrahedral Co_2C_2 core, a typical framework of alkyne-bridged dicobalt complexes. The dppm bridges two cobalt atoms and bends away from the benzimidazole moiety to prevent steric hindrance. In addition, the two substituents, the phosphanyl and benzimidazole, on the bridging alkyne bend away from the dicobalt moiety and reside on the same side, as predicted by the Dewar–Chatt–Duncanson model.[12] The oxidation of the phosphorus atom in **5_O** is evidenced by the formation of a P=O bond [P(3)–O(5) 1.490(4) Å]. The oxidized phosphane naturally loses its coordination capacity towards soft metals.[13] It also indicates that the phosphanyl site on **5** is electron-rich and suitable for coordination to soft metals.

Subsequently, an attempt was made to modify the benzimidazole moiety of **5** to an NHC-type ligand by reaction with benzyl bromide. This procedure is well prescribed in the literature as a general route to the preparation of N-heterocyclic carbenes from imidazole derivatives (Routes 1 and 2, Scheme 1).[8h,14] Nevertheless, an unexpected compound with a rather unusual conformation was formed as a bright-red precipitate (Route 1), which was characterized as [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-(R1)PC≡CCH_2-(R2)}] (**8**; R1 = Ph_2Bz; R2 = 3-$CoBr_3$-1*H*-benzimidazole). On the other hand, the existence of the targeted compound, [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-$Ph_2PC{\equiv}CCH_2$(IM)}$^+$]-Br^- (**9**; IM = 3-benzyl-1*H*-benzimidazole), was not certain.



Scheme 1. Preparation of cobalt-containing mono- or bidentate ligands. The existence of the complexes in brackets is speculative.

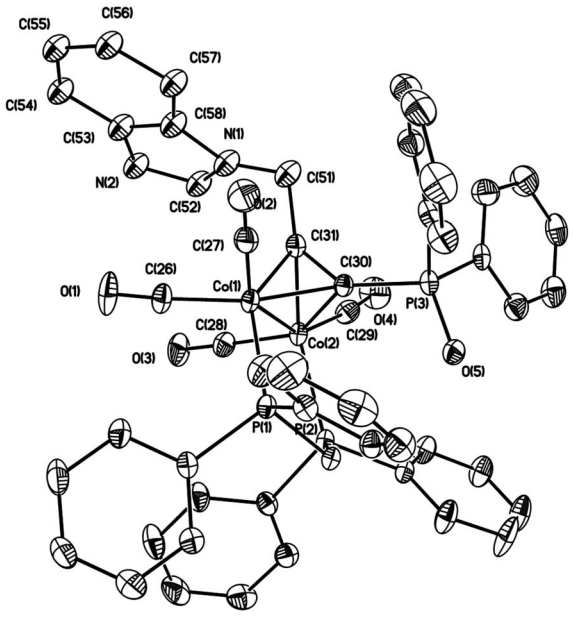


Figure 2. ORTEP drawing of **5_O**. Hydrogen atoms have been omitted for clarity.

The ^{1}H NMR spectrum of the crude reaction mixture shows a complicated pattern. Nevertheless, the observation of its oxidized counterpart [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}-{μ,η-$Ph_2P(=O)C{\equiv}CCH_2$(IM)}$^+$]Br^- (**9_O**; IM = 3-benzyl-1*H*-benzimidazole) in the reaction of **5_O** with benzyl bromide in a better-resolved ^{1}H NMR spectrum substantiates the possibility of the existence of **9**. Note that the oxidized phosphane site of **5_O** is not subjected to the attack of benzyl bromide. Therefore the reaction must take place at the benzimidazole site.

Complex **8** was further characterized by spectroscopic means as well as by single-crystal X-ray diffraction methods. The ^{31}P NMR spectrum exhibits two signals at δ = 30.5 and 36.9 ppm, in a ratio of 1:2, corresponding to the alkylated phosphane and dppm, respectively. The significant downfield shift of the former phosphane reflects its electron-deficient nature, which is consistent with its positively charged character. As revealed in the ORTEP diagram depicted in Figure 3, a pseudo-tetrahedral core Co_2C_2 was obtained and a benzyl group is present on the original phosphane site in **5**, as evidenced by the formation of a P–C bond [P(3)–C(44) 1.829(7) Å]. The phosphane site in **8** is in a tetrahedral environment and presumably cationic in nature. It is also observed that an unusual anionic $CoBr_3^-$ moiety is attached to the free nitrogen site of the imidazole moiety. Alternatively this can be viewed as a coordination of the imidazole unit with Co^{II}. The Co(3)–N(2) bond length is 2.041(5) Å, an indication of a genuine covalent bond yet a dative one. Although several complexes with an anionic $CoBr_3^-$ moiety attached to a pyridine moiety are known, to the best of our knowledge this is the first example of a metal-containing species in which the benzimidazole is attached to a $CoBr_3^-$ moiety. This cobalt atom is in a pseudo-tetrahedral environment and the nitrogen atom attached to the $CoBr_3^-$ moiety is in a trigonal environment and presumably anionic in nature. In a sense, complex **8** is a unique variation of a metal-containing zwitterion. Normally, zwitterions are polar with a high solubility in polar solvents. Nevertheless, **8** is soluble in organic solvents mainly due to its multiple organic substituents. For comparison, the reaction of benzyl bromide with an equimolar amount of triphenylphosphane and 1-methyl-1*H*-benzo[*d*]-imidazole was carried out in a one-pot reaction. Analysis of the products revealed that the attack of benzyl bromide on triphenylphosphane and 1-methyl-1*H*-benzo[*d*]imidazole occurs in a ratio of 89:11. This indicates that the phosphane site is more vulnerable towards electrophilic attack by benzyl bromide than the benzimidazole moiety.

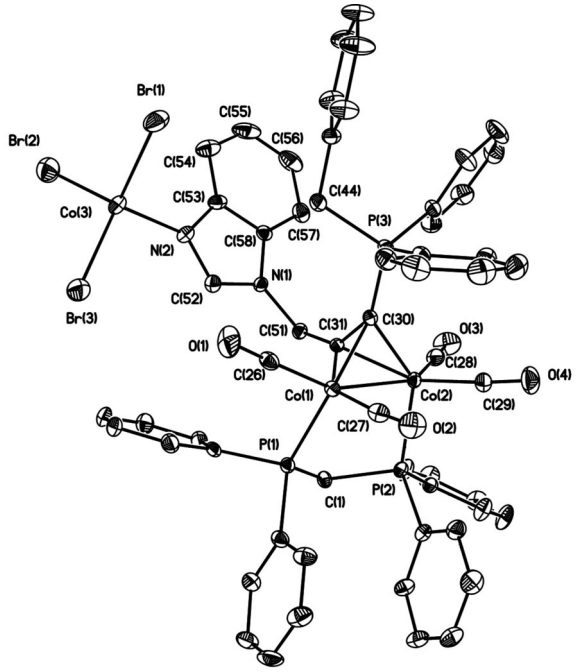
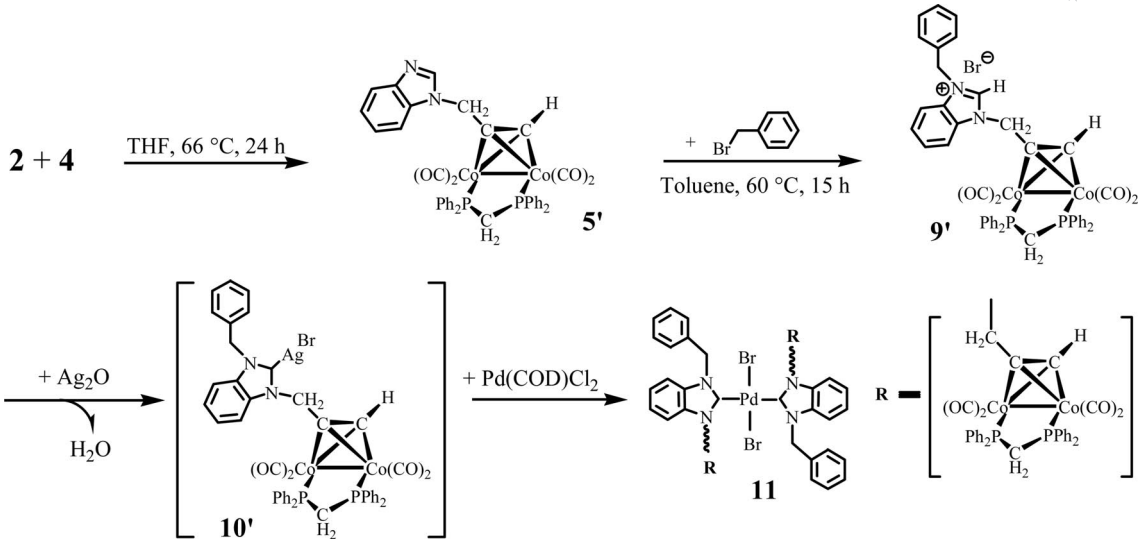


Figure 3. ORTEP drawing of **8**. Hydrogen atoms have been omitted for clarity.

In principle, the reaction path leading to the formation of an **8**-like compound should be blocked whereas the route for the attack of benzyl bromide on the phosphane site of a **5**-like compound is not available. This speculation was confirmed by the reaction of benzyl bromide with [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-$HC{\equiv}CCH_2$(IM)}] (**5′**; IM = 1*H*-benzimidazole) in which the PPh_2 unit of **5** is replaced by an inert H in **5′**. Complex **5'** was prepared by the procedure shown in Scheme 2. The reaction of **5′** with benzyl bromide indeed yielded a **9**-like compound, [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-$HC{\equiv}CCH_2$(IM′)}$^+$]Br^- (**9′**; IM′ = 3-benzyl-1*H*-benzimidazole). Subsequent treatment of **9′** with Ag_2O yielded the presumed carbene precursor [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-$HC{\equiv}CCH_2$(IM′)}]-[AgBr] (**10′**).[10a,15] The role of **10′** as carbene precursor was shown by the formation of the palladium complex [*trans*-({(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-$HC{\equiv}CCH_2$(IM′)})$_2$-



Scheme 2.

$PdBr_2$] (**11**) on treatment with [Pd(cod)Cl_2]. Interestingly, the solubility of **11** is poor in commonly used solvents such as toluene, CH_2Cl_2 and DMSO but good in THF.

The identity of complex **11** was first characterized by spectroscopic means and its structure determined further by single-crystal X-ray diffraction methods. In the ^{31}P NMR spectrum, only one singlet signal at 41.5 ppm was observed, which corresponds to the cobalt-coordinated dppm. The existence of the acetylenic proton is evidenced by the multiplet signal at δ = 6.61 ppm in the ^1H NMR spectrum. As revealed in the ORTEP diagram depicted in Figure 4, the Pd^{II} is centred in a square-planar environment. The two bulky carbene ligands are arranged in *trans* positions to keep them separated. The Pd(3)–C(52) bond length is 2.020(4) Å, a genuine dative bond. Interestingly, two bromides rather than chlorides are observed in **11**; it is believed that the chlorides were replaced by the excess bromide released during the formation of **11** because the formation of the side-product AgCl is thermodynamically more favourable than the formation of AgBr.

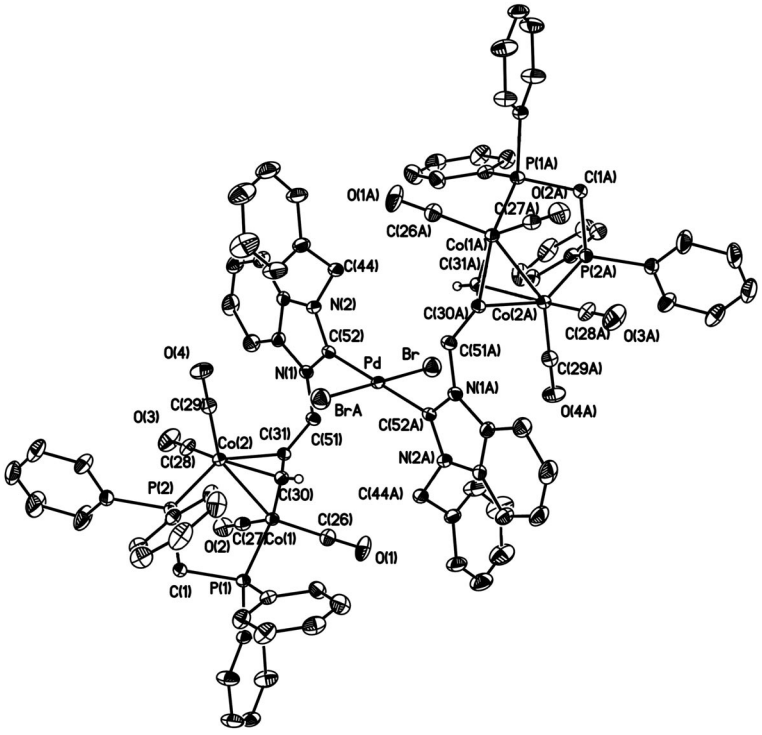
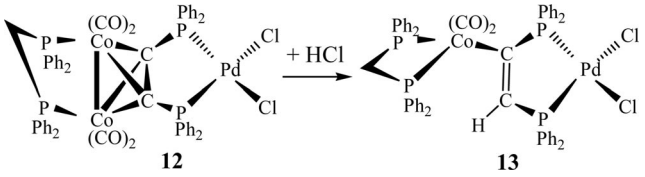


Figure 4. ORTEP drawing of **11**. Hydrogen atoms have been omitted for clarity.

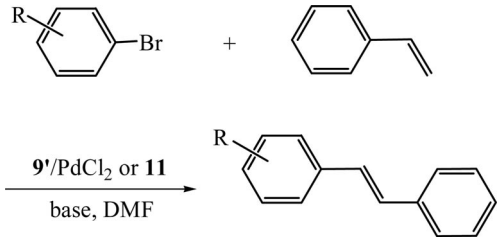
Until now, the reaction pathway for the formation of the unexpected **8** remained to be ascertained. The most perplexing question that might be raised is the source of the $CoBr_3^-$ moiety. In principle, one of the probable ways to obtain the $CoBr_3^-$ moiety is from the reaction of the bromide released from benzyl bromide with the Co_2C_2 framework. Interestingly, our previous work revealed some clues about the depletion of the cobalt atom from the Co_2C_2 skeleton. The novel palladium complex *cis*-dichlorido[1,2-bis(diphenylphosphanyl)vinyl-*P*,*P*′,*C*]palladium(II)-[bis(diphenylphosphanyl)methane-*P*,*P*′]cobaltacarbonyl (**13**) was obtained from the treatment of [{(μ-$Ph_2PCH_2PPh_2$)$Co_2(CO)_4$}-{($Ph_2PC{\equiv}CPPh_2$)$PdCl_2$}] (**12**) with hydrochloric acid (Scheme 3). The complex **13** was characterized by spectroscopic means as well as by single-crystal X-ray diffraction methods.[16] There are several unique features about this reaction. First, the dicobalt framework fragmented into a mono-cobalt moiety. Secondly, the bonding mode of the dppm ligand changed from bridging to chelating. Thirdly, one of the acetylenic carbon atoms became protonated. Fourthly, the palladium environment remained almost intact. Fifthly, the effective atomic number (EAN) rule was obeyed at the cobalt centre. Based on our previous work, it is assumed that the cobalt of the unusual anionic $CoBr_3^-$ moiety, which attaches to the free nitrogen site of the imidazole moiety, might derive from the depletion of dicobalt fragment by the addition of bromide.



Scheme 3.

Application of 11 or In Situ 9′/$PdCl_2$ (2:1) as a Catalyst Precursor in the Heck Reaction

As has been demonstrated, the catalytic performance of a palladium-catalysed cross-coupling reaction is determined by various influences such as the type of ligand and palladium salt employed, the ratio of ligand/palladium, the temperature, solvent, and base.[17] In principle, excellent efficiency only comes with the optimization of the most influential factors involved. Normally Heck reactions require more severe reaction conditions than Suzuki reactions.[18] Therefore it seems appropriate to employ **11** or in situ **9′**/$PdCl_2$ (2:1) as catalyst precursor in Heck reactions as this system has been proven to be more endurable at high reaction temperatures. The Heck reactions of substituted bromobenzenes with styrene were carried out at elevated temperature (Scheme 4). Because a high temperature is required, DMF, a high boiling-point solvent, was selected as the reaction media. For comparison of the catalytic efficiency with the published work of Hayashi and coworkers,[19] a similar procedure was used for the catalytic reactions under investigation. A suitable Schlenk tube was charged with 1.0 mmol of substituted bromobenzene, 1.0 mmol of styrene, 1.0 mL of DMF, 2.0 mmol of base, 1.0 mol-% of $PdCl_2$ and 1.0 mol-% of **11** (or in situ **9′**/$PdCl_2$ (2:1)) as catalyst precursor. The mixture was stirred at the designated reaction temperature and time depending on the reaction executed. The mixture was then worked up. Owing to steric hindrance, the *trans* form dominated over the *cis* form as the major product.



Scheme 4. Heck reaction catalysed by **11** or in situ **9′/**$PdCl_2$ (2:1).

As has been demonstrated, the type of base employed in Heck reactions is crucial to the catalytic efficiency.[20] It is also the most unpredictable ingredient among all the factors that affect the catalytic performance.[17b,21] The influence of the bases used in the Heck reactions catalysed by **11** or in situ **9′**/$PdCl_2$ (2:1) was examined (Table 1). As shown, acceptable results were obtained with K_2CO_3 or NaOAc as the base (entries 1 and 2). Quite a poor performance was observed by using Cs_2CO_3 as the base (entry 3). The catalytic performance was also poor when the heterocyclic compound 2-bromothiophene was used as the substrate; only 32% yield was observed under the same reaction conditions as used in entry 1. Similar catalytic efficiencies were obtained by employing purified **11** as the catalyst precursor (entries 6–8). This implies that the in situ addition of 2 molequiv. of **9′** to $PdCl_2$ yields **11** quantitatively.

Table 1. Heck reactions of bromobenzenes with styrene catalysed by **11** or in situ **9′/**$PdCl_2$ (2:1) employing various substituents, bases and reaction hours.[a]

Entry	Catalyst precursor	R	Base	Time [h]	Yield [%][b]
1	**9′**/$PdCl_2$ (2:1)	4-OMe	K_2CO_3	24	88 (74)
2	**9′**/$PdCl_2$ (2:1)	4-OMe	NaOAc	24	87 (79)
3	**9′**/$PdCl_2$ (2:1)	4-OMe	Cs_2CO_3	24	30 (24)
4	**9′**/$PdCl_2$ (2:1)	4-CHO	K_2CO_3	16	– (71)
5	**9′**/$PdCl_2$ (2:1)	H	K_2CO_3	24	– (85)
6	**11**	4-OMe	K_2CO_3	24	– (80)
7	**11**	4-CHO	K_2CO_3	24	<99 (81)
8	**11**	H	K_2CO_3	24	– (90)

[a] Reactions were conducted in DMF (1.0 mL) with base (2.0 equiv.) at 120 °C for the indicated time employing 1.0 mmol-% of **11** or in situ **9′**/$PdCl_2$ (2.0 mmol/1.0 mmol). [b] Conversion. Isolated yield given in parentheses as an average of two runs.

Conclusion

We have developed a general route for the preparation of some interesting cobalt-containing mono- or bidentate ligands with NHC- and/or P-coordinating sites. The appli-

cation of the monodentate ligand **9′** in Heck reactions gave reasonable efficiencies at an elevated temperature. The formation of an unexpected cobalt-containing zwitterionic complex **8** was observed and characterized.

Experimental Section

General: All operations were performed in a nitrogen-flushed glove box or in a vacuum system. Freshly distilled solvents were used. All product separations were performed by centrifugal thin-layer chromatography (CTLC, Chromatotron, Harrison model 8924) or by column chromatography. Most of the ^{1}H NMR spectra were recorded with a 300 MHz Varian VXR-300S spectrometer. In addition, some routine ^{1}H NMR spectra were recorded either with a Gemini-200 spectrometer at 200.00 MHz or a Varian-400 spectrometer at 400.00 MHz. The chemical shifts are reported in ppm relative to $CHCl_3$ (δ = 7.26 ppm), CH_2Cl_2 (δ = 5.30 ppm) or $CH_3C(=O)CH_3$ (δ = 2.09 ppm) as internal standards. ^{31}P and ^{13}C NMR spectra were recorded at 121.44 and 75.46 MHz, respectively. The ^{31}P and ^{13}C NMR chemical shifts are reported in ppm relative to H_3PO_4 (δ = 0.0 ppm) and $CHCl_3$ (δ = 77 ppm) or CH_2Cl_2 (δ = 53 ppm), respectively, as internal standards. Mass spectra were recorded with a JEOL JMS-SX/SX 102A GC/MS/MS spectrometer. Elemental analyses were performed with a Heraeus CHN-O-S-Rapid instrument.

Synthesis and Characterization of 1-Prop-2-ynyl-1*H*-benzimidazole (2): A 100 mL round-bottomed flask equipped with a magnetic stirring bar was charged with 1*H*-benzimidazole (3.307 g, 28.00 mmol), NaOH (1.120 g, 28.00 mmol) and THF (30 mL). The resulting mixture was then stirred at 50 °C for 1 h before it was cooled to 25 °C. Subsequently, 3-bromopropyne (3.729 g, 30.80 mmol) was added and the solution was stirred for another 12 h. After filtration, the resulting solution was concentrated and the solvent removed under reduced pressure. The title compound, 1-(prop-2-ynyl)-1*H*-benzimidazole (**2**), was isolated in a yield of 85.0% (3.712 g, 23.80 mmol).

Selected Spectroscopic Data for 2: ^{1}H NMR ($CDCl_3$): δ = 8.03 (s, 1 H, NCHN), 4.93 (s, 2 H, $NCH_2C{\equiv}CH$), 2.50 (s, 1 H, C≡CH), 7.26–7.84 (m, 4 H, arene) ppm. ^{13}C NMR ($CDCl_3$): δ = 143.57 (NCHN), 141.97, 133.02, 122.86, 122.15, 120.09, 109.38, 75.74 ($NCH_2C{\equiv}CH$), 74.57 ($NCH_2C{\equiv}CH$), 34.12 ($NCH_2C{\equiv}CH$) ppm.

Synthesis and Characterization of 1-[3-(Diphenylphosphanyl)prop-2-ynyl]-1*H*-benzimidazole (3): The same sized round-bottomed flask equipped with a magnetic stirring bar was charged with 1-(prop-2-ynyl)-1*H*-benzimidazole (**2**; 0.234 g, 1.50 mmol) and THF (10 mL). The resulting mixture was then stirred at –78 °C before 1.1 equiv. of *n*BuLi (0.66 mL, 2.5 M in hexane) was slowly added. In a dry box, diphenylchlorophosphane (0.330 g, 1.50 mmol) was added to the solution. Subsequently, the mixture was stirred at 25 °C for another 24 h. Then the solvent was removed under reduced pressure and the title compound, 1-[(3-diphenylphosphanyl)prop-2-ynyl]-1*H*-benzimidazole (**3**), was isolated in a yield of 50.4% (0.275 g, 0.75 mmol).

Selected Spectroscopic Data for 3: ^{1}H NMR ($CDCl_3$): δ = 8.04 (s, 1 H, NCHN), 5.13 (s, 2 H, $NCH_2C{\equiv}C$), 7.30–7.85 (m, 14 H, arene) ppm. ^{13}C NMR ($CDCl_3$): δ = 143.79 (NCHN), 99.80–134.77, 87.93 ($NCH_2C{\equiv}CH$), 84.47 ($NCH_2C{\equiv}CH$), 35.68 ($NCH_2C{\equiv}CH$) ppm. ^{31}P NMR ($CDCl_3$): δ = –33.77 (s, 1 P, $C{\equiv}CPPh_2$) ppm.

Synthesis and Characterization of [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}-{μ,η-$Ph_2PC{\equiv}CCH_2$(IM)}] (5; IM = 1*H*-benzimidazole): A 100 mL round-bottomed flask was charged with $[Co_2(CO)_8]$ (1.00 mmol, 0.342 g), dppm (1.00 mmol, 0.385 g) and toluene (10 mL). The solution was stirred at 60 °C for 6 h to give the yellow compound $[Co_2(CO)_6$(μ-*P*,*P*-dppm)]. Without further separation, the reaction flask was charged with 1 equiv. of 1-[(3-diphenylphosphanyl)prop-2-ynyl]-1*H*-benzimidazole (**3**; 0.340 g, 1.00 mmol) in toluene (5 mL). Subsequently the solution was stirred at 66 °C for another 24 h before the solvent was removed under reduced pressure. The residue was further separated by CTLC. A reddish-brown band was eluted with CH_2Cl_2/ethyl acetate (10:1) and was identified as the title compound **5** in 60.0% yield (0.60 mmol, 0.570 g).

Selected Spectroscopic Data for 5: ^{1}H NMR ($CDCl_3$): δ = 8.06 (s, 1 H, NCHN), 5.49 (s, 2 H, $NCH_2C{\equiv}C$), 3.35 (q, 1 H, dppm), 3.93 (s, 1 H, dppm), 6.97–7.82 (m, 34 H, arene) ppm. ^{13}C NMR ($CDCl_3$): δ = 204.44 (CO), 202.89 (CO), 143.30 (NCHN), 128.26–138.90, 122.36, 121.65, 120.73, 120.23, 109.84, 49.68 ($NCH_2C{\equiv}C$), 35.89 (dppm) ppm. ^{31}P NMR ($CDCl_3$): δ = –3.28 (s, 1 P, PPh_2), 38.98 (s, 2 P, dppm) ppm. $C_{52}H_{40}Co_2N_2O_5P_3$ (983.63): calcd. C 64.16, H 4.12, N 2.93; found C 60.05, H 4.23, N 2.24.

Reaction of 5 with Bromomethylbenzene: Compound **5** (0.955 g, 1.00 mmol) was placed in a 100 mL round-bottomed flask with bromomethylbenzene (1.10 mmol, 0.185 g) and THF (5 mL). The solution was stirred at 50 °C for 15 h. After filtration, the residue was washed with THF (10 mL) and diethyl ether (10 mL) before it was dried under reduced pressure. [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}-{μ,η-(R1)$PC{\equiv}CCH_2$(R2)}] (**8**; R1 = Ph_2Bz; R2: 3-$CoBr_3$-1*H*-benzimidazole) was isolated in a yield of 23% (0.320 g, 0.23 mmol).

Selected Spectroscopic Data for 8: ^{1}H NMR ($CDCl_3$): δ = 6.26 (s, 2 H, $NCH_2C{\equiv}C$), 6.18 (d, $J_{P\text{-}H}$ = 6.8 Hz, 2 H, $PCH_2C_6H_5$), 4.38 (q, 1 H, dppm), 3.78 (q, 1 H, dppm), 6.97–7.82 (m, 34 H, arene) ppm. ^{13}C NMR (CD_3OD): δ = 203.82 (CO), 199.63 (CO), 59.04, 58.02 ppm. ^{31}P NMR ($CDCl_3$): δ = 30.52 (s, 1 P, PCH_2Ph-$(Ph)_2$), 36.85 (s, 2 P, dppm) ppm. $C_{58}H_{46}Br_3Co_3N_2O_4P_3$ (1344.40): calcd. C 51.85, H 3.38, N 2.09; found C 53.43, H 4.35, N 2.00.

Synthesis and Characterization of [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}-{μ,η-$HC{\equiv}CCH_2$(IM)}] (5′; IM = 1*H*-Benzimidazole): A 100 mL round-bottomed flask equipped with a magnetic stirring bar was charged with $[Co_2(CO)_8]$ (1.00 mmol, 0.342 g), dppm (1.00 mmol, 0.385 g) and THF (10 mL). The solution was stirred at 60 °C for 6 h to give the yellow compound $[Co_2(CO)_6$(μ-*P*,*P*-dppm)] (**4**). Without further separation, the reaction flask was charged again with 1 mol equiv. of 1-prop-2-ynyl-1*H*-benzimidazole (**2**; 0.156 g, 1.00 mmol) in THF (5 mL). Subsequently, the solution was stirred at 66 °C for another 16 h before the solvent was removed under reduced pressure. The residue was further separated by CTLC. A red band eluted with CH_2Cl_2/ethyl acetate (3:1) was identified as the title compound **5′** in 75.0% yield (0.75 mmol, 0.557 g).

Selected Spectroscopic Data for 5′: ^{1}H NMR ($CDCl_3$): δ = 8.13 (s, 1 H, NCHN), 5.51 (s, 2 H, $NCH_2C{\equiv}C$), 5.58 (s, 1 H, C≡CH), 7.60 (s, 1 H, C_6H_4), 7.79 (s, 1 H, C_6H_4), 3.03 (m, 1 H, dppm), 3.57 (m, 1 H, dppm), 7.13–7.34 (m, 22 H, arene) ppm. ^{13}C NMR ($CDCl_3$): δ = 206.02 (CO), 202.40 (CO), 143.02 (NCHN), 137.58–135.50, 122.57, 121.60, 120.22, 110.04 (arene), 96.03, 72.99 ($C{\equiv}CH$), 49.43 ($NCH_2C{\equiv}C$), 41.83 (dppm) ppm. ^{31}P NMR ($CDCl_3$): δ = 42.91 (s, 2 P, dppm) ppm. $C_{39}H_{30}Co_2N_2O_4P_2$ (770.48): calcd. C 60.80, H 3.92, N 3.04; found C 60.88, H 4.24, N 2.95.

Reaction of 5′ with Bromomethylbenzene: Compound **5′** (0.830 g, 1.00 mmol) was placed in a 100 mL round-bottomed flask with bromomethylbenzene (1.10 mmol, 0.185 g) and toluene (5 mL). The solution was stirred at 60 °C for 15 h. After filtration, the residue was washed with toluene (10 mL) and diethyl ether (10 mL)

before it was dried under reduced pressure. Dark-red [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-HC≡CCH_2(IM′)}$^+$]Br^- (**9′**; IM′: 3-benzyl-1*H*-benzimidazole) was isolated in a yield of 85.0% (0.851 g, 0.85 mmol).

Selected Spectroscopic Data for 9′: ^{1}H NMR ($CDCl_3$): δ = 11.19 (s, 1 H, NCHN), 7.86 (d, $J_{H,H}$ = 8.4 Hz, 1 H, C_6H_4), 5.77 (s, 2 H, $NCH_2C_6H_5$), 5.87 (s, 2 H, NCH_2C≡C), 5.96 (m, 1 H, C≡CH), 3.63 (m, 1 H, dppm), 3.05 (m, 1 H, dppm), 7.13–7.61 (m, 28 H, arene) ppm. ^{13}C NMR ($CDCl_3$): δ = 205.82 (CO), 201.69 (CO), 141.92 (NCHN), 126.54–135.96, 113.44, 75.15, 52.52 (s, 2 C, N*C*H_2C≡C), 51.68 (s, 2 C, N*C*$H_2C_6H_5$), 41.59 (s, 1 C, dppm) ppm. ^{31}P NMR ($CDCl_3$): δ = 42.91 (s, 2 P, dppm) ppm. $C_{46}H_{37}BrCo_2N_2O_4P_2$ (941.51): calcd. C 58.68, H 3.96, N 2.98; found C 58.43, H 3.92, N 2.63.

Conversion of 9′ into a Carbene-Type Ligand and Reaction with [Pd(cod)Cl_2]: A 100 mL round-bottomed flask was charged with **9′** (1.882 g, 2.00 mmol) and CH_2Cl_2 (15 mL). The flask was wrapped in aluminium foil to avoid exposure to light. Then Ag_2O (0.462 g, 2.00 mmol) was added and the solution was stirred at 25 °C for 12 h. The solution was then filtered through Celite and dried under reduced pressure. A reddish-brown residue, presumed to be [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-HC≡CCH_2(IM′)}][AgBr] (**10′**), was collected. Compound **10′** was treated with dichloro(1,5-cyclooctadiene)palladium (0.028 g, 0.10 mmol) in THF (15 mL) at 25 °C and stirred for 12 h before filtration through Celite and drying under reduced pressure. The bright-red residue, [*trans*-({(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-HC≡CCH_2(IM′)})$_2$$PdBr_2$] (**11**), was washed with CH_2Cl_2 (10 mL). The yield of **11** was 67% (1.334 g, 0.67 mmol). Bright-red crystals suitable for X-ray crystallographic studies were obtained from THF solution.

Selected Spectroscopic Data for 11: ^{1}H NMR (THF): δ = 7.83 (d, $J_{H,H}$ = 12.0 Hz, 2 H, C_6H_4), 6.28 (s, 4 H, $NCH_2C_6H_5$), 6.40 (s, 4 H, NCH_2C≡C), 6.61 (m, 2 H, C≡CH), 3.44 (m, 2 H, dppm), 3.26 (m, 2 H, dppm), 6.91–7.60 (m, 56 H, arene) ppm. ^{31}P NMR ($CDCl_3$): δ = 41.52 (s, 2 P, dppm) ppm. ^{13}C NMR ([D_8]THF): δ = 208.55 (CO), 203.13 (CO), 184.19 [NC(Pd)N], 123.07–138.57, 112.59, 112.07, 77.75, 54.25, 51.03 ppm. $C_{92}H_{72}Br_2Co_4N_4O_8P_4Pd$ (1987.43): calcd. C 53.25, H 3.58, N 3.11; found C 55.45, H 4.14, N 2.25.

Preparation of 5_O and 9_O: Compound **5** (0.954 g, 1.00 mmol) dissolved in THF (5 mL) was placed in a 100 mL round-bottomed flask and H_2O_2 (3 mL) was then slowly added. The solution was stirred at 25 °C for 3 h. After filtration, the bright-red residue was washed with ethyl acetate (30 mL) before it was dried under reduced pressure. [{(μ-$PPh_2CH_2PPh_2$)$Co_2(CO)_4$}{μ,η-Ph_2P(=O)-C≡CCH_2(IM)}] (**5_O**; IM = 1*H*-benzimidazole) was isolated in a yield of 95.0% (0.921 g, 0.95 mmol). Oxide **5_O** (0.921 g, 0.95 mmol) was treated with bromomethylbenzene (1.10 mmol, 0.185 g) in toluene (5 mL) at 60 °C and stirred for 15 h. After filtration, the bright-red residue was washed with toluene and diethyl ether before it was dried under reduced pressure. [{(μ-PPh_2-CH_2PPh_2)$Co_2(CO)_4$}{μ,η-Ph_2P(=O)C≡CCH_2(IM)}$^+$]Br^- (**9_O**; IM = 3-benzyl-1*H*-benzimidazole) was isolated in a yield of 85% (0.921 g, 0.85 mmol).

Selected Spectroscopic Data for 5_O: ^{1}H NMR ($CDCl_3$): δ = 8.10 (s, 1 H, NCHN), 7.86 (d, $J_{H,H}$ = 2.4 Hz, 1 H, C_6H_4), 5.65 (t, 2 H, NCH_2C≡C), 5.65 (m, 1 H, dppm), 3.20 (m, 1 H, dppm), 6.86–7.71 (m, 33 H, arene) ppm. ^{13}C NMR ($CDCl_3$): δ = 205.38 (CO), 200.27 (CO), 143.73 (NCHN), 127.82–138.00, 107.5, 122.61, 121.92, 120.49, 109.72, 50.63, 35.59 (t, 1 C, dppm) ppm. ^{31}P NMR ($CDCl_3$): δ = 27.99 [s, 1 P, P(=0)CH_2Ph(Ph)$_2$], 36.99 (s, 2 P, dppm) ppm.

Selected Spectroscopic Data for 9_O: ^{1}H NMR ($CDCl_3$): δ = 10.94 (s, 1 H, NCHN), 7.79 (m, 1 H, C_6H_4), 5.80 (s, 2 H, $NCH_2C_6H_5$), 6.32 (s, 2 H, NCH_2C≡C), 5.69 (m, 1 H, dppm), 3.22 (m, 1 H, dppm), 6.91–7.59 (m, 38 H, arene) ppm. ^{13}C NMR ($CDCl_3$): δ = 206.40 (CO), 199.18 (CO), 125.12–137.68, 113.55, 113.05, 75.07, 73.73, 54.83 (N*C*H_2C≡C), 54.06 (N*C*$H_2C_6H_5$), 35.52 (dppm) ppm. ^{31}P NMR ($CDCl_3$): δ = 28.07 [s, 1 P, PCH_2Ph(Ph)$_2$], 37.29 (s, 2 P, dppm) ppm. $C_{58}H_{46}BrCo_2N_2O_5P_3$ (1141.69): calcd. C 61.02, H 4.06, N 2.45; found C 61.13, H 4.05, N 2.49.

General Procedure for the Heck Reactions: Heck reactions were performed according to the following procedure. Reactants including

Table 2. Crystal data for **5_O**, **8** and **11**.

Compound	**5_O**	**8**	**11**
Formula	$C_{52}H_{40}Co_2N_2O_6P_3$	$C_{58}H_{46}Br_3Co_3N_2O_4P_3$	$C_{92}H_{72}Br_2Co_4N_4O_8P_4Pd{\cdot}2CH_2Cl_2$
Formula mass	999.63	1344.40	2157.21
Crystal system	monoclinic	orthorhombic	monoclinic
Space group	*C*2/*c*	*Pbca*	P_{21}/c
a [Å]	28.128(4)	18.187(5)	13.0513(9)
b [Å]	12.6177(18)	17.336(5)	17.9369(13)
c [Å]	29.079(4)	35.433(10)	20.3915(14)
α [°]	90	90	90
β [°]	101.008(3)	90	104.0760(10)
γ [°]	90	90	90
V [Å^3]	10131(2)	11172(5)	4630.3(6)
Z	8	8	2
D_c [Mg/m^3]	1.311	1.599	1.547
λ(Mo-$K_α$) [Å]	0.71073	0.71073	0.71073
μ [mm^{-1}]	0.798	3.160	1.996
θ range [°]	1.43–26.02	1.72–26.07	1.97–26.03
Observed reflections [$F>4\sigma(F)$]	9938	11001	9095
No. of refined parameters	586	667	547
R_1 for significant reflections[a]	0.0778	0.0610	0.0558
wR_2 for significant reflections[b]	0.2563	0.1727	0.2040
GoF[c]	1.024	1.118	1.006

[a] $R_1 = |\Sigma(|F_o| - |F_c|)/|\Sigma F_o||$. [b] $wR_2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{1/2}$ with w = 0.1300, 0.1000 and 0.1850 for the crystal data of **5_O**, **8** and **11**, respectively. [c] GoF = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{rflns} - N_{params})]^{1/2}$.

palladium(II) chloride (1.7 mg, 0.01 mmol), **9′** (18.8 mg, 0.02 mmol) and a base (2.0 mmol) were placed in a 20 mL Schlenk flask. The flask was evacuated and back-filled with nitrogen before adding DMF (1.0 mL), the aryl bromide (1.0 mmol) and styrene (0.114 mL, 1.0 mmol). The solution was stirred at the designated temperature and time. Subsequently the mixture was filtered and concentrated in vacuo. The crude material was purified by CTLC on silica gel. A similar procedure was applied in the case of catalyst precursor **11** (19.91 mg, 0.01 mmol).

X-ray Crystallographic Studies: Suitable crystals of **5_O**, **8** and **11** were sealed in thin-walled glass capillaries under nitrogen and mounted on a Bruker AXS SMART 1000 diffractometer. Intensity data were collected in 1350 frames with increasing ω (width of 0.3° per frame). The space groups were determined on the basis of the Laue symmetries and systematic absences, and confirmed by using structure solution methods. The structures were solved by direct methods using the SHELXTL package.[22] All non-hydrogen atoms were located from successive Fourier maps and hydrogen atoms were refined by using the riding model. Anisotropic thermal parameters were used for all non-hydrogen atoms and fixed isotropic parameters were used for hydrogen atoms. The crystallographic data for **5_O**, **8** and **11** are summarized in Table 2.

CCDC-708000 (for **5_O**), -708001 (for **8**) and -708002 (for **11**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see also the footnote on the first page of this article): Spectroscopic data such as ^{1}H, ^{13}C, ^{31}P NMR, and mass spectra of **5**, **8**, **9′**, **9_O** and **11**.

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