1,3-Dialkyl- and 1,3-Diaryl-3,4,5,6-tetrahydropyrimidin-2-ylidene Rhodium(I) and Palladium(II) Complexes: Synthesis, Structure, and Reactivity

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Abstract: The synthesis of novel 1,3-diaryl- and 1,3-dialkylpyrimidin-2-ylidene-based N-heterocyclic carbenes (NHCs) and their rhodium(I) and palladium(II) complexes is described. The rhodium compounds bromo(cod)[1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene]rhodium (**7**), bromo(cod)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)rhodium (**8**) (cod = η^4-1,5-cyclooctadiene, mesityl = 2,4,6-trimethylphenyl), chloro(cod)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)rhodium (**9**), and chloro(cod)[1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene]rhodium (**10**) were prepared by reaction of [{Rh(cod)Cl}$_2$] with lithium *tert*-butoxide followed by addition of 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium bromide (**3**), 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate (**4**), 1,3-di-2-propyl-3,4,5,6-tetrahydropyrimidinium bromide (**6**), and 1,3-di-2-propyl-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate, respectively. Complex **7** crystallizes in the monoclinic space group $P2_1/n$, and **8** in the monoclinic space group $P2_1$. Complexes **9** and **10** were used for the synthesis of the corresponding dicarbonyl complexes dicarbonylchloro(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)-rhodium (**11**), and dicarbonylchloro[1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene]rhodium (**12**). The wavenumbers ν(CO I)/ν(CO II) for **11** and **12** were used as a quantitative measure for the basicity of the NHC ligand. The values of 2062/1976 and 2063/1982 cm^{-1}, respectively, indicate that the new NHCs are among the most basic cyclic ligands reported so far. Compounds **3** and **6** were additionally converted to the corresponding cationic silver(I) bis-NHC complexes [Ag(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2$]AgBr$_2$ (**13**) and [Ag{1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene}$_2$]AgBr$_2$ (**14**), which were subsequently used in transmetalation reactions for the synthesis of the corresponding palladium(II) complexes Pd(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2^{2+}$(Ag_2Br_2-Cl_4^{4-})$_{1/2}$ (**15**) and Pd[1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2$]-Cl_2 (**16**). Complex **15** crystallizes in the monoclinic space group $P2_1/c$, and **16** in the monoclinic space group C_2/c. The catalytic activity of **15** and **16** in Heck-type reactions was studied in detail. Both compounds are highly active in the coupling of aliphatic and aromatic vinyl compounds with aryl bromides and chlorides with turnover numbers (TONs) up to 2000000. Stabilities of **15** and **16** under Heck-couplings conditions were correlated with their molecular structure. Finally, selected kinetic data for these couplings are presented.

Keywords: C–C coupling · carbene ligands · homogeneous catalysis · palladium · rhodium

Introduction

The discovery of transition-metal complexes of N-heterocyclic carbenes (NHCs) by Öfele[1] and Wanzlick and Schönherr[2,3] in the 1960s, as well as the isolation of stable free carbenes by Arduengo et al.[4,5] in the early 1990s, initiated intense research in this area of chemistry. The corresponding metal complexes turned out to have interesting structural features, and NHCs were found to be highly basic[6], air- and moisture-stable substitutes[5] for phosphanes. In addition, the resulting metal complexes usually display better stability to air and moisture than the corresponding phosphane analogues. The work of Herrmann et al. and others almost revolutionized the area of catalysis by transition-metal complexes, in particular C–C bond-forming reactions such as Heck, Suzuki, and metathesis reactions.[7–14] The finding that NHCs based on saturated dihydroimidazol-2-ylidenes[15–17]

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rather than on unsaturated imidazol-2-ylidenes[11,18–22] even increased the catalytic activity of ruthenium-based metathesis catalysts suggests searching for even more basic NHCs. Recently, Herrmann et al. reported on an acyclic bis(di-2-propylamino)carbene, originally synthesized by Alder et al.,[23,24] and its ligand properties. This NHC proved to be the most basic so far reported.[25] Encouraged by these findings, by some excellent theoretical work[4,21,26,27] and by reports on the increased activity of metal complexes containing saturated imidazolylidenes,[15–17] we focused on NHCs other than 1,3-R_2-dihydroimidazol-2-ylidenes and elaborated a synthetic concept for the synthesis of new 1,3-diaryl- and 1,3-dialkyl-3,4,5,6-tetrahydropyrimidin-2-ylidenes. Here we report on their synthesis, ligand properties, and the synthesis of rhodium(I) and palladium(II) complexes. The latter were investigated for their catalytic activity in homogeneous Heck-type coupling reactions.

Results and Discussion

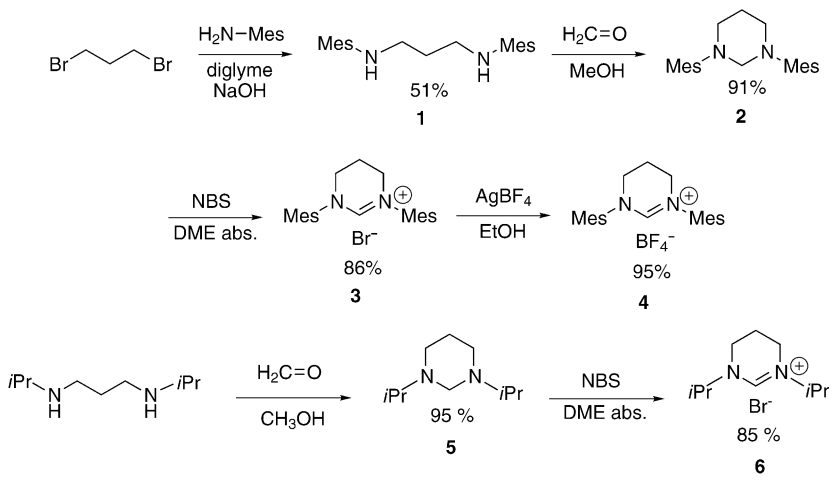
Synthesis of 1,3-dialkyl- and 1,3-diaryl-3,4,5,6-tetrahydropyrimidinium salts 1–6: 1,3-Dimesitylhexahydropyrimidine (**2**) was prepared by amination of 1,3-dibromopropane to yield 1,3-dimesitylaminopropane (**1**) followed by cyclization with aqueous formaldehyde. The corresponding NHC precursor 1,3-dimesityl-3,4,5,6-tetrahydropyrimidinium bromide (**3**) was accessible by reaction of **2** with *N*-bromosuccinimide (NBS).[28] Compound **3** was finally converted to the corresponding tetrafluoroborate **4** by treatment with $AgBF_4$ (Scheme 1). In analogy, 1,3-bis(2-propyl)hexahydropyrimidine (**5**) was prepared from 1,3-bis(2-propylamino)propane[23] and was finally subjected to cyclization to yield **6** (Scheme 1).

Synthesis of rhodium(I) complexes 7–12: The first Rh NHC complexes were reported by Herrmann et al.[10,29] Here, treatment of $[\{Rh(cod)Cl\}_2]$ (cod = cyclooctadiene) with a base (lithium *tert*-butoxide) followed by addition of **3** resulted in the formation of [RhBr(NHC)(cod)] (**8**) (NHC = 1,3-dimesityltetrahydropyrimidin-2-ylidene) in 73% yield. Analogously, the corresponding rhodium chloro complex [RhCl(NHC)(cod)] (**9**) was accessible from **4** in 74% yield (Scheme 2). Though sterically far less demanding, the NHC generated from **6** still allows the synthesis of mono-carbene complex [RhBr(NHC)(cod)] (**7**) (NHC = 1,3-bis(2-propyl)tetrahydropyrimidin-2-ylidene) in 84% yield. This is in accordance with findings by Herrmann et al., who were able to synthesize both the mono- and bis-NHC complexes of Rh^I using NHCs with low steric demand such as 1,3-dimethylimidazoline-2-ylidene.[10] Using 1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidinium tetrafluoroborate results in the formation of [RhCl(NHC)(cod)] (**10**) in 71% yield (Scheme 2). Though the above-described protocol was preferred, we note that treatment of **3** and **4** with lithium *tert*-butoxide at room temperature generates the corresponding free carbenes. Under these conditions, 3,4,5,6-tetrahydropyrimidin-2-ylidenes were sufficiently stable to allow the formation of the desired Rh complexes on addition of $[\{Rh(cod)Cl\}_2]$ at 50 °C in yields similar to those obtained with the other route. These findings may have implications for the synthesis of other metal complexes that do not tolerate the presence of a base.

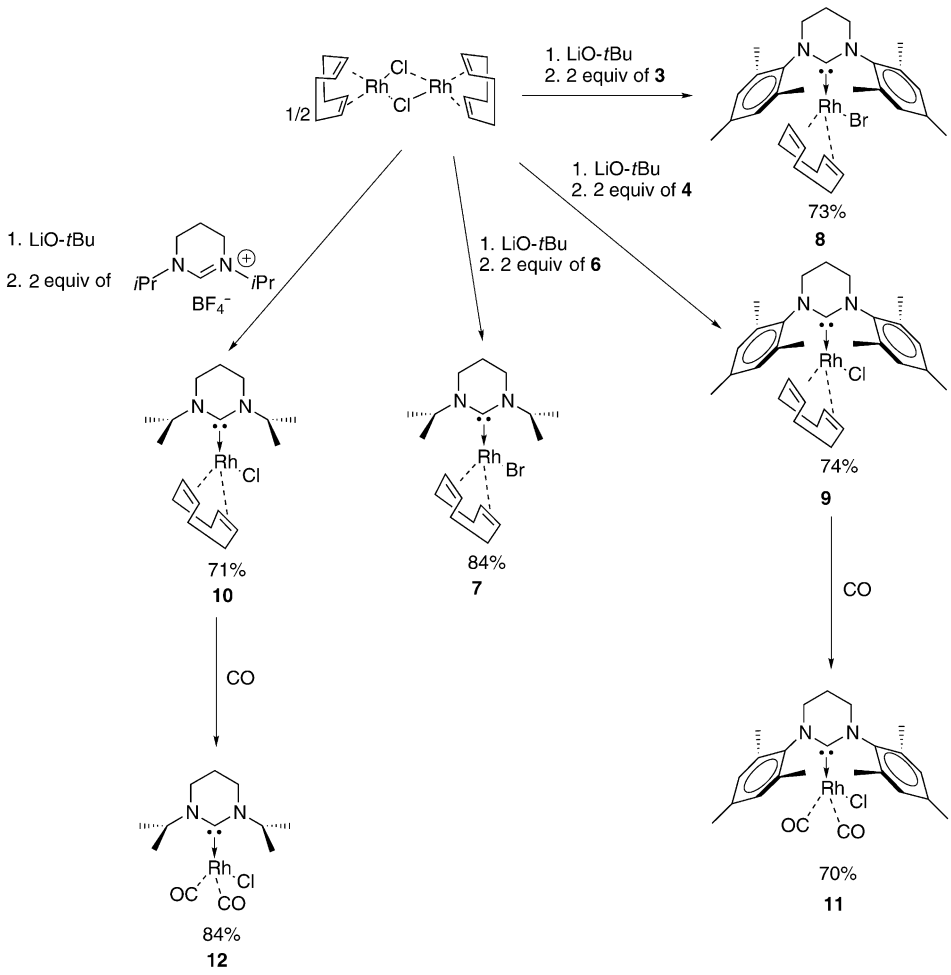
Crystals of **7** and **8** suitable for X-ray diffraction were obtained. The structures are shown in Figures 1 and 2. Complex **7** crystallizes as a mixture of Br and Cl complexes (0.6:0.4) in the monoclinic space group $P2_1/n$, $a = 1488.72(3)$, $b = 1410.67(2)$, $c = 1620.10(2)$ pm, $\alpha = 90$, $\beta = 116.946(2)$, $\gamma = 90°$, $Z = 4$. Crystallographic data and parameters are summarized in Table 1.

The $Rh{-}C_{NHC}$ distance (Rh(1)–C(9)) is 208.96(18) pm. This is longer than in [RhCl(NHC)(cod)] (NHC = 1,3-dimethylimidiazolin-2-ylidene), in which the Rh–C distance is 202.3(2) pm. The shortest distances of the cod ligand to rhodium were found to be 210.32(19) and 213.0(2) pm, respectively, for Rh(1)–C(1) and Rh(1)–C(2), respectively. Compound **8** crystallizes in the monoclinic space group $P2_1$, $a = 970.11(2)$ pm, $b = 1165.89(3)$ pm, $c = 1027.55(3)$ pm, $\alpha = 90°$, $\beta = 101.641(2)$, $\gamma = 90°$, $Z = 2$ (Table 1). The rhodium–C_{NHC} distance (Rh(1)–C(9)) of 204.7(3) pm is significantly shorter than that in **7**. The shortest distances between the cod ligand and rhodium (Rh(1)–C(2) 210.3(3), Rh(1)–C(1) 211.5(3) pm) are comparable to those in **7**. Selected distances and angles are given in Tables 2 and 3.

The significant difference in the $Rh{-}C_{NHC}$ distances is indicative of different basicities of the two ligands, though steric effects can neither be excluded nor quantified. To compare these two new NHCs with other known NHCs, the Rh^I NHC carbonyl complexes **11** and **12** were synthesized in 70 and 84% yield, respectively, by



Scheme 1. Synthesis of **1**–**6**. diglyme = diethyleneglycol dimethyl ether.



Scheme 2. Synthesis of Rh complexes **7**–**12**.

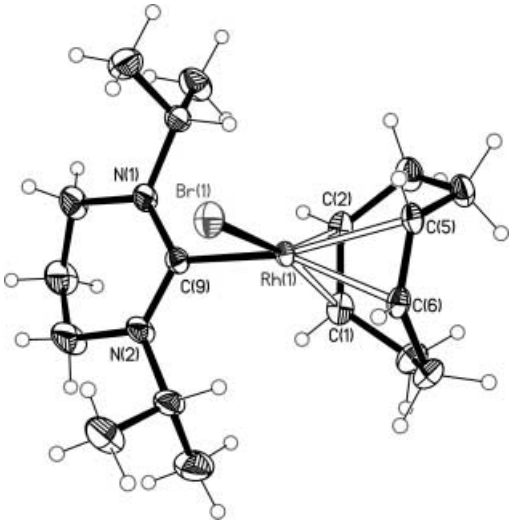


Figure 1. X-ray structure of **7**.

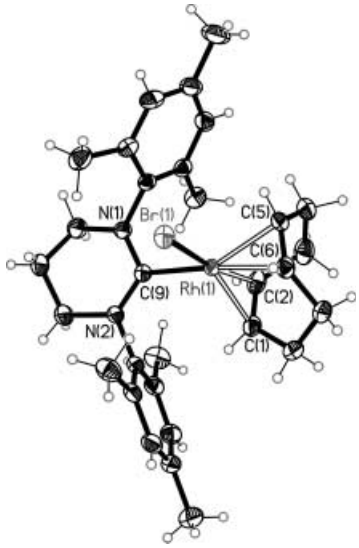


Figure 2. X-ray structure of **8**.

bubbling CO through a solution of **9** and **10** in THF/toluene (Scheme 2). The ν(CO I) and ν(CO II) values of Rh carbonyl complexes are an excellent measure for the basicity of a ligand.[25] The more basic the ligand, the more pronounced is σ donation to the metal center, and this results in lower values for both ν(CO I) and ν(CO II). The Rh carbonyl complexes **12** and particularly **11** show low values for both ν(CO I) and ν(CO II) and have the lowest values for ν(CO II) ever reported for Rh carbonyl complexes of gener-

Table 1. Crystal data and structure refinement for **7** and **8**.

	7	**8**
formula	$C_{30}H_{40}Br_{0.6}Cl_{0.4}N_2Rh{\cdot}CH_2Cl_2$	$C_{18}H_{32}BrN_2Rh{\cdot}CH_2Cl_2$
M_r	678.60	544.20
crystal system	monoclinic	monoclinic
space group	$P2_1/n$ (No. 14)	$P2_1$ (No. 4)
a [pm]	1488.72(3)	970.11(2)
b [pm]	1410.67(2)	1165.89(3)
c [pm]	1620.10(2)	1027.55(3)
α [°]	90	90
β [°]	116.946(2)	101.641(2)
γ [°]	90	90
V [nm^3]	3.03298(8)	1.13830(5)
Z	4	2
T [K]	233(2)	233(2)
ρ_{calcd} [Mg m^{-3}]	1.486	1.588
μ [mm^{-1}]	1.588	2.745
color, habit	orange prism	yellow prism
no. of rflns with $I>2\sigma(I)$	5264	4300
GOF on F^2	1.024	1.064
R indices ($I>2\sigma(I)$)	$R_1=0.0230$	$R_1=0.0215$
	$wR_2=0.0554$	$wR^2=0.0514$

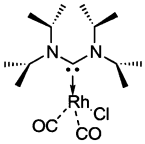
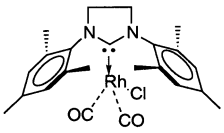
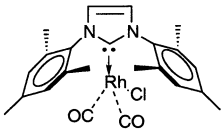
Table 2. Bond lengths [pm] and angles [°] for **7**.

Rh(1)–C(9)	208.96(18)	Rh(1)–C(1)	210.32(19)	Rh(1)–C(2)	213.0(2)
Rh(1)–C(5)	216.15(19)	Rh(1)–C(6)	222.92(19)	Rh(1)–Br(1)	249.99(3)
Rh(1)–Cl(1)	249.99(3)	N(1)–C(9)	134.6(2)	N(2)–C(9)	134.9(2)
C(9)-Rh(1)-C(1)	100.07(7)	C(9)-Rh(1)-C(2)	95.50(8)	C(1)-Rh(1)-C(2)	38.40(9)
C(9)-Rh(1)-C(5)	149.56(7)	C(1)-Rh(1)-C(5)	96.10(8)	C(2)-Rh(1)-C(5)	81.47(8)
C(9)-Rh(1)-C(6)	173.21(7)	C(1)-Rh(1)-C(6)	80.03(8)	C(2)-Rh(1)-C(6)	88.77(8)
C(5)-Rh(1)-C(6)	36.39(8)	C(9)-Rh(1)-Br(1)	90.73(5)	C(1)-Rh(1)-Br(1)	145.96(7)
C(2)-Rh(1)-Br(1)	171.31(6)	C(5)-Rh(1)-Br(1)	90.09(5)	C(6)-Rh(1)-Br(1)	85.61(5)
C(9)-N(1)-C(13)	122.20(15)	C(9)-N(1)-C(10)	123.38(16)	C(13)-N(1)-C(10)	114.36(15)
C(9)-N(2)-C(19)	122.44(15)	C(9)-N(2)-C(12)	125.90(16)	C(12)-N(2)-C(19)	111.60(15)
N(1)-C(9)-N(2)	115.30(16)				

Table 3. Bond lengths [pm] and angles [°] for **8**.

Rh(1)–C(9)	204.7(3)	Rh(1)–C(2)	210.3(3)	Rh(1)–C(1)	211.5(3)
Rh(1)–C(6)	219.7(3)	Rh(1)–C(5)	223.4(3)	Rh(1)–Br(1)	251.61(4)
N(1)–C(9)	135.4(4)	N(2)–C(9)	134.3(4)	C(9)-Rh(1)-C(2)	91.48(12)
C(9)-Rh(1)-C(1)	91.41(13)	C(2)-Rh(1)-C(1)	38.76(13)	C(9)-Rh(1)-C(6)	156.36(11)
C(2)-Rh(1)-C(6)	96.89(12)	C(1)-Rh(1)-C(6)	81.66(12)	C(9)-Rh(1)-C(5)	167.25(12)
C(2)-Rh(1)-C(5)	80.90(12)	C(1)-Rh(1)-C(5)	89.00(12)	C(6)-Rh(1)-C(5)	36.06(12)
C(9)-Rh(1)-Br(1)	89.62(9)	C(2)-Rh(1)-Br(1)	155.95(9)	C(1)-Rh(1)-Br(1)	165.22(10)
C(6)-Rh(1)-Br(1)	91.57(8)	C(5)-Rh(1)-Br(1)	93.23(8)	C(9)-N(1)-C(10)	122.8(3)
C(9)-N(1)-C(13)	120.1(2)	C(10)-N(1)-C(13)	116.5(3)	C(9)-N(2)-C(12)	123.8(3)
C(9)-N(2)-C(16)	119.3(3)	C(12)-N(2)-C(16)	116.5(3)	N(1)-C(9)-N(2)	117.6(3)

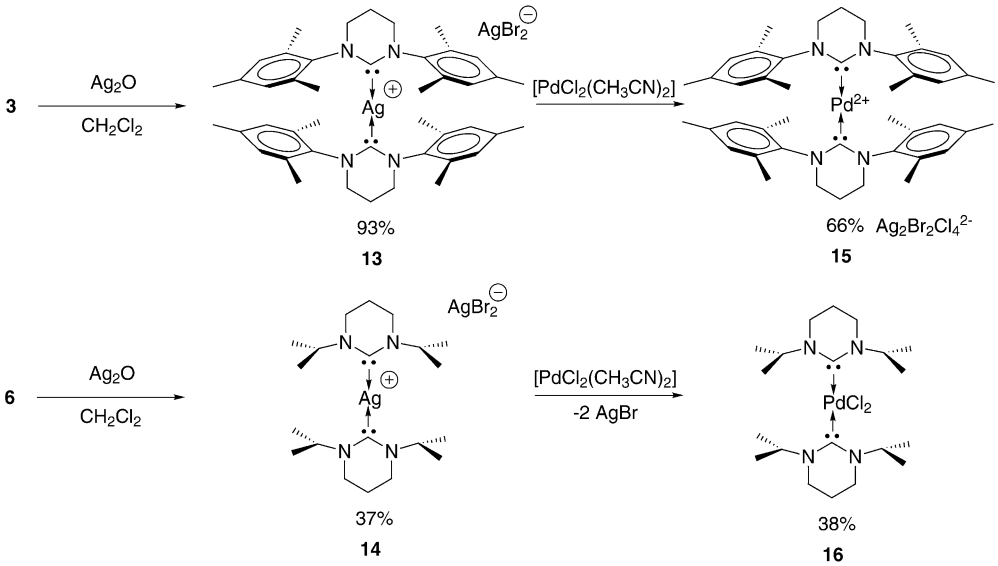
Table 4. ν(CO I) and ν(CO II) [cm^{-1}] for Rh carbonyl complexes.

Compound	ν(CO I)	ν(CO II)	Ref.
11	2062	1976	this work
12	2063	1982	this work
	2057	1984	–[25]
	2081	1996	–[25]
	2076	2006	–[25]

al formula [RhCl(NHC)(CO)$_2$], where NHC is an N-heterocyclic carbene (Table 4).

This indicates that the corresponding free carbenes 1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene and 1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene are NHCs with very high, if not the highest, basicity reported so far, particularly since steric effects can be ruled out in the latter. If this were true than catalytically active metal complexes should exhibit high activity in catalytic reactions if steric factors were still absent. Rhodium complexes are indeed relevant to many areas of catalysis such as hydrosilylation, ethylene/CO copolymerization, hydroformylation, and hydrogenation. Nevertheless, we decided to prepare palladium complexes of our new carbenes for two reasons. First, a broad variety of data on catalysis is available for "standard" palladium NHC complexes. Second, we were interested whether 3,4,5,6-tetrahydropyrimidin-2-ylidenes would facilitate a synthetic route that involves formation of silver(I) carbenes.

Synthesis of bis-NHC complexes of silver(I) and palladium(II) 13–16: The formation of NHC complexes of mercury and palladium by treatment of the imidazolium chlorides with the corresponding metal acetate was already demonstrated by Wanzlick and Schönherr et al. and Herrmann et al.[3,10] Though the free carbenes can be generated by reaction of **3** and **6**, respectively, with potassium *sec*-amylate, we chose a synthetic approach that entailed formation of Ag^I bis-NHC complexes followed by transmetalation. Thus, the corresponding palladium complexes were accessible via the silver intermediates as described by Lin et al.,[30,31] Crabtree et al.[32], and Coleman[33]. For this purpose, compounds **3** and **6** were treated with freshly prepared silver(I) oxide to yield the corresponding cationic silver(I) bis-NHC complexes [Ag(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2$]AgBr$_2$ (**13**) and [Ag(1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2$]AgBr$_2$ (**14**). Reaction of these compounds with [PdCl$_2$(CH$_3$CN)$_2$] resulted in the palladium(II) complexes [Pd(1,3-dimesityl-3,4,5,6-tetrahydropyri-



Scheme 3. Synthesis of **13**–**16**.

midin-2-ylidene)$_2$]$^{2+}$($Ag_2Br_2Cl_2^{4-}$)$_{1/2}$ (**15**) and [$PdCl_2$(1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2$] (**16**) in 84 and 42% yield, respectively (Scheme 3). Crystals of **15** and **16** suitable for X-ray diffraction were obtained. The structures are shown in Figures 3 and 4.

Compound **15** crystallizes in the monoclinic space group $P2_1/c$, $a=2719.11(7)$, $b=1613.44(3)$, $c=2280.11(6)$, $\alpha=90$, $\beta=109.255(2)$, $\gamma=90°$, $Z=8$. Its asymmetric unit contains two dicationic Pd(NHC)$_2$ complexes, one disordered solvent molecule (acetone), and an $Ag_2X_6^{4-}$ (X=Cl, Br) counteranion[34]. Interestingly, the two halide ions are separated from the dicationic Pd center for steric reasons. These findings were additionally supported by FABMS measurements, in which only the cationic species $C_{44}H_{57}N_4Pd$ ([M+H−2Cl]$^+$) was observed. Implications for the catalytic activity are discussed below. Since **15** was synthesized from the bromine-containing precursor **13** and [$PdCl_2(CH_3CN)_2$], an occupational disorder of the halide atoms with a total disorder of 0.527:0.473 for Cl:Br was observed in $Ag_2X_6^{4-}$. Compound

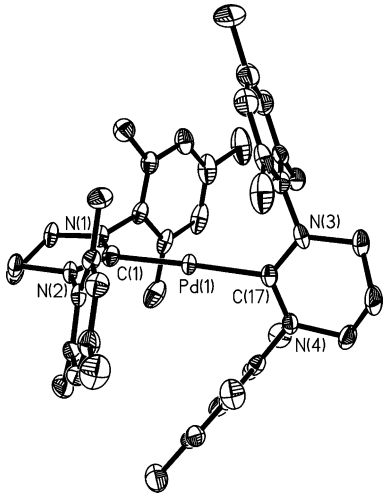


Figure 3. X-ray structure of **15** (without ($Ag_2Br_2Cl_4^{4-}$)$_{1/2}$).

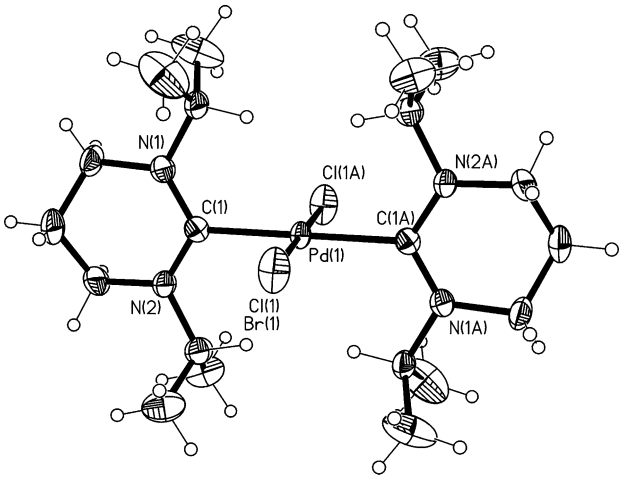


Figure 4. X-ray structure of **16**.

16 crystallizes in the monoclinic space group $C2/c$, $a=2235.22(3)$, $b=815.95(5)$, $c=1686.34(4)$ pm, $\alpha=90$, $\beta=125.505(2)$, $\gamma=90°$, $Z=4$. As it was synthesized from the bromine-containing precursor **14** and [$PdCl_2(CH_3CN)_2$] the crystal showed an occupational disorder of halide ions of 5:1 for Cl(1):Br(1). In contrast to **15**, an almost perfect square-planar ligand arrangement (C(1)-Pd(1)-Cl(1) 92.06°) around the Pd center with both halo ligands coordinated to the metal was observed. Consequently, both a cationic species with one chloro ligand attached to the Pd center, namely, $C_{20}H_{40}ClN_4Pd$ ([M+H−HCl]$^+$), and the halogen-free species [M+H−2HCl]$^+$ were observed by FABMS. Crystallographic data and parameters for **15** and **16** are summarized in Table 5. Selected bond lengths and angles for **15** and **16** are listed in Tables 6 and 7, respectively.

Heck reactions: Heck reactions[35–38] are among the most prominent C–C bond-forming reactions.[37,38] Phosphane-based systems,[39–41] palladacycles,[42–46] and NHC-based systems[20,47–50] are among to the most reactive here. Despite

Table 5. Crystal data and structure refinement for **15** and **16**.

	15	**16**
formula	$C_{44}H_{56}AgBr_{1.42}Cl_{1.58}N_4Pd\cdot 0.5$ acetone	$C_{20}H_{40}Br_{0.33}Cl_{1.67}N_4Pd$
M_r	1053.68	528.67
crystal system	monoclinic	monoclinic
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)
a [pm]	2719.11(7)	2235.22(3)
b [pm]	1613.44(3)	815.95(5)
c [pm]	2280.11(6)	1686.34(4)
α [°]	90	90
β [°]	109.255(2)	125.505(2)
γ [°]	90	90
V [nm^3]	9.4435(4)	2.50373(17)
Z	8	4
T [K]	233(2)	233(2)
ρ_{calcd} [Mg m^{-3}]	1.482	1.403
μ [mm^{-1}]	2.121	1.463
color, habit	brown plate	colorless prism
no. of rflns with $I>2\sigma(I)$	8904	1622
GOF on F^2	1.178	1.089
R indices ($I>2\sigma(I)$)	$R_1=0.0539$	$R_1=0.0241$
	$wR^2=0.1041$	$wR^2=0.0550$

Table 6. Bond lengths [pm] and angles [°] for **15**.

Pd(1)–C(17)	209.5(8)	Pd(1)–C(1)	209.9(8)	Pd(2)–C(33)	209.1(7)
Pd(2)–C(49)	209.6(7)	C(17)-Pd(1)-C(1)	177.7(3)	C(33)-Pd(2)-C(49)	178.0(3)
N(2)-C(1)-N(1)	117.4(7)	N(2)-C(1)-Pd(1)	122.2(6)	N(1)-C(1)-Pd(1)	120.4(6)
N(4)-C(17)-N(3)	117.8(7)	N(4)-C(17)-Pd(1)	119.1(6)	N(3)-C(17)-Pd(1)	123.1(7)
N(6)-C(33)-N(5)	117.3(7)	N(6)-C(33)-Pd(2)	122.7(5)	N(5)-C(33)-Pd(2)	119.9(5)
N(5)-C(34)-C(35)	109.4(7)	N(8)-C(49)-N(7)	117.3(7)	N(8)-C(49)-Pd(2)	118.9(6)
N(7)-C(49)-Pd(2)	123.7(5)	N(7)-C(50)-C(51)	109.6(7)		

Table 7. Bond lengths [pm] and angles [°] for **16**.

Pd(1)–C(1)#1	206.2(3)	Pd(1)–C(1)	206.2(3)	Pd(1)–Cl(1)	234.81(6)
Pd(1)–Cl(1)#1	234.81(6)	Pd(1)–Br(1)#1	234.81(6)	C(1)#1-Pd(1)-C(1)	180.00(14)
C(1)#1-Pd(1)-Cl(1)	87.94(7)	C(1)-Pd(1)-Cl(1)	92.06(7)	C(1)#1-Pd(1)-Cl(1)#1	92.06(7)
C(1)-Pd(1)-Cl(1)#1	87.94(7)	Cl(1)-Pd(1)-Cl(1)#1	180.0	C(1)#1-Pd(1)-Br(1)#1	92.06(7)
C(1)-Pd(1)-Br(1)#1	87.94(7)	Cl(1)-Pd(1)-Br(1)#1	180.0	Cl(1)#1-Pd(1)-Br(1)#1	0.00(3)
N(1)-C(1)-N(2)	118.2(2)	N(1)-C(1)-Pd(1)	120.76(18)	N(2)-C(1)-Pd(1)	120.90(19)

the excellent yields that have been reported for phosphane-based coupling systems,[51] a major advantage of NHC-based catalysts is that they are far less prone to oxidation than their phosphane analogues, and this allows prolonged use and reuse. Comparison of **15** and **16** with existing catalyst systems in terms of reactivity was expected to provide more information about the general applicability of this type of ligands in organometallic catalysis in general. The data obtained for the Heck reaction of aryl bromides and chlorides with styrene and butyl acrylate are summarized in Table 8. Kinetic data for key compounds are summarized in Figure 5.

Heck-type reactions with aryl iodides and activated aryl bromides can in principle be accomplished with colloidal, ligand-free Pd by maintaining a Pd concentration of less than 0.1 mol %.[52–55] As in the case of ligand-based Heck-type couplings,[56] anionic Pd^0 and Pd^{II} species have been proposed to be the active species. Compound **16** is a less active catalyst for activated aryl bromides such as 4-bromoacetophenone (Table 8, entries 13 and 14) than its mesityl counterpart **15** (Table 8, entries 1–4). Thus, turnover frequencies (TOFs) of 10 and 2 s^{-1} were found for **15** and **16**, respectively, in the coupling of butyl acrylate and 4-bromoacetophenone. This is in accordance with the "ranking" obtained by IR spectroscopy on **11** and **12** and suggests that no ligand-free species, which would exhibit identical reactivity, are present. High TONs were observed for activated aryl bromides with **15**, which reached 2000000 even when the system was "recharged" and thus illustrate both high stability and activity of the system (Table 8, entry 4). Interestingly, though less active, **16** allows the coupling of a broader variety of aryl halides without formation of Pd black (Table 8, entries 13–19). Pd^0 was observed with **15** in the coupling of bromobenzene, 4-bromoanisole, and 4-chloroacetophenone with butyl acrylate (Table 8, entries 9, 10, and 12). In view of the crystal structure, this is attributed to hampered formation of the species $(NHC)_2PdArX$. For steric reasons, one might speculate that with **15** the active species is (NHC)Pd formed by (temporary) loss of one NHC, rather than free Pd, since the latter is certainly not expected to be active in the coupling of aryl bromides and particularly aryl chlorides. At low catalyst concentration and reaction rates, as is the case for deactivated aryl bromides and aryl chlorides, backdiffusion of the NHC ligand does not take place, and low TONs and formation of Pd black result. Further evidence is provided by use of a supported version of **15** in which both NHC ligands are attached to a support. Such a system certainly facilitates the reformation of a $(NHC)_2Pd^0$ species. In no case was formation of Pd black observed with the same set of substrates.[57] In addition, the supports could be reused, and the activity of a filtered reaction mixture was low compared to the support. This strongly suggests that the true active species are ligand-bound and not colloidal Pd. Further evidence was obtained by adding Hg^{II} to mixtures of 4-bromoacetophenone and butyl acrylate. Both **15** and **16** were still active and reached TONs of up to 86000 with 0.001 mol % of catalyst. Finally, and in contrast to **15**, compound **16**, which has a readily accessible Pd core, was found to be quite efficient in the coupling of aryl chlorides in the presence of tetrabutylammonium bromide (TBAB; Table 8, entries 11 and 18) and allowed high conversion (>90 %) to be reached over less than 10 h. In fact, its reactivity respectively rivals and exceeds those of other NHC-based systems[50] and phosphane-based systems, which have been reported to achieve TONs of around 25–38 in the reaction of 4-chloroacetophenone and styrene with 3

Table 8. Summary of Heck-type couplings. All reactions were carried out in dimethylacetamide (DMAc) using anhydrous sodium acetate as base (1.5 mol equiv).

Entry	CH=CH_2R	ArX	Catalyst	mol%	T [°C]	t [h]	Conversion [%]	TON
1	butyl acrylate	4-bromoacetophenone	**15**	0.05	145	1	100	2000
2	butyl acrylate	4-bromoacetophenone	**15**	0.001	145	6.5	97	97300
3	butyl acrylate	4-bromoacetophenone	**15**	0.0001[a]	145	21	98	997000
4	butyl acrylate	4-bromoacetophenone	**15**	0.00005	145	190	$\geq$99	2×10^6
5	styrene	4-bromoacetophenone	**15**	0.001	145	30	93[b]	93300
6	styrene	bromobenzene	**15**	0.05	145	41	90[c]	1800
7	styrene	bromobenzene	**15**	0.0001	145	65	56[c]	560000
8	styrene	4-bromoanisole	**15**	0.05	145	86	60[d]	1200
9	butyl acrylate	bromobenzene	**15**	0.05	145	–	Pd black	$\leq$200
10	butyl acrylate	4-bromoanisole	**15**	0.05	145	–	Pd-black	$\leq$200
11	butyl acrylate	4-chloroacetophenone	**15**	1[a]	150	86	32	32
12	butyl acrylate	4-chloroacetophenone	**15**	0.05	145	–	Pd black	$\leq$200
13	butyl acrylate	4-bromoacetophenone	**16**	0.05	147	22.5	100	2000
14	butyl acrylate	4-bromoacetophenone	**16**	0.0001	145	90	52	515000
15	butyl acrylate	bromobenzene	**16**	0.05	145	67	92	1800
16	butyl acrylate	bromobenzene	**16**	0.0001	145	66	49	489000
17	butyl acrylate	4-bromoanisole	**16**	0.05	145	4	63	63
18	butyl acrylate	4-chloroacetophenone	**16**	1[a]	150	8	91	91
19	butyl acrylate	4-chloroacetophenone	**16**	1[a]	150	22.3	100	100

[a] Tetrabutylammonium bromide (0.2 equiv) was added. [b] 19% 1,1-diphenylethene. [c] 7% 1,1-diphenylethene. [d] 14% 1,1-diphenylethene.

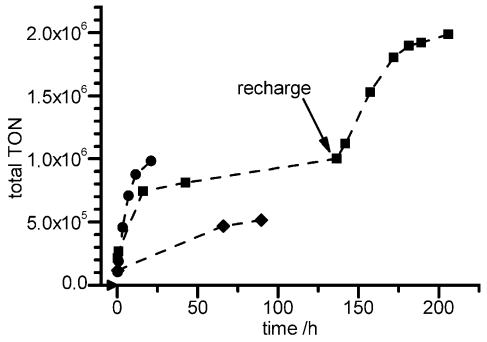


Figure 5. Kinetics of Heck-type coupling between 4-bromoacetophenone and butyl acrylate at 145°C in DMAc. With 0.0001 mol% of **15** (○), 0.0001 mol% of **16** (◆), or 0.0001 mol% of **15** and 0.2 mol% of TBAB (■) as catalyst.

and 0.3 mol% Pd, respectively, under optimized conditions.[39,41,51] It also competes with the activity of coupling systems consisting of an alkyl phosphane and a palladacyle.[45] The positive effect of TBAB on reaction kinetics has already been described by various groups[58–62] and is best illustrated by comparing the reaction kinetics of 4-bromoacetophenone and butyl acrylate, as shown in Figure 5 (see also Table 8, entries 3 and 4). Compound **15** proved to be significantly more active on addition of TBAB; the TON increased from 10 to 20 s^{-1}.

Conclusion

We have synthesized a new class of N-heterocyclic carbenes based on 1,3-disubstituted pyrimidin-2-ylidenes. They have high basicity and allow the synthesis of mono- and bis-NHC complexes of Rh and Pd, respectively. The bis-NHC palladium(II) complexes are highly active catalysts for Heck-type reactions of aryl bromides and chlorides, and in some cases TONs of up to 2000000 can be obtained. Current work focuses on the heterogenization of these ligands and their metal complexes on various supports, evaluation of the catalytic activity of these systems in various C–C and C–heteroatom bond-forming reaction, and the synthesis of other metal complexes relevant to catalysis.

Experimental Section

All experiments involving transition metals were performed under a nitrogen atmosphere in a MBraun glove box or by standard Schlenk techniques. Reagent-grade THF, toluene, and pentane were distilled from sodium benzophenone ketyl under argon. Dichloromethane and chloroform were distilled from calcium hydride under argon. 1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate was synthesized according to a published procedure.[23] All other reagents were commercially available and used as received. Column chromatography was performed with silica gel 60 (220–440 mesh, Fluka, Buchs, Switzerland). NMR spectra were recorded at 25°C on a Bruker Spektrospin 300 at 300.13 MHz for ^{1}H and at 75.47 MHz for ^{13}C and referenced to the solvent peaks ($CDCl_3$: $\delta=7.24$, 77.0 ppm; CD_2Cl_2: $\delta=5.32$, 54.0 ppm). FTIR spectra were recorded on a Bruker Vector 22 using ATR technology. GC-MS measurements were carried out on a Shimadzu GCMS QP 5050 with a SPB-5 fused silica column (30 m × 0.25 mm × 25 μm film thickness) and helium as carrier gas. Mass spectra were recorded on a Finnigan MAT 95S using FAB ionization (Cs gun: 20 kV, 3 μA; *m*-nitrobenzyl alcohol matrix). Elemental analyses were performed at the Institute of Physical Chemistry, University of Vienna, Austria, and at the Mikroanalytisches Labor, Technische Universität München, Garching, Germany.

***N,N'*-Dimesitylpropane-1,3-diamine (1)**: 1,3-Dibromopropane (4.100 g, 20.31 mmol) and 2,4,6-trimethylaniline (mesitylamine, 5.910 g, 43.71 mmol) were dissolved in diethyleneglycol dimethyl ether, and the mixture was stirred at 140°C. During the reaction a brown precipitate formed. The reaction was monitored by GC-MS. After 6 h no further conversion was observed. The reaction mixture was allowed to cool to room temperature. Dichloromethane (100 mL) and 15% aqueous sodium hydroxide solution (30 mL, 110 mmol) were added, and the reaction mixture was stirred until the solids had completely dissolved. The dark red organic phase was separated, washed with water (3 × 100 mL), and dried over sodium sulfate. After evaporation of the solvents in vacuo, a dark

red oil remained. The product was purified by column chromatography on silica gel 60 with diethyl ether/pentane (1/2) as eluent ($R_f = 0.3$). All product fractions were pooled and evaporated to dryness to give the product as an off-white powder (3.307 g, 10.40 mmol, 51%). Alternatively, the product can be purified by repeated recrystallization from pentane and diethyl ether/pentane. FTIR (ATR mode): $\tilde{\nu} = 3358$ (w), 2960 (w) 2912 (m), 2848 (m), 1610 (w), 1590 (w), 1480 (s), 1434 (s), 851 (s), 726 (s), 689 cm^{-1} (s); ^1H NMR ($CDCl_3$): $\delta = 6.82$ (s, 4H, aromatic H), 3.05 (t, 4H, $2 \times NCH_2$, $^3J(H,H) = 6.78$ Hz), 3.0–2.8 (br s, 2H, NH), 2.26 (s, 12H, *o*-CH_3 of Mes), 2.23 (s, 6H, *p*-CH_3 of Mes), 1.89 ppm (quint, 2H, CH_2, $^3J(H,H) = 6.78$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 143.5$, 131.4, 129.7, 129.4 (all aromatic C), 47.0 ($2 \times NCH_2$), 32.5 (CH_2), 20.5, 18.3 ppm (both CH_3 of Mes); GC-MS (EI) calcd for $C_{21}H_{30}N_2$: *m/z*: 310.24; found: 310.25; elemental analysis (%) calcd for $C_{21}H_{30}N_2$: C 81.24, H 9.74, N 9.02; found: C 81.14, H 9.69, N 9.01.

1,3-Dimesitylhexahydropyrimidine (2): Compound **1** (1.308 g, 4.211 mmol) was dissolved in methanol and treated with 36.5% aqueous formaldehyde solution (0.386 g, 4.63 mmol formaldehyde) diluted with methanol (2 mL). The reaction mixture was stirred at 45°C. A white precipitate formed during the reaction. Conversion was complete after 16 h, as indicated by GC-MS. The precipitate was filtered off. Recrystallization of the crude product from ethanol yielded 1.231 g of colorless crystals (3.832 mmol, 91%). FTIR (ATR mode): $\tilde{\nu} = 2944$ (w), 2913 (w), 2822 (w), 1478 (s), 1393 (m), 1320 (m), 1248 (m), 1205 (s), 849 cm^{-1} (s); ^1H NMR ($CDCl_3$): $\delta = 6.81$ (s, 4H, aromatic H), 4.23 (s, 2H, NCH_2N), 3.21 (t, 4H, NCH_2), 2.35 (s, 12H, *o*-CH_3 of Mes), 2.23 (s, 6H, *p*-CH_3 of Mes), 1.86 ppm (m, 2H, CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 145.2$, 136.8, 134.1, 129.4 (all aromatic C), 69.7 (NCH_2N), 49.8 (NCH_2), 27.9 (CH_2), 20.6, 19.8 ppm (both CH_3 of Mes); GC-MS (EI) calcd for $C_{22}H_{30}N_2$: *m/z*: 322.24; found: 322.25.

1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium bromide (3): Compound **2** (0.823 g, 2.56 mmol) was dissolved in absolute dimethoxyethane and treated with *N*-bromosuccinimide (NBS, 0.455 g, 2.56 mmol). The reaction mixture was stirred at room temperature for 3 h. A yellow precipitate formed, which was filtered off, washed with pentane, and dried in vacuo to yield 0.881 g (2.20 mmol, 86%) of **3** as a yellow powder. FTIR (ATR mode): $\tilde{\nu} = 2976$ (w), 2914 (w), 1648 (s), 1479 (w), 1312 (s), 1209 cm^{-1} (s); ^1H NMR ($CDCl_3$): $\delta = 7.54$ (s, 1H, N^+=CH), 6.91 (s, 4H, aromatic H), 4.18 (t, 4H, NCH_2), 2.57 (m, 2H, CH_2),), 2.39 (s, 12H, *o*-CH_3 of Mes), 2.24 ppm (s, 6H, *p*-CH_3 of Mes); ^{13}C NMR ($CDCl_3$): $\delta =$ 153.6 (N^+=CH), 140.5, 136.4, 134.6, 130.1 (all aromatic C), 47.0 (NCH_2), 21.0 (CH_3 of Mes), 19.6 (CH_2), 18.0 ppm (CH_3 of Mes); elemental analysis (%) calcd for $C_{22}H_{29}BrN_2$: C 65.83, H 7.28, N 6.98; found: C 65.52, H 7.62, N 6.90.

1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate (4): Compound **3** (1.500 g, 3.737 mmol) was dissolved in ethanol and treated with a solution of silver tetrafluoroborate (0.728 g, 3.737 mmol) in ethanol. Immediately, a yellow precipitate of silver bromide formed. After stirring for a few minutes, the precipitate was filtered off and washed with ethanol. Finally, the solution was concentrated to a few milliliters and the product crystallized as 1.450 g of white crystals. (3.550 mmol, 95%). FTIR (ATR mode): $\tilde{\nu} = 1657$ (s), 1478 (w), 1316 (s), 1093 (s), 1051 (s); ^1H NMR ($CDCl_3$): $\delta = 7.48$ (s, 1H, N^+=CH), 6.93 (s, 4H, aromatic H), 3.88 (t, 4H, NCH_2), 2.54 (m, 2H, CH_2), 2.28 (s, 12H, *o*-CH_3 of Mes), 2.25 ppm (s, 6H, *p*-CH_3 of Mes); ^{13}C NMR ($CDCl_3$): $\delta = 153.9$ (N^+=CH), 140.5, 136.3, 134.3, 130.1 (all aromatic C), 46.3 (NCH_2), 20.9 (CH_3 of Mes), 19.2 (CH_2), 17.4 ppm (CH_3 of Mes); elemental analysis (%) calcd for $C_{22}H_{29}BF_4N_2$: C 64.72, H 7.16, N 6.86; found: C 64.52, H 7.39, N 6.81.

1,3-Bis(2-propyl)hexahydropyrimidine (5): 1,3-Bis(2-propyl)propane-1,3-diamine (1.162 g, 7.338 mmol) was dissolved in absolute methanol (3 mL). 36.5% aqueous formaldehyde solution (0.734 g, 8.81 mmol formaldehyde) diluted with methanol (2 mL) was added, and the mixture was stirred at 47°C for 2 h. After that time the reaction was complete, as indicated by GC-MS. The product was dried in vacuo to give a colorless liquid in 95% yield (1.190 g, 6.71 mmol). ^1H NMR ($CDCl_3$): $\delta = 3.23$ (s, 2H, NCH_2N), 2.68 (hept, 2H, NCH, $^3J(H,H) = 6.84$ Hz), 2.47 (t, 4H, NCH_2, $^3J(H,H) = 5.49$ Hz), 1.60 (quint, 2H, CH_2, $^3J(H,H) = 5.49$), 0.98 ppm (d, 12H, CH_3, $^3J(H,H) = 6.84$ Hz); ^{13}C NMR ($CDCl_3$): $\delta = 70.4$ (NCH_2N), 52.3 (NCH_2), 47.7 (NCH), 24.7 (CH_2), 19.0 ppm (CH_3); GC-MS (EI) calcd for $C_{10}H_{22}N_2$: *m/z*: 170.18, found: 170.20.

1,3-Bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium bromide (6): Compound **5** (1.190 g, 6.986 mmol) was dissolved in absolute 1,2-dimethoxyethane and treated with NBS (1.243 g, 6.986 mmol). The reaction mixture was stirred at room temperature for 2 h, during which a yellow precipitate formed. The volatile compounds were removed in vacuo and a brown, oily residue remained. The pure product was obtained after column chromatography on silica gel 60 with dichlormethane/ethanol (6/1) as eluent. The product eluted in the second fraction ($R_f = 0.2$). The product fractions were combined and evaporated to dryness to yield 1.480 g of **6** as a brown powder (5.938 mmol, 85%). FTIR (ATR mode): $\tilde{\nu} = 3405$ (w), 2964 (m), 2882 (m), 1671 (s), 1324 (m), 1123 cm^{-1} (m); NMR ($CDCl_3$): $\delta = 9.40$ (s, 1H, N^+=CH), 4.36 (hept, 2H, NCH, $^3J(H,H) = 6.39$), 3.31 (t, 4H, NCH_2, $^3J(H,H) = 5.94$), 2.05 (quint, 2H, CH_2, $^3J(H,H) = 5.94$ Hz), 1.27 ppm (d, 12H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 151.5$ (N^+=C), 56.0 (NCH), 38.2 (NCH_2), 20.1 (CH_3), 19.1 ppm (CH_2).

Bromo(η^4-1,5-cyclooctadiene){1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene}rhodium (7): [{Rh(cod)Cl}$_2$] (120 mg, 244 μmol) was dissolved in THF (5 mL), and lithium *tert*-butoxide (47 mg, 590 μmol) was added with vigorous stirring. The mixture was stirred for a further 30 min at room temperature, and then **6** (134 mg, 536 μmol) was added. The reaction mixture was stirred overnight at 55°C, after which time TLC showed no further conversion. The solvent was removed in vacuo. The product was purified by column chromatography on silica gel 60 with dichloromethane/ethanol (250/4) as mobile phase. The product eluted as a yellow band in the second fraction ($R_f = 0.6$). The product fractions were pooled and evaporated to dryness to yield a yellow solid (0.189 g, 411 μmol, 84%). Yellow crystals suitable for X-ray analysis were obtained by layering pentane over a dilute solution of **7** in dichloromethane at −36°C. FTIR (ATR mode): $\tilde{\nu} = 2963$ (m), 2928 (m), 2873 (m), 2832 (m), 1506 (s), 1449 (m), 1363 (m), 1304 (s), 1162 (s), 1078 cm^{-1} (m); ^1H NMR ($CDCl_3$): $\delta = 6.35$ (hept, 2H, NCH), 4.84 (m, 2H, cod CH), 3.37 (m, 2H, cod CH), 3.05–2.85 (m, 4H, NCH_2), 2.26 (m, 4H, cod CH_2), 1.90–1.65 (m, 6H, CH_2 + cod CH_2), 1.29 ppm (d, 12H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 203.7$ (d, NCN, $^1J(^{103}Rh,^{13}C) = 45$ Hz,), 94.4 (d, cod CH, $^1J(^{103}Rh,^{13}C) = 6.5$ Hz), 69.0 (d, cod CH, $^1J(^{103}Rh,^{13}C) = 15.5$ Hz), 57.1, 37.8, 32.3, 29.0, 21.0, 20.3, 19.7 ppm (cod CH_2, NCH_2, CH_2, NCH, CH_3); elemental analysis (%) calcd for $C_{18}H_{32}BrN_2Rh$: C 47.07, H 7.02, N 6.10; found: C 47.39, H 7.00, N 6.01.

Bromo(η^4-1,5-cyclooctadiene)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)rhodium (8): [{Rh(cod)Cl}$_2$] (120 mg, 244 μmol) was dissolved in THF (4 mL), and lithium *tert*-butoxide (47 mg, 590 μmol) was added with vigorous stirring. The mixture was stirred for a further 30 min at room temperature, and then **3** (215 mg, 536 μmol) was added. After a few minutes a clear, yellow solution formed, which was stirred for 5 h at room temperature. After this time, TLC showed no further conversion. The solvent was removed in vacuo. The product was purified by column chromatography on silica gel 60 with dichloromethane/ethanol (250/8) as mobile phase. **8** eluted as a yellow band in the second fraction ($R_f = 0.3$). The product fractions were pooled and evaporated to dryness to yield a yellow solid in 73% yield. (0.219 g, 356 μmol). Yellow crystals suitable for X-ray analysis were obtained by layering pentane over a dilute solution of **8** in dichloromethane at −36°C. FTIR (ATR mode): $\tilde{\nu} = 2879$ (m), 1477 (s), 1433 (m), 1298 (s), 1198 (m), 851 cm^{-1} (m); ^1H NMR ($CDCl_3$): $\delta = 6.97$ (m, 4H, aromatic H), 4.32, 4.20 ($2 \times$ br s, 2H, cod CH), 3.3–3.1 (m, 6H, NCH_2 + cod CH), 2.7–2.1 (m, 20H, $CH_2 + CH_3$ of Mes), 1.5–1.2 ppm (m, 8H, cod CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 211.1$ (d, NCN, $^1J(^{103}Rh,^{13}C) = 45$ Hz,), 141.8, 141.7, 137.3 (all aromatic C), 93.8 (d, cod CH, $^1J(^{103}Rh,^{13}C) = 7.5$ Hz), 93.4 (d, cod CH, $^1J(^{103}Rh,^{13}C) = 6.8$ Hz), 67.7 (d, cod CH, $^1J(^{103}Rh,^{13}C) = 15.1$ Hz), 66.9 (d, cod CH, $^1J(^{103}Rh,^{13}C) =$ 15.1 Hz), 47.9, 47.6, 32.2, 32.2, 27.6, 27.4, 21.1, 21.0, 20.9 ppm (cod CH_2, NCH_2, CH_2, CH_3 of Mes).

Chloro(η^4-1,5-cyclooctadiene)(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)rhodium (9): [{Rh(cod)Cl}$_2$] (120 mg, 244 μmol) was dissolved in THF (4 mL), and then lithium *tert*-butoxide (47 mg, 590 μmol) was added with stirring. The mixture was stirred for a further 30 min at room temperature, and then **4** (219 mg, 536 μmol) was added. A clear, yellow solution formed immediately. The reaction mixture was stirred for 1 h at 53°C, then the solvent was removed in vacuo. The product was obtained after column chromatography on silica gel 60 with dichloromethane/THF/ethanol (400/17/3) as solvent. The product eluted as a yellow band in the second fraction ($R_f = 0.4$). The product fractions were pooled and

evaporated to dryness to give a yellow powder in 74% yield (0.206 g, 397 μmol). Yellow crystals were grown from dichloromethane/pentane. FTIR (ATR mode): $\tilde{\nu}$ = 2880 (m), 1478 (s), 1434 (m), 1299 (s), 1198 (m), 1026 (m), 851 (m), 804 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ = 6.97 (m, 4H, aromatic H), 4.19 (s, 2H, cod CH), 3.32 (t, 4H, NCH_2), 3.18 (s, 2H, cod CH), 2.7–2.0 (m, 20H, CH_2+CH_3 of Mes), 1.6–1.1 ppm (m, 8H, cod CH_2); ^{13}C NMR ($CDCl_3$): δ = 210.8 (d, NCN, $^1J(^{103}Rh,^{13}C)$ = 53 Hz), 141.6, 137.4, 128.4 (br) (all aromatic C), 94.0 (d, cod CH, $^1J(^{103}Rh,^{13}C)$ = 7.2 Hz), 67.0 (d, cod CH, $^1J(^{103}Rh,^{13}C)$ = 14.4 Hz), 47.6, 32.3, 27.4, 27.4, 21.2, 20.9, 19.6 ppm (br) (cod CH_2, NCH_2, CH_2, CH_3 of Mes); elemental analysis (%) calcd for $C_{30}H_{40}ClN_2Rh$: C 63.55, H 7.11, N 4.94; found: C 63.22, H 7.00, N 4.91.

Chloro(η⁴-1,5-cyclooctadiene){1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene}rhodium (10): [{Rh(cod)Cl}$_2$] (80 mg, 164 μmol) was dissolved in THF (5 mL), and lithium *tert*-butoxide (32 mg, 400 μmol) was added with vigorous stirring. The mixture was stirred for a further 30 min at room temperature, then 1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium tetrafluoroborate (134 mg, 536 μmol) was added. A clear, orange solution formed within minutes. The reaction mixture was stirred overnight at 55 °C. After this time TLC showed no further conversion. The solvent was removed in vacuo. The product was purified by column chromatography on silica gel 60 with dichloromethane/ethanol (250/8) as solvent. The product eluted as a yellow band in the second fraction (R_f = 0.3). The product fractions were pooled and evaporated to dryness to yield a yellow solid (0.096 g, 230 μmol, 71%). FTIR (ATR mode): $\tilde{\nu}$ = 2963 (m), 2929 (m), 2872 (m), 1505 (m), 1440 (m), 1364 (m), 1303 (s), 1158 (m), 1076 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ = 6.44 (hept, 2H, NCH, ^3J(H,H) = 6.84 Hz), 4.77 (m, 2H, cod CH), 3.30 (m, 2H, cod CH), 3.05–2.85 (m, 4H, NCH_2), 2.30 (m, 4H, cod CH_2), 1.90–1.65 (m, 6H, CH_2+cod CH_2), 1.29 ppm (d, 12H, CH_3, ^3J(H,H) = 6.84 Hz); ^{13}C NMR ($CDCl_3$): δ = 204.1 (d, NCN, $^1J(^{103}Rh,^{13}C)$ = 46 Hz,), 95.0 (d, cod CH, $^1J(^{103}Rh,^{13}C)$ = 6.5 Hz), 68.0 (d, cod CH, $^1J(^{103}Rh,^{13}C)$ = 15.5 Hz), 57.3, 37.7, 32.5, 28.8, 21.0, 20.4, 19.8 ppm (cod CH_2, NCH_2, CH_2, NCH, CH_3); elemental analysis (%) calcd for $C_{18}H_{32}ClN_2Rh$: C 52.12, H 7.78, N 6.75; found: C 52.01, H 7.60, N 6.38.

Dicarbonylchloro(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)rhodium (11): Compound **9** (50 mg, 88 μmol) was dissolved in a mixture of THF (3 mL) and toluene (3 mL) in a Schlenk flask. The flask was removed from the dry box, and carbon monoxide was bubbled through the solution for 50 min. A color change from orange to pale yellow was observed. The reaction mixture was stirred at room temperature for 10 min and then concentrated to dryness to give an orange powder in 70% yield (32 mg, 62 μmol). FTIR (ATR mode): $\tilde{\nu}$ = 2062 ($\tilde{\nu}$(CO I)), 1976 ($\tilde{\nu}$(CO II)); ^1H NMR ($CDCl_3$): δ = 6.90 (m, 4H, aromatic H), 3.43 (t, 4H, NCH_2), 2.40–2.25 ppm (m, 20H, CH_2+CH_3 of Mes); ^{13}C NMR ($CDCl_3$): δ = 202.3 (d, NCN, $^1J(^{103}Rh,^{13}C)$ = 41 Hz), 185.5 (d, CO, $^1J(^{103}Rh,^{13}C)$ = 52 Hz), 183.6 (d, CO, $^1J(^{103}Rh,^{13}C)$ = 76 Hz), 141.2, 138.4, 137.9, 136.3, 134.1, 130.0, 129.0, 128.9, 128.2, 125.2 (all aromatic C), 46.8 (NCH_2), 21.4, 21.0, 20.7, 19.4, 18.4, 18.2 ppm (NCH_2, CH_2, CH_3 of Mes). FABMS calcd for $C_{24}H_{29}ClN_2O_2Rh$ [M+H]$^+$: m/z: 515.09; found m/z: 486.1 [M+H−HCO], 479.1 [M+H−HCl].

Dicarbonylchloro[1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene]rhodium (12): Compound **10** (50 mg, 120 μmol) was dissolved in a mixture of THF (3 mL) and toluene (3 mL) in a Schlenk flask. The flask was removed from the dry box and carbon monoxide was bubbled through the solution for 50 min. The reaction mixture was stirred at room temperature for 1.5 h and then concentrated to dryness giving a yellow powder in 84% yield (37 mg, 101 μmol). FTIR (ATR mode) 2063 (ν(CO I)), 1982 (ν(CO II)); ^1H NMR ($CDCl_3$): δ = 5.47 (hept, 2H, NCH, ^3J(H,H) = 6.57 Hz), 3.07 (m, 4H, NCH_2), 2.0–1.7 (m, 2H; CH_2), 1.25–1.10 ppm (2×d, 12H, CH_3 of 2-Pr, ^3J(H,H) = 6.57 Hz); ^{13}C NMR ($CDCl_3$): δ = 192.8 (d, N-C-N, $^1J(^{103}Rh,^{13}C)$ = 38 Hz), 186.4 (d, CO, $^1J(^{103}Rh,^{13}C)$ = 53 Hz), 183.5 (d, CO, $^1J(^{103}Rh,^{13}C)$ = 77 Hz), 58.2 (NCH of 2-Pr), 38.0 (NCH_2), 20.5 (CH_2), 19.4, 19.0 ppm (CH_3 of 2-Pr). FABMS calcd for $C_{12}H_{21}ClN_2O_2Rh$: m/z: 363.03 [M+H]$^+$, found: m/z: 334.0 [M+H−HCO], 327.0 [M+H−HCl]; elemental analysis (%) calcd for $C_{12}H_{20}ClN_2O_2Rh$: C 39.74, H 5.56, N 7.72; found: C 39.41, H 5.47, N 7.60.

[Ag(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2$][AgBr$_2$] (13): *Silver oxide*: Silver nitrate (1.01 g, 5.94 mmol) was dissolved in water (10 mL) and heated to 80 °C. Sodium hydroxide (0.24 g, 6.00 mmol) was dissolved in 5 mL of water and also heated to 80 °C. On mixing the two solutions, a dark brown precipitate of Ag_2O formed immediately. The precipitate was filtered off, washed with hot water (3×20 mL) and boiling ethanol (3×20 mL), and dried in vacuo.

[Ag(1,3-Dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2$][AgBr$_2$] (***13***): Compound **3** (0.564 g, 1.41 mmol) was dissolved in absolute dichloromethane (35 mL), and then freshly prepared silver(I) oxide (0.166 g, 0.717 mmol) was added. The reaction mixture was stirred for 22 h at room temperature, during which an almost clear solution formed. The reaction mixture was filtered, and then the filtrate was concentrated to 1 mL. On addition of diethyl ether (80 mL), a white precipitate formed. The precipitate was filtered off, washed with diethyl ether, and dried in vacuo. The product was stored in the dark. Yield: 0.663 g (93%, 1.31 μmol, white solid). FTIR (ATR mode): $\tilde{\nu}$ = 2945 (w), 2908 (w), 1731 (w), 1661 (w), 1605 (w), 1515 (s), 1478 (m), 1443 (m), 1300 (m), 1203 (m), 1024 (m), 856 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ = 6.90 (s, 8H, aromatic H), 3.37 (t, 8H, NCH_2, ^3J(H,H) = 5.94 Hz), 2.31 (quint, 4H, CH_2), 2.25, 2.23 ppm (2×s, 36H, CH_3 of Mes); ^{13}C NMR ($CDCl_3$): δ = 142.7, 138.2, 134.3, 129.9 (all aromatic C), 43.9 (NCH_2), 21.0 (CH_3 of Mes), 20.7 (CH_2), 17.8 ppm (CH_3 of Mes); FABMS calcd for $C_{44}H_{56}N_4Ag$: m/z: 749.35 [M^+]; found: m/z: 749.35 (98.5%).

[Ag{1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene}$_2$]AgBr$_2$ (14): Silver(I) oxide was prepared as described for **13**. **6** (0.193 g, 0.775 mmol) was dissolved in absolute dichloromethane (15 mL), and then freshly prepared silver (I) oxide (0.0897 g, 0.387 mmol) was added. The reaction mixture was stirred for 26 h at room temperature, but remained a suspension. The reaction mixture was brought into a dry box. The solid components were filtered off and the filtrate was concentrated to 1 mL. On addition of diethyl ether, an off-white solid precipitated. The precipitate was filtered off, washed with diethyl ether, and dried in vacuo to yield 0.101 g of product (37%, 287 μmol). FTIR (ATR mode): $\tilde{\nu}$ = 2972 (w), 2952 (w), 2909 (w), 2878 (w), 1681 (m), 1523 (m), 1464 (m), 1445 (m), 1370 (m), 1343 (m), 1314 (m), 1232 (m), 1216 (m), 1161 (m), 1094 (s), 1045 (s), 1034 cm^{-1} (m); ^1H NMR ($CDCl_3$): δ = 4.3–4.1 (m, 2H, NCH), 3.26, 2.94 (2×t, 4H, NCH_2), 2.01, 1.80 (2×quint, 2H, CH_2), 1.22, 1.10 ppm (2×d, 12H, CH_3); ^{13}C NMR ($CDCl_3$): δ = 55.8 (NCH), 38.0 (NCH_2), 20.1 (CH_3), 19.0 ppm (CH_2); FAB calcd for $C_{20}H_{40}N_4Ag$ [M^+]: m/z: 443.23; found m/z: 443.2 (100%) [M^+].

[PdCl$_2$(1,3-dimesityl-3,4,5,6-tetrahydropyrimidin-2-ylidene)$_2$] (15): Compound **13** (0.300 g, 295 μmol) was dissolved in dichloromethane and treated with a solution of [$PdCl_2(CH_3CN)_2$] (77 mg, 295 μmol) in dichloromethane. A clear red solution formed. The reaction mixture was stirred at room temperature for 5 h. During that time silver bromide precipitated. Then the reaction mixture was stirred at 45 °C for 3 h. The precipitate was filtered off, and the filtrate was concentrated to dryness and finally purified by passage over a short column of silica 60 with acetone as eluent. Recrystallization from dichloromethane/pentane yielded 203 mg of red crystals (66%, 196 μmol). The precipitate consisted of pure AgBr. It could be dissolved in concentrated ammonia and reprecipitated by addition of concentrated nitric acid. Crystals of **15** suitable for X-ray analysis were obtained by crystallization from acetone/diethyl ether. FTIR (ATR mode): $\tilde{\nu}$ = 2916 (w), 1518 (s), 1478 (m), 1441 (m), 1302 (s), 1203 (m), 851 cm^{-1} (s); ^1H NMR (CD_2Cl_2): δ = 6.91 (s, 8H, aromatic H), 3.18 (t, 8H, NCH_2, ^3J(H,H) = 5.64 Hz), 2.34 (s, 12H, p-CH_3 of Mes), 2.21 (m, 4H, CH_2), 1.81 ppm (s, 24H, o-CH_3 of Mes); ^{13}C NMR (CD_2Cl_2): δ = 144.3, 139.9, 136.7, 131.4 (aromatic C), 45.5, 45.5 (NCH_2), 22.7, 22.4, 19.4 ppm (CH_3 of Mes+CH_2); FABMS calcd for $C_{44}H_{57}Cl_2N_4Pd$: m/z: 817.30 [M^++H]$^+$; found: m/z: 747.5 (100%) [M^++H−2Cl]); elemental analysis (%) calcd for $C_{88}H_{112}Pd_2Ag_2Br_3Cl_3N_8$: C 51.39, H 5.49, N 5.45; found: C 51.61, H 5.59, N 5.41.

[Pd{1,3-bis(2-propyl)-3,4,5,6-tetrahydropyrimidin-2-ylidene}$_2$]Cl$_2$ (16): Compound **15** (0.173 g, 242 μmol) was dissolved in dichloromethane and treated with a solution of [$PdCl_2(CH_3CN)_2$] (63 mg, 240 μmol) in dichloromethane. On mixing, a beige precipitate of silver bromide formed immediately, and the solution changed its color from orange to pale yellow. The reaction mixture was stirred for 30 min at room temperature. Then silver bromide was removed by filtration of the mixture through glass-fiber paper. The filtrate was concentrated to dryness and passed over a short column of silica 60 with acetone as eluent. Recrystallization from dichloromethane/pentane gave the product as yellow crystals in 38% yield (50 mg, 92 μmol). FTIR (ATR mode): $\tilde{\nu}$ = 2967 (m), 2869 (m), 1525 (s), 1449 (m), 1362 (m), 1306 (s), 1169 cm^{-1} (s); ^1H NMR ($CDCl_3$):

$\delta = 6.31$ (m, 4H, NCH), 2.97 (t, 8H, NCH_2), 1.79 (m, 4H, CH_2), 1.32–1.22 ppm (m, 24H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 192.5$, 192.1 (Pd=C), 56.5, 56.4, 56.3 (NCH), 37.6, 37.5, 37.5 (NCH_2), 20.8, 20.7, 19.8, 19.7, 19.6, 19.5 ppm (CH_3+CH_2); FABMS calcd for $C_{20}H_{41}Cl_2N_4Pd$: *m/z*: 513.17 $[M^+ + H]^+$; found *m/z*: 477.2 $[M^+ + H - HCl]$, 441.3 (100%) $[M^+ + H - 2HCl]$; elemental analysis (%) calcd for $C_{20}H_{40}Cl_{0.67}Br_{0.33}N_4Pd$: C 45.44, H 7.63, N 10.60; found: C 45.46, H 7.62, N 10.59.

Typical procedure for Heck reactions: Aryl halide (10 mmol), vinyl compound (12 mmol), anhydrous sodium acetate (15 mmol), and *tert*-butylbenzene (160 mg) as internal standard were dissolved in dimethylacetamide (DMAc; 10 mL). Then the mixture was heated to 145 °C. The actual temperature was measured directly in the Schlenk tube. A GC-MS spectrum was recorded for this mixture. The catalyst dissolved in DMAc (1 mL) was added. A few milliliters of sample were withdrawn in definite time intervals. These samples were diluted with dichloromethane, filtered through glass-fiber paper, and analyzed by GC-MS. The conversion was calculated as $1 - A_{ArX}(t)A_{std}(t_0)/A_{ArX}(t_0)A_{std}(t)$ (A = area).

Crystal structure determination on 7, 8, 15, and 16: Single crystals of **7** and **8** suitable for X-ray analysis were obtained by slow crystallization from dichloromethane/pentane, and those of **15** and **16** from acetone/diethyl ether. Data were collected on a Nonius Kappa CCD using graphite-monochromatized $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) and a nominal crystal to area detector distance of 36 mm. Intensities were integrated using DENZO and scaled with SCALEPACK.[63] Several scans in ϕ and ω directions were made to increase the number of redundant reflections, which were averaged in the refinement cycles. This procedure replaces in a good approximation an empirical absorption correction. The structures were solved with direct methods (SHELXS86) and refined against F^2 (SHELX97).[64] The function minimized was $\Sigma[w(F_o^2 - F_c^2)^2]$ with the weight defined as $w^{-1} = [\sigma^2(F_o^2) + (xP)^2 + yP]$ and $P = (F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms at C(1), C(2), C(5), and C(6) were found and refined with bond restraints (d_{C-H} around 95 pm) and isotropic displacement parameters; all others were placed on calculated positions. For compound **7** a disorder in the ratio 3:2 occurs by exchange of the bromine atom Br(1) at the metal center by chlorine Cl(1). The ratio was determined by using a free variable which refines the ratio of occupation for two different halogens on the same position. In the last refinement cycles the ratio was fixed at the determined value. Another 3:2 disorder exists for the two chlorine atoms of a solvent molecule: Cl2:Cl2A and Cl3:Cl3A are split into two positions. Further crystallographic data are collected in Table 1. For compound **15**, each Cl/Br pair in $Ag_2X_6^{4-}$ was refined with equal coordinates and displacement parameters, and free variables were used to refine the occupation factors at each position. Another 1:1 disorder occurred for the solvent acetone by rotating around 50° about C(65).

CCDC-212219, CCDC-212220, CCDC-222718 and CCDC-222717 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or deposit@ccdc.cam.uk).

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[1] K. Öfele, *J. Organomet. Chem.* **1968**, *12*, P42-P43.
[2] H.-W. Wanzlick, *Angew. Chem.* **1962**, *74*, 129–134; *Angew. Chem. Int. Ed. Engl.* **1962**, *1*, 75–80.
[3] H. W. Wanzlick, H. J. Schönherr, *Angew. Chem.* **1968**, *80*, 154–155; *Angew. Chem. Int. Ed. Engl.* **1968**, *7*, 141–142.
[4] A. J. Arduengo III, H. V. Rasika Dias, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1992**, *114*, 5530–5534.
[5] A. J. Arduengo III, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.* **1991**, *113*, 361–363.
[6] R. W. Alder, P. R. Allen, S. J. Williams, *Chem. Commun.* **1995**, 1267–1268.
[7] W. A. Herrmann, C. Köcher, *Angew. Chem.* **1997**, *109*, 2256–2282; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2162–2187.
[8] T. Weskamp, V. P. W. Böhm, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *600*, 12–22.
[9] M. Regitz, *Angew. Chem.* **1996**, *108*, 791–794; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 725–728.
[10] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Chem. Eur. J.* **1996**, *2*, 772–780.
[11] J. Huang, E. D. Stevens, S. P. Nolan, J. L. Petersen, *J. Am. Chem. Soc.* **1999**, *121*, 2674–2678.
[12] J. Huang, H.-J. Schanz, E. D. Stevens, S. P. Nolan, *Organometallics* **1999**, *18*, 5375–5380.
[13] D. S. McGuinness, K. J. Cavell, B. W. Skelton, A. H. White, *Organometallics* **1999**, *18*, 1596–1605.
[14] D. S. McGuinness, K. J. Cavell, *Organometallics* **2000**, *19*, 741–748.
[15] C. W. Bielawski, R. H. Grubbs, *Angew. Chem.* **2000**, *112*, 3025–3028; *Angew. Chem. Int. Ed.* **2000**, *39*, 2903–2906.
[16] M. Scholl, S. Ding, C. W. Lee, R. H. Grubbs, *Org. Lett.* **1999**, *1*, 953–956.
[17] M. Scholl, T. M. Trnka, J. P. Morgan, R. H. Grubbs, *Tetrahedron Lett.* **1999**, *40*, 2247–2250.
[18] T. Weskamp, W. C. Schattenmann, M. Spiegler, W. A. Herrmann, *Angew. Chem.* **1998**, *110*, 2631–2633; *Angew. Chem. Int. Ed.* **1998**, *37*, 2490–2492.
[19] T. Weskamp, F. J. Kohl, W. Hieringer, D. Gleich, W. A. Herrmann, *Angew. Chem.* **1999**, *111*, 2573–2576; *Angew. Chem. Int. Ed.* **1999**, *38*, 2416–2419.
[20] V. P. W. Böhm, C. W. K. Gstöttmayr, T. Weskamp, W. A. Herrmann, *J. Organomet. Chem.* **2000**, *595*, 186–190.
[21] M. Tafipolsky, W. Scherer, K. Öfele, G. Artus, B. Pedersen, W. A. Herrmann, G. S. McGrady, *J. Am. Chem. Soc.* **2002**, *124*, 5865–5880.
[22] T. Weskamp, F. J. Kohl, W. A. Herrmann, *J. Organomet. Chem.* **1999**, *582*, 362–365.
[23] R. W. Alder, M. E. Blake, C. Bortolotti, S. Bufali, C. P. Butts, E. Linehan, J. M. Oliva, G. Orpen, M. J. Quayle, *Chem. Commun.* **1999**, 241–242.
[24] R. W. Alder, M. E. Blake, S. Bufali, C. P. Butts, A. G. Orpen, J. Schütz, S. J. Williams, *J. Chem. Soc. Perkin Trans. 1* **2001**, 1586–1593.
[25] K. Denk, P. Sirsch, W. A. Herrmann, *J. Organomet. Chem.* **2002**, *649*, 219–224.
[26] C. Heinemann, T. Müller, Y. Apeloig, H. Schwarz, *J. Am. Chem. Soc.* **1996**, *118*, 2023–2038.
[27] A. H. Cowley, *J. Organomet. Chem.* **2001**, *617–618*, 105–109.
[28] L. R. Orelli, M. B. Garcia, I. A. Perillo, *Heterocycles* **2000**, *53*, 2437–2450.
[29] W. A. Herrmann, J. Fischer, K. Öfele, G. R. J. Artus, *J. Organomet. Chem.* **1997**, *530*, 259–262.
[30] C. K. Lee, J. C. C. Chen, K. M. Lee, C. W. Liu, I. J. B. Lin, *Chem. Mater.* **1999**, *11*, 1237–1242.
[31] H. M. J. Wang, C. Y. L. Chen, I. J. B. Lin, *Organometallics* **1999**, *18*, 1216–1223.
[32] A. R. Chianese, X. Li, M. C. Janzen, J. W. Faller, R. H. Crabtree, *Organometallics* **2003**, *22*, 1663–1667.
[33] K. S. Coleman, H. T. Chamberlayne, S. Turberville, M. L. H. Green, A. R. Cowley, *Dalton Trans.* **2003**, 2917–2922.
[34] J. F. Bringley, M. Rajeswaran, EP-A, EP 1324119 A1, **2003** [*Chem. Abstr.* 139: 76296].
[35] W. Cabri, I. Candiani, *Acc. Chem. Res.* **1995**, *28*, 2–7.
[36] G. T. Crisp, *Chem. Soc. Rev.* **1998**, *27*, 427–436.
[37] J. G. de Vries, *Can. J. Chem.* **2001**, *79*, 1086–1092.
[38] A. de Meijere, F. E. Meyer, *Angew. Chem.* **1994**, *106*, 2473–2506; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2379–2411.
[39] A. F. Littke, G. C. Fu, *J. Am. Chem. Soc.* **2001**, *123*, 6989–7000.
[40] T. H. Riermeier, A. Zapf, M. Beller, *Top. Catal.* **1997**, *4*, 301–309.
[41] A. F. Littke, G. C. Fu, *Angew. Chem.* **2002**, *114*, 4350–4386; *Angew. Chem. Int. Ed.* **2002**, *41*, 4176–4211.
[42] W. A. Herrmann, C. Broßmer, K. Öfele, C.-P. Reisinger, T. Priermeier, M. Beller, H. Fischer, *Angew. Chem.* **1995**, *107*, 1989–1992; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1844–1847.

[43] W. A. Herrmann, V. P. W. Böhm, *J. Organomet. Chem.* **1999**, *572*, 141–145.
[44] W. A. Herrmann, C. Broßmer, C.-P. Reisinger, T. H. Riermeier, K. Öfele, M. Beller, *Chem. Eur. J.* **1997**, *3*, 1357–1364.
[45] A. Zapf, M. Beller, *Chem. Eur. J.* **2001**, *7*, 2908–2915.
[46] W. A. Herrmann, C. P. Reisinger, K. Öfele, C. Broßmer, M. Beller, H. Fischer, *J. Mol. Catal.* **1996**, *108*, 51–56.
[47] W. A. Herrmann, V. P. W. Böhm, C. W. K. Gstöttmayr, M. Grosche, C.-P. Reisinger, T. Weskamp, *J. Organomet. Chem.* **2001**, *617–618*, 616–628.
[48] W. A. Herrmann, C.-P. Reisinger, M. Spiegler, *J. Organomet. Chem.* **1998**, *557*, 93–96.
[49] J. Schwarz, V. P. W. Böhm, M. G. Gardiner, M. Grosche, W. A. Herrmann, W. Hieringer, G. Raudaschl-Sieber, *Chem. Eur. J.* **2000**, *6*, 1773–1780.
[50] A. M. Magill, D. S. McGuinness, K. J. Cavell, G. J. P. Britovsek, V. C. Gibson, A. J. P. White, D. J. Williams, A. H. White, B. W. Skelton, *J. Organomet. Chem.* **2001**, *617–618*, 546–560.
[51] A. F. Littke, G. C. Fu, *J. Org. Chem.* **1999**, *64*, 10–11.
[52] M. Beller, H. Fischer, K. Kühlein, C.-P. Reisinger, W. A. Herrmann, *J. Organomet. Chem.* **1996**, *520*, 257–259.
[53] A. Biffis, M. Zecca, M. Basato, *Eur. J. Inorg. Chem.* **2001**, 1131–1133.
[54] A. H. M. de Vries, J. M. C. A. Mulders, J. H. M. Mommers, H. J. W. Henderickx, J. G. de Vries, *Org. Lett.* **2003**, *5*, 3285–3288.
[55] Q. Yao, E. P. Kinney, Z. Yang, *J. Org. Chem.* **2003**, *68*, 7528–7531.
[56] C. Amatore, A. Jutand, *Acc. Chem. Res.* **2000**, *33*, 314–321.
[57] M. Mayr, M. R. Buchmeiser, *Macromol. Rapid. Commun.* **2004**, *25*, 231–236.
[58] W. A. Herrmann, M. Elison, J. Fischer, C. Köcher, G. R. J. Artus, *Angew. Chem.* **1995**, *107*, 2602–2605; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 2371–2374.
[59] G. T. Crisp, M. G. Gebauer, *Tetrahedron* **1996**, *52*, 12465–12474.
[60] M. R. Buchmeiser, K. Wurst, *J. Am. Chem. Soc.* **1999**, *121*, 11101–11107.
[61] J. Silberg, T. Schareina, R. Kempe, K. Wurst, M. R. Buchmeiser, *J. Organomet. Chem.* **2000**, *622*, 6–18.
[62] M. R. Buchmeiser, T. Schareina, R. Kempe, K. Wurst, *J. Organomet. Chem.* **2001**, *634*, 39–46.
[63] Z. Otwinowski, W. Minor, *Methods in Enzymology, Vol. 276*, Academic Press, New York, **1997**.
[64] G. M. Sheldrick, Program package SHELXTL V.5.1, Bruker Analytical X-Ray Instruments Inc., Madison, **1997**.

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