Arylation of Carbonyl Compounds Catalyzed by Rhodium and Iridium 1,3-R_2-Tetrahydropyrimidin-2-ylidenes: Structure-Reactivity Correlations

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Abstract: Six different well-defined rhodium and iridium N-heterocyclic carbene complexes, i.e., RhCl(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**1**), RhBr(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**2**), RhCl[1,3-di(2-propyl)tetrahydropyrimidin-2-ylidene](COD) (**3**), IrCl(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**4**), Rh(CF_3COO)(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**5**), and IrBr[1,3-di(2-propyl)tetrahydropyrimidin-2-ylidene](COD) (**6**) (COD = 1,5-cyclooctadiene, mesityl = 2,4,6-trimethylphenyl) have been used as catalysts for the arylation of aldehydes and α,β-unsaturated ketones using different arylboronic acids. Compounds **1**–**4** and **6** were prepared by reaction of $[RhCl(COD)]_2$ and $[IrCl(COD)]_2$, respectively, with a base and the corresponding 1,3-R_2-tetrahydropyrimidinium salt. Compound **5** was prepared by reaction of 1.0 equivalents of CF_3COOAg with **1**. The use of an excess of CF_3COOAg resulted in the replacement of Rh(I) by Ag(I) and yielded Ag(1,3-dimesityltetrahydropyrimidin-2-ylidene)$^+Rh_2(CF_3COO)_3(COD)^-$ (**8**). Compounds **4** and **8** were characterized by X-ray analysis. The activity of the rhodium complexes increased in the order **5** > **3** > **1** > **2**, indicating the necessity of strongly electron-withdrawing groups at the metal centers, thus increasing their nucleophilicity. In due consequence, the "softer" iridium complexes **4** and **6** exhibited significantly reduced catalytic activity albeit with enhanced selectivity. The syntheses of the metal complexes as well as a detailed study on their reactivity in the arylation of carbonyl compounds using equimolar amounts of arylboronic acid and carbonyl compound in the presence of 0.08–1 mol % catalyst are presented.

Keywords: arylations; N-heterocyclic carbenes; homogeneous catalysis; iridium; rhodium

Introduction

Transition metal N-heterocyclic carbene (NHC) complexes are widely used in molecular organometallic catalysis.[1–4] Current effort focuses on structural variations in N-heterocyclic carbenes. Beside altering the substituents at both nitrogens, the synthesis of different saturated and unsaturated imidazol-2-ylidenes[5–8] and imidazolin-2-ylidenes,[9–11] respectively, and non-cyclic structures need to be mentioned.[12] Recently, we reported on NHCs based on 1,3-R_2-tetrahydropyrimidin-2-ylidenes (R = mesityl, 2-propyl) and the synthesis of various Rh, Ag, and Pd complexes therefrom.[13,14] In addition, Grubbs–Hoveyda-type catalysts of the general formula RuX_2(1,3-dimesityltetrahydropyrimidin-2-ylidene)[CH-2-(2-PrO-5-NO_2-C_6H_3)] (X = Cl, CF_3COO) were synthesized and found to be highly active metathesis catalysts.[15] In view of the high reactivity of both the Pd and Ru complexes, we were interested whether the same applied to the corresponding Rh and Ir complexes based on this type of ligands.

So far, NHC complexes of both Rh and Ir have already been described by Herrmann et al.,[16,17] Nolan et al.,[18] and others.[19–25] Rh-NHC complexes have mainly been used in hydroformylation,[26] carbonyl hydrosilylation[27] and C=C hydrosilylation.[21] Ir-NHC complexes were used in the Oppenauer-type oxidation of alcohols,[23] and as hydrogenation catalysts.[18]

Miyaura et al. were the first to report on the Rh(I)-catalyzed addition of aryl- and 1-alkenylboronic acids, respectively, to enones and aldehydes to yield the corresponding ketones and secondary alcohols, respective-

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ly.[28,29] The reasons for applying transition metal catalysis for these types of reaction are quite obvious. While this reaction may conveniently be accomplished without any catalyst with unsubstituted carbonyl compounds and aryllithium and Grignard reagents, respectively, the use of transition metal catalysts in combination with boronic acids widened the scope of this reaction to substituted carbonyl compounds as well as aryl- and alkenylboronic acids. Using phosphane-based ligands and 3 mol % of metal, turnover numbers (TONs) up to 30 and excellent yields up to 95% were achieved. The use of highly basic ligands such as triethylphosphine or tri-*tert*-butylphosphine resulted in increased yields and reaction rates even at room temperature. Important enough, this was realized using only 1 equivalent of phosphine with respect to Rh.[30] Larger amounts significantly impeded any reaction, indicating the necessity of a mono-ligated Rh center. Alternatively, potassium aryltrifluoroborates were used, nevertheless, a ligand or catalyst loading of 3 mol % was required, too.[31] Extending the scope of this reaction to asymmetric catalysis, Hayashi et al. reported on the use of chiral ligands such as (*S*)-BINAP in asymmetric 1,4-additions of alkenyldioxaborolanes to α,β-unsaturated ketones, which allowed an enantiomeric excess (ee) up to 95% and TONs of 10–30 using catalyst loadings of 3–10 mol %.[32,33]

In 2001, Fürstner et al. reported on the use of a mixture of $RhCl_3 \cdot 3\,H_2O$ and various N-heterocyclic carbenes formed *in situ* as catalysts in the arylation and vinylation of aldehydes.[34] The corresponding Rh(III)-NHC complexes formed during reaction were proposed to be the active catalysts. Using this *in situ* approach, turnover numbers (TONs) were in the range of 50–100. In view of these highly significant results and the high reactivity of the above-mentioned transition metal 1,3-R_2-tetrahydropyrimidin-2-ylidene Pd and Ru complexes in related reactions we investigated the utility of both Rh(I)- and Ir(I)-1,3-R_2-tetrahydropyrimidin-2-ylidenes of the general formula MX(NHC)(COD) [M = Rh, Ir; X = Cl, Br, CF_3COO; NHC = 1,3-bis(2-propyl)tetrahydropyrimidin-2-ylidene, NHC = 1,3-dimesityltetrahydropyrimidin-2-ylidene; COD = cycloocta-1,5-diene] in the arylation of various carbonyl compounds including electron-rich and -poor aldehydes and α,β-unsaturated ketones. Since RhCl(1,3-dimesityltetrahydropyrimidin-2-ylidene)$(CO)_2$ and RhCl[1,3-di(2-propyl)tetrahydropyrimidin-2-ylidene]$(CO)_2$ had already been found to be the Rh(I) complexes with the lowest value for the ν(CO II) band,[13] a fact highly indicative for pronounced binding capabilities of the NHCs,[12] we focused on the corresponding Rh(I)-X complexes (X=Cl, Br, CF_3COO). The results with regards to the role of the metal, the substituents at the NHC, i.e., 2-propyl and mesityl, and the X group on both reactivity and selectivity will be discussed.

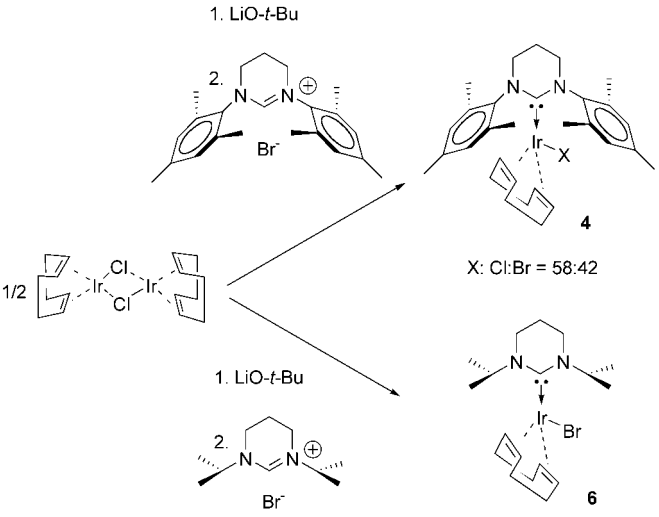
Results and Discussion

Synthesis of Rh and Ir Catalysts

Generally speaking, both rhodium- and iridium-NHC complexes may be obtained either *via* transmetallation of the corresponding silver (I) complexes[19,24,35] or directly *via* reaction of $[RhCl(COD)]_2$ and $[IrCl(COD)]_2$, respectively, with a base and the corresponding 1,3-R_2-tetrahydropyrimidinium salt. The latter route was chosen for the synthesis of RhCl(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**1**), RhBr(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**2**) and RhCl-[1,3-di-(2-propyl)tetrahydropyrimidin-2-ylidene](COD) (**3**) (COD = cycloocta-1,5-diene) as already described in a previous disclosure.[13] The iridium catalysts IrCl(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**4**) and IrBr[1,3-di(2-propyl)tetrahydropyrimidin-2-ylidene]-(COD) (**6**) were prepared in an analogous way (Scheme 1). It is worth mentioning that the use of 1,3-dimesityltetrahydropyrimidinium bromide yields a mixture of IrCl(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**4**) and IrBr(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (Figure 1). Nevertheless, pure **4** may be prepared by using 1,3-dimesityltetrahydropyrimidinium tetrafluoroborate.

Compound **4** derived from 1,3-dimesityltetrahydropyrimidinium bromide crystallizes in the triclinic space group $P\bar{1}$ (No. 2), $a = 945.44(3)$ pm, $b = 1288.84$ (5) pm, $c = 1447.55$ (6) pm, $\alpha = 68.690$ (2)°, $\beta = 80.451$ (2)°, $\gamma = 74.681$ (2)°. Relevant bond lengths and angles are summarized in Table 1.

Reaction of compound **1** with 1.0 equiv. of CF_3COOAg resulted in the formation of Rh(CF_3COO)-(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**5**) (Scheme 2). All attempts to prepare Rh(CF_3COO)-



Scheme 1. Synthesis of compounds **4** and **6**.

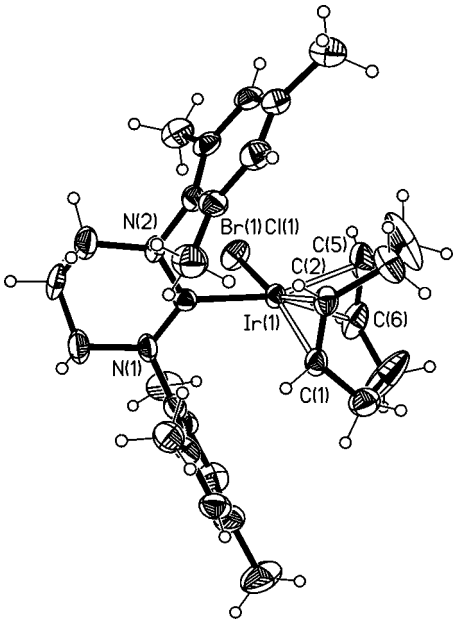


Figure 1. X-ray structure of **4**.

Table 1. Selected bond lengths [pm] and angles [°] for **4**.

Ir(1)–C(9)	205.8(5)
Ir(1)–C(1)	210.3(6)
Ir(1)–C(2)	211.4(6)
Ir(1)–C(6)	216.2(6)
Ir(1)–C(5)	216.4(6)
Ir(1)–Cl(1)	245.00(10)
C(9)–Ir(1)–Br(1)	87.40(15)

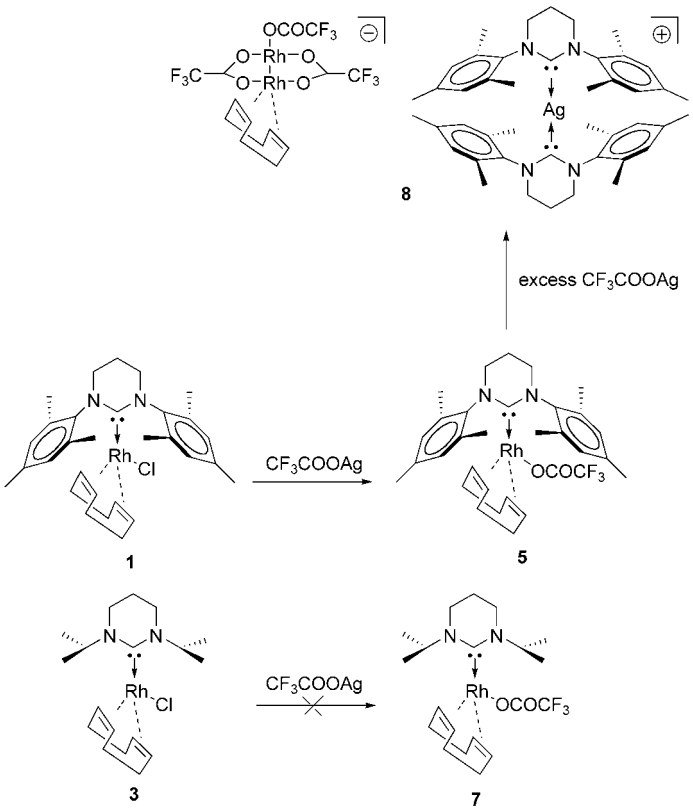
Table 2. Selected bond lengths [pm] and angles [°] for **8**.

Ag(1)–C(15)	210.7(3)
Ag(1)–C(31)	211.1(3)
Rh(1)–Rh(2)	293.80(4)
C(15)–Ag(1)–C(31)	178.89(12)

[1,3-di-(2-propyl)tetrahydropyrimidin-2-ylidene](COD) (**7**) in an analogous way failed. Immediate decomposition was observed.

Interestingly, the use of any excess of CF_3COOAg in the reaction with **1** leads to the immediate replacement of Rh(I) by Ag(I) and formation of Ag(1,3-dimesityltetrahydropyrimidin-2-ylidene)$^+$ $Rh_2(CF_3COO)_3(COD)^-$ (**8**), which was also characterized by X-ray analysis (Figure 2). Compound **8** crystallizes in the monoclinic space group $P2_1/n$ (No. 14), $a = 1115.27(2)$ pm, $b = 2076.83$ (2) pm, $c = 2608.33$ (4) pm, $\alpha = 90°$, $\beta = 97.200$ (1)°, $\gamma = 90°$. Relevant bond lengths and angles are summarized in Table 2.

The fact that Rh(I) is replaced by Ag(I) is indicative for the high affinity of Ag(I) for NHCs based on tetrahydropyrimidin-2-ylidenes and supports the synthetic approach chosen for the synthesis of compounds **1**–**3**, **4** and **6**.



Scheme 2. Synthesis of compounds **5** and **8** and attempted synthesis of **7**.

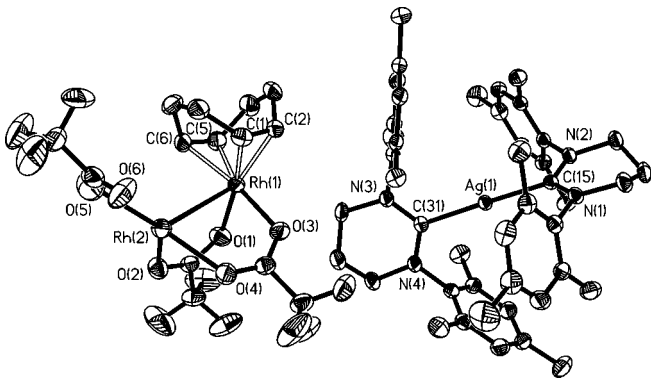
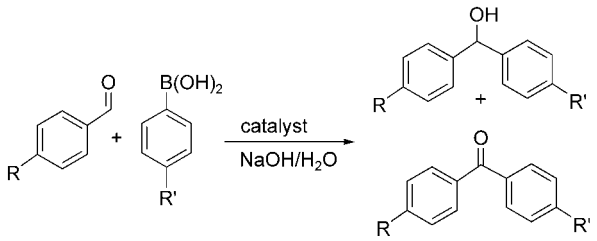


Figure 2. X-ray structure of **8**.

Reactivity in Carbonyl Arylations

For all reactions, oxygen-free reaction conditions were chosen and turned out to be a prerequisite as shown by a few reactions carried out in the presence of air. The latter did not result in the formation of any product. In a



Scheme 3. Arylation of carbonyl compounds.

first step, compound **1** was used in various arylation reactions (Scheme 3, Table 3, entries 1–9).

Using 0.4–0.7 mol % of **1**, TONs were in the range of 20–140. Such reactivity already exceeds that of the original Rh-phosphane-based systems and is comparable to the one reported by Fürstner.[34] As already observed by Miyaura et al.[28–30], the presence of an electron-withdrawing group in the aromatic aldehyde and a donating group in the arylboronic acid facilitated the reaction and

Table 3. Summary of carbonyl arylations using catalysts **1**–**6**.

Entry	Ar′-B(OH)$_2$ Ar′ =	Carbonyl compound	Catalyst [mol %]	TON	Yield [%]	Ratio[c]
1	4-(CH_3O)-C_6H_4-	2-ferrocenylbenzaldehyde	**1** (0.60)	140	83	100 : 0
2	4-(CH_3O)-C_6H_4	furfural	**1** (0.40)	75	30	100 : 0
3	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**1** (0.70, 0.50[a])	80 (140[a])	55 (70[a])	82 : 18
4	4-(CH_3O)-C_6H_4-	2-OH-benzaldehyde	**1** (0.30)	70 (120[a])	22 (36[a])	0 : 100
5	4-(CH_3O)-C_6H_4-	cyclohex-2-en-1-one	**1** (0.70)	110[a]	77[a]	0 : 100
6	4-CH_3-C_6H_4-	4-F-benzaldehyde	**1** (0.40)	100 (250[a, b])	41 (99[a, b])	95 : 5
7	4-CH_3-C_6H_4-	2-OH-benzaldehyde	**1** (0.60)	23 (107[a])	14 (64[a])	0 : 100
8	4-vinyl-C_6H_4-	4-F-benzaldehyde	**1** (0.50)	100 (200[a])	53 (99[a, b])	72 : 28
9	4-vinyl-C_6H_4-	2-OH-benzaldehyde	**1** (0.50)	50 (140[a])	24 (70[a])	0 : 100
10	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**2** (0.80)	110[a]	88[a]	75 : 25
11	4-(CH_3O)-C_6H_4-	cyclohex-2-en-1-one	**2** (0.80)	100[a]	80[a]	0 : 100
12	4-(CH_3O)-C_6H_4-	2-OH-benzaldehyde	**2** (1.2)	50[a]	60[a]	0 : 100
13	4-CH_3-C_6H_4-	4-F-benzaldehyde	**2** (0.5)	200[a, b]	>99[a, b]	82 : 18
14	4-CH_3-C_6H_4-	2-OH-benzaldehyde	**2** (1.3)	50[a]	66[a]	0 : 100
15	4-vinyl-C_6H_4-	4-F-benzaldehyde	**2** (0.5)	200[a, b]	99[a, b]	77 : 23
16	4-vinyl-C_6H_4-	2-OH-benzaldehyde	**2** (2.4)	40[a, b]	96[a, b]	0 : 100
17	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**3** (0.10)	430[a]	43[a]	100 : 0
18	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**3** (0.80)	125[a, b]	>99[a, b]	100 : 0
19	4-(CH_3O)-C_6H_4-	2-OH-benzaldehyde	**3** (0.50)	140[a]	70[a]	0 : 100
20	4-(CH_3O)-C_6H_4-	cyclohex-2-en-1-one	**3** (1.0, 0.90[a])	47 (70[a])	47 (66[a])	0 : 100
21	4-CH_3-C_6H_4-	4-F-benzaldehyde	**3** (0.50)	190[a, b]	95[a, b]	100 : 0
22	4-CH_3-C_6H_4-	2-OH-benzaldehyde	**3** (0.80)	64[a]	51[a]	0 : 100
23	4-vinyl-C_6H_4-	2-OH-benzaldehyde	**3** (0.80)	100[a]	80[a]	0 : 100
24	4-vinyl-C_6H_4-	4-F-benzaldehyde	**3** (0.50)	22[a]	11[a]	100 : 0
25	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**4** (0.50)	40[a]	20[a]	100 : 0
26	4-(CH_3O)-C_6H_4-	2-OH-benzaldehyde	**4** (0.70)	9[a]	6[a]	0 : 100
27	4-(CH_3O)-C_6H_4-	cyclohex-2-en-1-one	**4** (0.50)	6[a]	3[a]	0 : 100
28	4-(CH_3O)-C_6H_4-	2-ferrocenylbenzaldehyde	**5** (0.11)	340	37	100 : 0
29	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**5** (0.08)	950[a, b]	76	100 : 0
30	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**5** (0.1)	990[a, b]	99[a, b]	100 : 0
31	4-(CH_3O)-C_6H_4-	2-OH-benzaldehyde	**5** (0.080)	375[a]	30[a]	0 : 100
32	4-(CH_3O)-C_6H_4-	cyclohex-2-en-1-one	**5** (0.13)	590[a]	76[a]	0 : 100
33	4-CH_3-C_6H_4-	4-F-benzaldehyde	**5** (0.080)	1230[a, b]	99[a, b]	100 : 0
34	4-CH_3-C_6H_4-	2-OH-benzaldehyde	**5** (0.12)	420[a]	50[a]	0 : 100
35	4-vinyl-C_6H_4-	4-F-benzaldehyde	**5** (0.080)	1230[a, b]	99[a, b]	100 : 0
36	4-vinyl-C_6H_4-	2-OH-benzaldehyde	**5** (0.12)	340[a]	41[a]	0 : 100
37	thiophen-2-yl	4-F-benzaldehyde	**5** (0.13)	760[a, b]	99[a, b]	71 : 29
38	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**6** (0.90)	22[a]	20[a]	100 : 0
39	4-(CH_3O)-C_6H_4-	4-F-benzaldehyde	**6** (4.9)	20[a, b]	>99[a, b]	100 : 0
40	4-(CH_3O)-C_6H_4-	2-OH-benzaldehyde	**6** (0.70)	4[a]	3[a]	0 : 100
41	4-CH_3-C_6H_4-	2-OH-benzaldehyde	**6** (0.90)	40[a]	36[a]	0 : 100

TONs are based on isolated yields unless stated otherwise.
[a] TON determined by GC-MS.
[b] Yield > 90%.
[c] RR′CHOH:RR′CO.

vice versa.[30] However, considerable reactivity was also observed for benzaldehyde substituted with the electron-donating ferrocene moiety at the 2-position (Table 3, entry 1). 100% 1,4-addition was observed with cyclohex-2-enone (Table 3, entry 5). Replacement of the chlorine in **1** by Br as realized in **2** gave significantly lower TONs (Table 3, entries 10–16) for most substrates compared to **1**. Switching from Rh(I) to Ir(I) as realized in complex **4**, drastically reduced reactivity resulting in TONs = 40 (Table 3, entries 25–27). Nevertheless, replacement of the 1,3-dimesityltetrahydropyrimidin-2-ylidene moiety by the 1,3-di-(2-propyl)tetrahydropyrimidin-2-ylidene group as realized in **3** had a significant influence on reactivity. With one exception (Table 3, entry 24), TONs between 70 and 430 were realized (Table 3, entries 17–24). These findings clearly illustrate the improved reactivity of the 1,3-di-(2-propyl)tetrahydropyrimidin-2-ylidene-based Rh(I) complex **3**. Replacement of Rh(I) by Ir(I) in **3** as exemplified with catalyst **6** gave similar results as observed with **4**. Reactivity in selected arylation reactions was again comparably low, thus TONs < 40 were obtained again (Table 3, entries 39–41). From this set of data, some conclusions can already be drawn. First, the 1,3-di-(2-propyl)tetrahydropyrimidin-2-ylidene ligand appears favorable over the 1,3-dimesityltetrahydropyrimidin-2-ylidene one. Second, the Rh(I) complexes are by far more reactive than the corresponding "softer" Ir complexes[36–39]. Third, an X-ligand with pronounced electron-withdrawing capabilities favoring the reductive elimination and C–C bond formation appeared favorable. If this was true, then the corresponding CF_3COO-substituted Rh(I) complex **5** should in fact exhibit superior reactivity. The results obtained with **5** in various arylation reactions are summarized in Table 3, entries 28–37. As can be deduced therefrom, catalyst **5** displayed high activity, allowing TONs up to 1230. In fact, most coupling reactions allowed TONs between 600 and 1200. In addition, reactions summarized in Table 3, entries 6, 8, 13, 15, 16, 18, 21, 30, 33, 35, 37, were realized in virtually quantitative (i.e., > 95%) yield.

The fact that excess of CF_3COOAg in the reaction with **1** did not yield **5** but resulted in the formation of **8** deserves particular attention. Due to the high affinity of Ag(I) to the 1,3-dimesityltetrahydropyrimidin-2-ylidene ligand, any rearrangement in a coupling reaction catalyzed by **5** could not totally be excluded. In order to make sure that an Rh(I)-NHC complex was in fact the active species, a control experiment was performed. Thus, 4-methoxybenzeneboronic acid and 4-F-benzaldehyde were converted into the corresponding alcohol with a TON of 125 using 0.4 mol % of a mixture of [RhCl(COD)] and CF_3COOAg. Similar TONs (120) were obtained with [RhCl(COD)] without the use of CF_3COOAg. Thus, both systems gave TONs by far lower than that realized with **5**, clearly underlining the role of both the NHC and CF_3COO ligand.

In terms of selectivity, a few interesting points need to be summarized. As already mentioned, the arylation of cyclohex-2-enone proceeds *via* 1,4-addition throughout. Interestingly, the secondary alcohol formed in the reaction of 2-hydroxybenzaldehyde with an arylboronic acid was quantitatively oxidized to the corresponding ketone with any of the catalysts **1**–**6** formally forming thermodynamically stable 2-hydroxy-α,β-unsaturated ketones even in the absence of any air. However, catalysts **1**, **2**, and **5** were found to partially oxidize the resulting secondary alcohols to the corresponding ketones, too (Table 3, entries 3, 6, 8, 10, 13, 15, and 37). This was not observed for the less reactive Ir-based catalysts **4** and **6** as well as for **3**.

Conclusion

In summary, we demonstrated the feasibility of Rh- and Ir-NHC complexes of the general formula MX(NHC)(COD) [M = Rh, Ir; X = Cl, Br, CF_3COO; NHC = 1,3-bis(2-propyl)tetrahydropyrimidin-2-ylidene, NHC = 1,3-dimesityltetrahydropyrimidin-2-ylidene; COD = cycloocta-1,5-diene] to catalyze the arylation of aldehydes and α,β-unsaturated ketones. Important findings were that (i) the tetrahydropyrimidin-2-ylidene ligand results in catalysts with high catalytic activity; (ii) 2-propyl groups at both nitrogens are superior over mesityl groups at the same position; (iii) the activity of the catalyst strongly correlates with the electron-withdrawing properties of the X group, indicating the necessity of a highly nucelophilic metal center; (iv) the use of iridium results in less active yet more selective catalysts with lowered tendency of oxidizing the resulting secondary alcohols; and (v) reactions can be carried out using a 1:1 ratio of the arylboronic acid and carbonyl compound. Our results clearly show the way for more reactive catalysts, thus allowing significant reductions in the amount of catalyst.

Experimental Section

General Remarks

NMR data were obtained at 300.13 MHz for proton and at 75.74 MHz for carbon in the indicated solvent at 25 °C on a Bruker Spectrospin 300 and are listed in parts per million downfield from tetramethylsilane for proton and carbon. IR spectra were recorded on a Bruker Vector 22 using ATR technology. GC-MS investigations were carried out on a Shimadzu GCMS-QP5050, using a SPB-5 fused silica column (30 m × 0.25 mm × 25 μm film thickness). Elemental analyses were carried out at the Mikroanalytisches Labor, Anorganisch-Chemisches Laboratorium, Technische Universität München. Further instrumentation is described elsewhere.[40] Mass spectra were recorded on a Finnigan MAT 95S using FAB ionization (Cs-gun: 20 kV, 3 μA, matrix: *m*-nitrobenzylic alcohol).

The syntheses of 1,3-dimesityltetrahydropyrimidinium tetrafluoroborate, 1,3-dimesityltetrahydropyrimidinium bromide, 1,3-di(2-propyl)tetrahydropyrimidinium tetrafluoroborate, 1,3-di(2-propyl)tetrahydropyrimidinium bromide, RhCl(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**1**), RhBr(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (**2**), and RhCl[1,3-di(2-propyl)tetrahydropyrimidin-2-ylidene](COD) (**3**) are described elsewhere.[13] Syntheses of catalysts **4**–**8** and reactions were performed under an argon atmosphere by standard Schlenk techniques or in an N_2-filled dry-box (MBraun, Germany) unless stated otherwise. Reagent grade diethyl ether, pentane, THF and dimethoxyethane (DME) were distilled from sodium benzophenone ketyl under argon. Reagent grade dichloromethane was distilled from calcium hydride under argon. Other solvents and reagents were used as purchased. Deionized water was used throughout.

IrBr(1,3-dimesityltetrahydropyrimidin-2-ylidene)-(COD) (4)

LiO-*t*-Bu (29 mg, 362 μmol) dissolved in 2 mL of THF was added to a solution of $[Ir(COD)Cl]_2$ (100 mg, 148 μmol) suspended in 1 mL of THF. After stirring the mixture at room temperature for 40 min, 1,3-dimesityltetrahydropyrimidinium bromide (131.4 mg, 327 μmol), dissolved in 2 mL of THF, was added. The mixture was heated to 60 °C and stirred for 12 hours. The solvent was evaporated under vacuum and the residue was purified by chromatography on silica 60 using CH_2Cl_2/ethanol (250:1) as eluent. Yield: 40 mg (59 μmol, 20%).

Crystals of **4** suitable for X-ray analysis were obtained from CH_2Cl_2. Using 1,3-dimesityltetrahydropyrimidinium bromide, the product was roughly a 1:1 mixture of the corresponding iridium chloro and bromo complexes, respectively (see X-ray structure). In order to obtain analytical data for a well-defined compound, the pure chloro complex was prepared using 1,3-dimesityltetrahydropyrimidinium tetrafluoroborate. FT-IR (ATR mode): $\nu = 2881$ (m), 1609 (w), 1477 (s), 1435 (s), 1375 (w), 1293 (s), 1258 (m), 1199 (m), 1078 (m), 1024 (m), 843 (m), 806 (s), 703 cm^{-1} (m); ^1H NMR (THF-d_8): $\delta = 6.91$ (m, 4H, aromatic H), 3.76 (m, 2H, CH_{COD}), 3.43 (m, 4H, NCH_2), 2.88 (m, 2H, CH_{COD}), 2.35–2.10 (m, 20H, CH_2 + Mes CH_3), 1.51–1.20 ppm (m, 8H, $CH_{2\ COD}$); ^{13}C NMR (THF-d_8): $\delta =$ 191.4 (s, NCN), 142.9, 137.8, 135.9, 128.9 (all aromatic C), 79.2 (s, CH_{COD}), 51.3 (s, CH_{COD}), 49.2 (s, NCH_2), 32.8, 28.9, 21.2, 20.9, 17.9 ($CH_{2\ COD}$, CH_2, Mes CH_3); FABMS: calcd. for $C_{30}H_{40}ClIrN_2$: $m/z = 656.25$; found: 656.25 [$M^{\circ+}$], 621.74 [$M^+ - Cl$].

Rh(CF_3COO)(1,3-dimesityltetrahydropyrimidin-2-ylidene)(COD) (5)

Compound **1** (50 mg, 88 μmol) was dissolved in THF (1 mL) and the solution was cooled to −36 °C. A chilled solution of silver trifluoroacetate (19.5 mg, 88 μmol) in THF (1 mL) was added dropwise. A white precipitate of silver chloride formed immediately. THF (0.5 mL) was added and the reaction mixture was stirred for 75 min at room temperature. Silver chloride was then removed by filtration through celite. The solvent was removed under vacuum, the residue was dissolved in dichloromethane and the solution was quickly filtered through glass-fiber paper. Yellow crystals were obtained by layering diethyl ether and pentane over a dichloromethane solution of **5** at −36 °C; yield: 37 mg (57 μmol, 65%).

The compound decomposes rapidly if dissolved in non-coordinating solvents. FT-IR (ATR mode): $\nu = 2920$ (m), 2872 (m), 2828 (m), 1676 (s), 1607 (m), 1485 (s), 1436 (s), 1404 (m), 1299 (s), 1181 (s), 1125 (s), 1029 (m), 959 (m), 838 (m), 715 cm^{-1} (m); ^1H NMR (THF-d_8): $\delta = 7.04$ (m, 4H, aromatic H), 4.74 (m, 2H, CH_{COD}), 3.37 (m, 4H, NCH_2), 2.98 (m, 2H, CH_{COD}), 2.47–2.14 (m, 20H, CH_2 + Mes CH_3), 1.57–1.15 ppm (m, 8H, $CH_{2\ COD}$); ^{13}C NMR (THF-d_8): $\delta = 210.2$ [d, NCN, $^1J(^{103}Rh,^{13}C) =$ 48 Hz], 160.8 [q, CO, $^2J(^{19}F,^{13}C) = 34$ Hz], 143.0, 138.1 (s, aromatic CH), 136.0, 130.8, 129.4 (br, aromatic C), 117.2 [q, CF_3, $^1J(^{19}F,^{13}C) = 292$ Hz], 94.2 [d, CH_{COD}, $^1J(^{103}Rh,^{13}C) = 8$ Hz], 65.6 [d, CH_{COD}, $^1J(^{103}Rh,^{13}C) = 16$ Hz], 48.4 (s, NCH_2), 32.6 (s), 28.2 (s), 21.9 (br), 21.9 (br), 21.0 (s) (CH_2, Mes CH_3), 18.8 (br, $CH_{2\ COD}$); elemental analysis: calcd. for $C_{32}H_{40}F_3N_2O_2Rh$: C 59.63, H 6.25, N 4.35; found: C 59.51, H 6.38, N 4.40.

IrBr(1,3-di(2-propyl)tetrahydropyrimidin-2-ylidene)-(COD) (6)

$[Ir(COD)Cl]_2$ (100 mg, 149 μmol) was dissolved in THF (3 mL). Lithium *tert*-butoxide (69 mg, 863 μmol) was added and the mixture stirred for 30 min. 1,3-Di(2-propyl)-3,4,5,6-tetrahydropyrimidin-1-ium bromide (81 mg, 325 μmol) was added and the reaction mixture stirred for 7 h at 55 °C. The solvent was removed under vacuum. The product was purified by column chromatography on silica gel 60 using dichloromethane:ethanol (250:8) as mobile phase. The product eluted as a yellow band in the first fraction. The product fractions were pooled and evaporated to dryness to afford a yellow solid; yield: 111 mg (202 μmol, 68%). FT-IR (ATR mode): $\nu = 2963$ (m), 2924 (m), 2872 (m), 1501 (s), 1448 (m), 1364 (m), 1307 (s), 1201 (m), 1159 (s), 1077 (s), 1016 (m), 807 cm^{-1} (m); ^1H NMR ($CDCl_3$): $\delta = 6.00$ [hept, 2H, NCH, $^3J(H,H) =$ 6.7 Hz], 4.40 (m, 2H, CH_{COD}), 3.13–2.98 (m, 6H, NCH_2 + CH_{COD}), 2.12 (m, 4H, $CH_{2\ COD}$), 1.90–1.79 (m, 2H, CH_2), 1.68–1.42 (m, 4H, $CH_{2\ COD}$), 1.25 (m, 12H, CH_3); ^{13}C NMR ($CDCl_3$): $\delta = 198.4$ (s, NCN), 79.0 (s, CH_{COD}), 56.5 (s, CH_{COD}), 52.5 (s, NCH_2), 38.3, 33.0, 29.6, 21.1, 20.4, 19.3 (s, CH_2, Mes CH_3, $CH_{2\ COD}$); FABMS: calcd. for $C_{18}H_{33}BrIrN_2$: $m/z =$ 549.02; found: $m/z = 549.0$ [$M + H^+$].

Reaction of 1 with Excess of CF_3COOAg (8)

Compound **1** (50 mg, 88 μmol) was dissolved in THF (1 mL) and the solution was cooled to −36 °C. A chilled solution of silver trifluoroacetate (10 equivs. with respect to **1**) in THF (1 mL) was added dropwise. A white precipitate of silver chloride formed immediately. THF (1 mL) was added and the reaction mixture was stirred for 90 min at room temperature. Silver chloride was then removed by filtration through celite. The solvent was removed under vacuum and the residue was washed with a little diethyl ether. The product was re-dissolved in dichloromethane and the solution was quickly filtered through glass-fiber paper. Yellow crystals were obtained by layering diethyl ether and pentane over the dichloromethane-solution of **8** at −36 °C. Yield: 34 mg (24 μmol, 27%).

The compound decomposes rapidly if dissolved in non-coordinating solvents. FT-IR (ATR mode): $\nu = 2918$ (m), 2849 (m), 1673 (s), 1611 (w), 1516 (m), 1472 (m), 1432 (m), 1376 (w), 1336 (w), 1302 (m), 1188 (s), 1139 (s), 1032 (m), 996 (m), 969 (m), 841 (m), 719 cm^{-1} (m); ^1H NMR (THF-d_8): $\delta = 6.96$ (m, 8H, aromatic H), 4.16 (m, 4H, CH_{COD}), 3.19 [t, 8H, NCH_2, $^3J(H,H) = 5.70$ Hz], 2.66–2.53 (m, 4H, $CH_{2\ COD}$), 2.32 (s, 12 H, Mes-*p*-CH_3), 2.15–2.07 (m, 4H, CH_2), 1.81 (s, 24H, Mes-*o*-CH_3), 1.72–1.66 (m, 4 H, $CH_{2\ COD}$); ^{13}C NMR (THF-d_8): $\delta = 206.3$ [d, NCN, $^1J(^{109}Ag,^{13}C) = 199$ Hz], 206.3 [d, NCN, $^1J(^{107}Ag,^{13}C) = 173$ Hz], 162.9 [q, CO, $^2J(^{19}F,^{13}C) = 35$ Hz], 143.7, 138.8, 135.9, 130.4 (s, aromatic CH), 118.9 [q, CF_3, $^1J(^{19}F,^{13}C) = 288$ Hz], 80.2 [d, CH_{COD}, $^1J(^{103}Rh,^{13}C) = 14$ Hz], 44.4 (br, NCH_2), 31.5 (s), 21.2 (br), 21.1 (br) (CH_2, Mes CH_3), 18.0 (br, CH_{2COD}). Crystals suitable for X-ray analysis were obtained from methylene chloride:diethyl ether:pentane.

Standard Procedure for the Reaction of an Arylboronic Acid with a Carbonyl Compound

The catalyst (for the amount refer to Table 3) and arylboronic acid (0.53 mmol) were dissolved in DME (2.2 mL). Tetradecane (0.7 equivs. with respect to the arylboronic acid) as an internal standard as well as the carbonyl compound (1 equiv. with respect to the arylboronic acid), sodium hydroxide (2 equivs. with respect to the arylboronic acid) and water (0.6 mL) were added. The mixture was stirred at 80 °C until no further conversion was monitored by GC-MS. Diethyl ether was added and the reaction mixture was extracted with water. The organic phases were pooled and dried over sodium sulfate. After evaporating the solvent under vacuum the residue was purified by column chromatography on silica gel 60 using pentane:diethyl ether as mobile phase.

Determination of Yields

All products were characterized by their mol peak and fragmentation in GC-MS. Additionally, all products except (4-fluorophenyl)-(thiophen-2-yl)-methanol were isolated once and characterized by NMR (see Supplementary Information). Standard solutions of these isolated products were used for the calibration of the GC-MS. Together with the measurement of educt conversion both yields and TONs were determined accurately.

X-ray Crystallographic Study of 4 and 8:

Compound **4**: ($C_{30}H_{40}Br_{0.42}Cl_{0.58}IrN_2 \cdot x\ CH_2Cl_2$) triclinic space group $P\bar{1}$ (No. 2), $a = 945.44(3)$ pm, $b = 1288.84$ (5) pm, $c = 1447.55$ (6) pm, $\alpha = 68.690$ (2)°, $\beta = 80.451$ (2)°, $\gamma = 74.681$ (2)°, $V = 1.58008$ (10) nm^3, $Z = 2$, $\rho_{calc} = 1.597$ g cm^{-3}, $T = 233$ (2) K, $\mu = 4.996$ mm^{-1}, Mo-K_α radiation ($\lambda = 71.073$ pm), yellow plate $0.35 \times 0.15 \times 0.03$ mm. 7950 reflections were collected on a Nonius KappaCCD diffractometer with 3994 reflections $> 2\sigma(I)$, $R1 = 0.0305$.

Compound **8**: ($C_{58}H_{68}AgF_9N_4O_6Rh_2$) monoclinic space group $P2_1/n$ (No. 14), $a = 1115.27(2)$ pm, $b = 2076.83$ (2) pm, $c = 2608.33$ (4) pm, $\alpha = 90°$, $\beta = 97.200$ (1)°, $\gamma = 90°$, $V = 5.99384$ (15) nm^3, $Z = 4$, $\rho_{calc} = 1.553$ g cm^{-3}, $T = 233$ (2) K, $\mu = 0.947$ mm^{-1}, Mo-K_α radiation ($\lambda = 71.073$ pm), colorless prism $0.4 \times 0.1 \times 0.1$ mm. 31056 reflections were collected on a Nonius Kappa CCD diffractometer with 8706 reflections $> 2\sigma(I)$, $R1 = 0.0357$.

Both structures were solved and refined using hydrogen atoms calculated with isotropic displacement parameters 1.2 and 1.5 times higher than of the carbon atoms and hydrogen atoms found and refined at the carbon atoms C1, C2, C5, C6. Refinement details: 0.42:0.58 occupation disorder of Br1:Cl1 and 1:1 position disorder of solvent dichloromethane at C25-Cl2-Cl3:C25A-Cl2A-Cl3A in **4**. 7:3 position disorder of the fluorine of one CF_3 group in **8**.

Further crystallographic data for **4** and **8** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 241277 and 241276. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44) 1223–336033; e-mail: deposit@ccdc.cam.ac.uk).

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