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Graphical abstract synopsis

(N-Ru-C)-cycloruthenates are easily prepared at room temperature on reaction of arylimines with [RuCl$_2$(p-cymene)]$_2$ and KOAc in methanol, via ortho arene C-H activation/deprotonation by acetate. The presence of a Ru-Cl remaining bond, instead of a Ru-OAc bond, is crucial for compound isolation. This preparative method was applied to 2-phenyl oxazoline, benzo[h]quinoline, 2-phenylpyridine and 1-phenylpyrazole derivatives.
Cycloruthenation of aryl imines and N-heteroaryl benzenes via C-H bond activation with Ru(II) and acetate partners

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In the memory of professor Alexander Shilov
for his creative and inspiring work on C-H bond activation

Abstract. The reaction of arylimines with [RuCl₂(p-cymene)]₂ and 4 equiv. of KOAc at room temperature in methanol leads to the formation of N-Ru-C cycloruthenates RuCl(arylmine-κC,N)(p-cymene) 3a-3d via ortho C-H activation/deprotonation by acetate. The presence of the stable Ru-Cl bond rather than a labile Ru-OAc bond is crucial for the isolation of the complexes. This preparative method of cyclometallates was applied to 2-phenyl oxazoline, and benzo[h]quinoline and to the improved synthesis of 2-phenylpyridine and 1-phenylpyrazole derivatives. The molecular structures of three cycloruthenates are reported.

Keywords: N-Ru-C cycloruthenates, C-H bond activation, C-H bond deprotonation, arylimines, ruthenium-acetate.

1 Introduction
Since the initial creative work of Alexander Shilov on C-H bond activation of alkanes with Pt(II) and Pt(IV) 1,2 catalysts leading especially to alcohols, 2 many transition metal complexes have been shown to promote the activation of C-H bonds via various processes and to further
lead to catalytic functionalizations of aromatic systems and alkanes. Among these molecular metal catalysts, after the useful contribution of ruthenium(0) species in the Murai reaction, the easily prepared, inexpensive and stable ruthenium(II) complexes are now offering easy and diverse catalytic functionalizations of sp² C-H as well as sp³ C-H bonds.

Ruthenium(II)-catalyzed sp² C-H bond functionalization of functional aromatic compounds has known since 2001 a tremendous development due to the control of direct (hetero)arylation with aryl and heteroaryl halides for the preparation of polyfunctional molecules and polydentate ligands and for the access to polyfunctional alkenes via catalytic alkenylation. For catalytic functionalization of arene C-H bonds the mechanism based on kinetics was shown to be favoured by nitrogen containing functional/directing groups and to take place via an initial, easy ortho C-H bond deprotonation by carbonate only or by carboxylate as a proton shuttle to form a cyclometallated ruthenium(II) intermediate. The oxidative addition of arylhalide to the orthometallacycle followed by the reductive C-C bond formation is a more energy demanding step that can be also performed in water as solvent.

The first preparations of (N,C)-cyclometallated ruthenium(II) complexes were made by transmetallations from mercury salts. Then they were performed more directly by C-H bond deprotonation of N-containing functional arenes as reported by Pfeffer et al. and Davies et al. Thus the cyclometallated ruthenium(II) complexes arising from the deprotonation of arylmethylamines, 1-aminotetralin, and N-containing heterocycles such as phenylpyrrolidine, phenylpyridine, oxazolines, pyrazole were successfully isolated. By contrast the preparation of cycloruthenates of arylimines with ruthenium(II) complexes was not straightforward in spite of the easiness of their Ru(II)-catalyzed ortho arylations. Cationic ruthenium(II) cyclometallated benzylideneanilines PhC(R)=NPh (R = H, Me) were first obtained on reaction with RuCl₂(PMe₃)₃(C₆Me₆)/ 2AgBF₄. By contrast benzodiazepine reacted with [RuCl₂(p-cymene)]₂ and NEt₃ to generate the (N,C)-ruthenacycle involving the benzodiazepine arylimine moiety.

Davies showed that the acetate ligand of RuCl(OAc)(p-cymene) complex could promote the formation at room temperature of (N,C)-cyclometallated complexes from aldimines but only when they contained a N-alkyl group and in the presence of an excess of
benzaldehyde. This methodology could not be used for the preparation of cyclometallated ruthenium(II) complexes from arylideneanilines, which easily led by contrast to their rhodium and iridium cyclometallated derivatives. For the later the regioselectivity of C-H bond deprotonation was shown to be mostly sensitive to steric effects. Orthometallation of aryloxazolines appeared less favorable than that of alkylimines. It occurred only with iridium complexes and not with ruthenium or rhodium derivatives.

The ruthenium(II) catalyzed direct ortho C-H bond diarylations of N-arylimines with arylhalides by action of both acetate and PPh₃ ligands were successfully performed in NMP, and more surprisingly in water with higher activity of the catalyst. The first step of this reaction is expected to be the formation of the orthometallated intermediate via the C-H bond deprotonation, which motivated the search for the conditions to form and isolate the N-aryl imine cycloruthenation intermediates.

We now describe the general and facile access to a variety of cyclometallated ruthenium(II) complexes first of arylimines, following our preliminary report, on reaction with [RuCl₂(p-cymene)]₂ at room temperature in the presence of KOAc in methanol. It will be shown that these complexes are stable when a Ru-Cl bond is retained. This ortho C-H bond activation by deprotonation with acetate can be applied to functional arenes equipped of a nitrogen-containing heterocyclic directing group such as pyridine, pyrazole, oxazoline and benzo[h]quinoline and three of these cyclometallate complexes are characterized by X-ray structure analysis.

2 Experimental
2.1 General
All reagents were obtained from commercial sources and used as received. THF and dichloromethane were dried over Braun MB-SPS-800 solvent purification system, and stored under an argon atmosphere. Methanol (anhydrous, HPLC grade, Aldrich) was used as received. Technical grade petroleum ether (40-60 °C b.p.) and ethyl acetate were used for chromatography column. Analytical TLC was performed on Merck 60F254 silica gel plates (0.25 mm thickness). Column chromatography was performed on Acros Organics Ultrapure silica gel (mesh size 40-60µm, 60A).
$^1$H NMR spectra were recorded in CDCl$_3$ at ambient temperature on Bruker DPX-200, AVANCE I 300, AVANCE III 400 spectrometers at 200.1, 300.1 and 400.1 MHz, using the solvent as the internal standard (CDCl$_3$, 7.26 ppm). $^{13}$C NMR spectra were obtained at 50, 75 and 100 MHz and referenced to the internal solvent signals (CDCl$_3$, central peak at 77.2 ppm). Chemical shift ($\delta$) and coupling constants ($J$) are given in ppm and in Hz, respectively. The peak patterns are indicated as follows: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet, and br. for broad. Infrared spectra were recorded on a Bruker IFS28 spectrometer using KBr pellets. HRMS were measured on Waters Q-TOF 2, at the CRMPO (Centre régional de mesures physiques de l'Ouest), Université de Rennes 1.

2.2 General procedures for the reactions of imines with [RuCl$_2$(p-cymene)]$_2$

[RuCl$_2$(p-cymene)]$_2$ (0.1 mmol, 61.2 mg), imine (0.2 mmol), KOAc (0.4 mmol, 40 mg) and methanol (5 mL) were introduced in a dried Schlenck tube under argon, equipped with magnetic stirring bar and the mixture was stirred at ambient temperature for 20 h. The solvent was then evaporated under vacuum and the desired product was purified by chromatography column on silica gel (0.5 mol% Et$_3$N) with a mixture of petrol ether/ethyl acetate as the eluent.

[RuCl(C$_6$H$_4$-1-C(H)=N(4-CH$_3$C$_6$H$_4$-kC,C,N)}(p-cymene)] (3a)

This compound was prepared from the imine 2a. The complex 3a was purified by chromatography column on silica gel with a mixture of petrol ether/ethyl acetate as the eluent (75:25), and was isolated as an orange solid (83 mg, 90 %). R$_f$ (petroleum ether/EtOAc 70:30) = 0.45.

$^1$H NMR (400 MHz, CDCl$_3$): $\delta$ = 8.20 (d, 1H, $J$ = 7.6 Hz, H$_6$), 8.10 (s, 1H, H$_7$), 7.66 (d, 2H, $J$ = 8.4 Hz, H$_{11}$), 7.54 (d, 1H, $J$ = 7.6 Hz, H$_3$), 7.23-7.17 (m, 3H, H$_{10}$, H$_4$ or H$_5$), 7.02 (t, 1H, $J$ = 7.4 Hz, H$_4$ or H$_5$), 5.48 (d, 1H, $J$ = 6.0 Hz, cymene), 5.22 (d, 1H, $J$ = 6.0 Hz, cymene), 4.87 (d, 1H, $J$ = 6 Hz, cymene), 4.83 (d, 1H, $J$ = 6.0 Hz, cymene), 2.43-2.36 (m, 4H, H$_{13}$, CHMeMe’), 2.08 (s, 3H, Me cymene), 0.99 (d, 3H, $J$ = 6.8 Hz, CHMeMe’), 0.85 (d, 3H, $J$ = 6.8 Hz, CHMeMe’). The protons H$_3$, H$_6$, H$_{10}$ have been assigned from a COSY experiment. $^{13}$C$^1$H$^1$ NMR (100 MHz, CDCl$_3$): $\delta$ = 189.2 (C-Ru), 171.7, 152.8, 146.2, 139.3, 137.3, 130.3, 129.8, 129.4, 122.6, 122.3, 102.5, 100.7, 92.7, 89.6, 82.9, 82.4, 31.0, 23.1, 21.6, 21.3, 18.9. IR: $\nu
(C=N) 1579 cm\(^{-1}\). HRMS (ESI): \(m/z\) calcd for C\(_{24}\)H\(_{26}\)N\(^{35}\)ClNa\(^{102}\)Ru [M+ Na]\(^+\) 488.0695, found 488.0708. \(m/z\) calcd for C\(_{24}\)H\(_{26}\)N\(^{102}\)Ru [M- Cl]\(^+\) 430.1109, found 430.1112.

\[\text{[RuCl\{4-OMeC\(_6\)H\(_4\})-1-C(H)=N(4-CH\(_3\)C\(_6\)H\(_4\)-kC,N\}]\{(p-cymene)\}} (3b)\]

This compound was prepared from the imine 2b (45 mg, 0.2 mmol). The complex 3b was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate as the eluent (70:30), and was isolated as a red solid (77 mg, 77 %). \(R_f\) (petroleum ether/EtOAc 70:30) = 0.30.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 7.97\) (s, 1H, H\(_7\)), 7.72 (d, 1H, \(J = 2.4\) Hz, H\(_6\)), 7.63 (d, 2H, \(J = 8.4\) Hz, H\(_{11}\)), 7.48 (d, 1H, \(J = 8.4\) Hz, H\(_3\)), 7.19 (d, 2H, \(J = 8.4\) Hz, H\(_{10}\)), 6.56 (dd, 1H, \(J = 2.4\) Hz, \(J = 8.4\) Hz, H\(_4\)), 5.44 (d, 1H, \(J = 6.0\) Hz, cymene), 5.18 (d, 1H, \(J = 5.7\) Hz, cymene), 4.83 (m, 2H, cymene), 3.92 (s, 3H, OMe), 2.41-2.35 (m, 4H, H\(_{13}\), C\(_3\)H\(_7\)MeMe'), 2.08 (s, 3H, Me cymene), 0.99 (d, 3H, \(J = 6.9\) Hz, CH\(_{3}\)MeMe'), 0.85 (d, 3H, \(J = 6.9\) Hz, CHMeMe').

\(13\)C\({}\(^{1}\)H\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 191.5\) (C-Ru), 170.2, 160.3, 152.8, 139.7, 136.8, 131.1, 129.3, 123.6, 122.3, 109.0, 102.3, 100.1, 92.4, 89.2, 83.0, 82.2, 55.3, 30.9, 23.1, 21.6, 21.2, 18.9. IR: \(v\) (C=N) 1578 cm\(^{-1}\). HRMS (ESI): \(m/z\) calcd for C\(_{25}\)H\(_{28}\)N\(^{35}\)Cl\(^2\)Na\(^{102}\)Ru [M+ Na]\(^+\) 518.0801, found 518.0817. \(m/z\) calcd for C\(_{25}\)H\(_{28}\)N\(^{102}\)Ru [M- Cl]\(^+\) 460.1212, found 460.1212.

\[\text{[RuCl\{4-CIC\(_6\)H\(_4\})-1-C(H)=N(4-CH\(_3\)C\(_6\)H\(_4\)-kC,N\}]\{(p-cymene)\}} (3c)\]

This compound was prepared from the imine 2c (45.8 mg, 0.2 mmol). The complex 3c was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate as the eluent (75:25), and was isolated as a red solid (52 mg, 52 %). \(R_f\) (petroleum ether/EtOAc 70:30) = 0.65.

\(^1\)H NMR (300 MHz, CDCl\(_3\)): \(\delta = 8.15\) (d, 1H, \(J = 1.8\) Hz, H\(_6\)), 8.06 (s, 1H, H\(_7\)), 7.63 (d, 2H, \(J = 8.1\) Hz, H\(_{11}\)), 7.45 (d, 1H, \(J = 7.8\) Hz, H\(_3\)), 7.22 (d, 2H, \(J = 8.1\) Hz, H\(_{10}\)), 7.01-6.97 (m, 1H, H\(_4\)), 5.47 (d, 1H, \(J = 6.0\) Hz, cymene), 5.22 (d, 1H, \(J = 6.0\) Hz, cymene), 4.90 (d, 1H, \(J = 6.0\) Hz, cymene), 4.85 (d, 1H, \(J = 6.0\) Hz, cymene), 2.42-2.33 (m, 4H, H\(_{13}\), C\(_3\)H\(_7\)MeMe'), 2.10 (s, 3H, Me cymene), 0.98 (d, 3H, \(J = 6.9\) Hz, CH\(_{3}\)MeMe'), 0.85 (d, 3H, \(J = 6.9\) Hz, CHMeMe').

\(13\)C\({}\(^{1}\)H\) NMR (75 MHz, CDCl\(_3\)): \(\delta = 190.5\) (C-Ru), 170.8, 152.5, 144.5, 138.5, 137.6, 136.0, 130.4, 129.5, 123.0, 122.2, 103.1, 100.9, 92.9, 89.4, 83.7, 82.6, 31.0, 23.0, 21.7, 21.3, 19.0. IR: \(v\) (C=N) 1578 cm\(^{-1}\). HRMS (ESI): \(m/z\) calcd for C\(_{25}\)H\(_{28}\)NO\(^{35}\)Cl\(^2\)Na\(^{102}\)Ru [M+ Na]\(^+\) 518.0801, found 518.0817. \(m/z\) calcd for C\(_{25}\)H\(_{28}\)N\(^{102}\)Ru [M- Cl]\(^+\) 460.1212, found 460.1212.

\[\text{[RuCl\{C\(_6\)H\(_4\})-1-C(CH\(_3\))=N(4-OCH\(_3\)C\(_6\)H\(_4\)-kC,N\}]\{(p-cymene)\}} (3d)\]

This compound was prepared from the imine 2d (45 mg, 0.2 mmol). The complex 3d was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl
acetate (70:30) as the eluent, and was isolated as a red solid (72 mg, 73 %). Rf (petroleum ether/EtOAc 70:30) = 0.35

1H NMR (300 MHz, CDCl₃): δ = 8.20 (d, 1H, J = 7.5 Hz, H₃ or H₆), 7.46 (d, 1H, J = 7.5 Hz, H₃ or H₆), 7.30-7.18 (m, 3H, H₁₁, H₄ or H₅), 7.05-6.96 (m, 3H, H₁₀, H₄ or H₅), 5.33 (d, 1H, J = 6.0 Hz, cymene), 4.95 (d, 1H, J = 6.0 Hz, cymene), 4.63 (d, 2H, J = 6.0 Hz, cymene), 3.91 (s, 3H, OMe), 2.57-2.48 (m, 1H, CH₂MeMe’), 2.27 (s, 3H, H₁₄), 2.02 (s, 3H, Me cymene), 1.01 (d, 3H, J = 6.9 Hz, CHMeMe’), 0.83 (d, 3H, J = 6.9 Hz, CHMeMe’).

13C{¹H} NMR (100 MHz, CDCl₃): δ = 188.3 (C-Ru), 179.6, 157.8, 147.4, 146.4, 139.3, 130.1, 128.3, 121.9, 116.5, 114.8, 102.9, 102.6, 92.8, 90.4, 80.3, 80.2, 55.6, 30.8, 23.0, 21.3, 18.8, 16.9. IR: ν (C=N) 1578 cm⁻¹. HRMS (ESI): m/z calcd for C₂₅H₂₈NO₃₅ClNa₁₀₂Ru [M+ Na]⁺ 518.0801, found 518.0811. m/z calcd for C₂₅H₂₈NO₁₀₂Ru [M- Cl]⁺ 460.1214, found 460.1211.

2.3 Reaction of 2-phenyl-2-oxazoline with [RuCl₂(p-cymene)]₂: preparation of complex 5.

This compound was prepared from 2-phenyl-2-oxazoline 4 (0.2 mmol, 26.3 µL). The desired complex 5 was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (30:70) as the eluent, and was isolated as a green solid (32.7 mg, 40%). Rf (petroleum ether/EtOAc 30:70) = 0.25

1H NMR (300 MHz, CDCl₃): δ = 8.15 (d, 1H, J = 7.5 Hz, H₃ or H₆), 7.35 (d, 1H, J = 7.5 Hz, H₃ or H₆), 7.22 (t, 1H, J = 7.5 Hz, H₄ or H₅), 6.98 (t, 1H, J = 7.5 Hz, H₄ or H₅), 5.56 (d, 1H, J = 5.7 Hz, cymene), 5.46 (d, 1H, J = 5.7 Hz, cymene), 5.19 (d, 1H, J = 5.7 Hz, cymene), 4.99 (d, 1H, J = 5.7 Hz, cymene), 4.78-4.67 (m, 2H, H₁₄), 4.26-4.08 (m, 2H, H₁₁), 2.06 (s, 3H, Me cymene), 1.10 (d, 3H, J = 6.9 Hz, CHMeMe’), 1.00 (d, 3H, J = 6.9 Hz, CHMeMe’).

13C{¹H} NMR (75 MHz, CDCl₃): δ = 182.7 (C-Ru), 174.2, 139.3, 130.9, 130.7, 126.4, 122.3, 101.3, 99.3, 88.1, 87.5, 81.8, 81.0, 70.8, 54.4, 31.2, 22.8, 22.2, 19.1. IR: ν (C=N) 1632 cm⁻¹. HRMS (ESI): m/z calcd for C₁₉H₂₂NO₃⁵ClNa₁₀₂Ru [M+ Na]⁺ 440.0331, found 440.0336; m/z calcd for C₁₉H₂₂NO₁₀₂Ru [M- Cl]⁺ 382.0745, found 482.0755.

2.4 Reaction of benzo[h]quinoline with [RuCl₂(p-cymene)]₂ : preparation of complex 7.

This compound was prepared from benzo[h]quinolone 6 (0.2 mmol, 35.8 mg). The desired complex 7 was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (50:50) as the eluent, and was isolated as a dark green solid (41.9 mg, 47 %). Rf (petroleum ether/EtOAc 1:1) = 0.20.

1H NMR (300 MHz, CDCl₃): δ = 9.48 (d, 1H, J = 5.1 Hz, H₂), 8.41 (d, 1H, J = 6.9 Hz), 8.18 (d, 1H, J = 7.8 Hz), 7.78 (d, 1H, J = 8.7 Hz), 7.63-7.42 (m, 4H), 5.74 (d, 1H, J = 5.7 Hz, cymene), 5.66 (d, 1H, J = 6.0 Hz, cymene), 5.30 (d, 1H, J = 6.0 Hz, cymene), 5.13 (d, 1H, J = 6.0 Hz, cymene), 2.50 (m, 1H, CHMeMe’), 2.04 (s, 3H, Me cymene), 0.97 (d, 3H, J = 6.9 Hz,
CHMeMe’), 0.84 (d, 3H, J = 6.9 Hz, CHMeMe’). \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (75 MHz, CDCl\(_3\)): \(\delta = 178.4\) (C-Ru), 155.3, 152.5, 140.5, 136.6, 135.4, 133.9, 129.7, 129.3, 126.9, 122.8, 121.1, 120.9, 101.5, 99.6, 89.7, 89.3, 83.6, 82.5, 30.9, 22.7, 21.8, 18.9. \(\text{HRMS (ESI): } m/z \text{ calcd for } C_{23}H_{22}N_3S\text{Ru} [\text{M+ Na}]^+ 472.0382, \text{ found } 472.0390.\) \(m/z \text{ calcd for } C_{23}H_{22}N_3S\text{Ru} [\text{M- Cl}]^+ 414.0796, \text{ found } 414.0797.\)

### 2.5 Reaction of 2-Phenylpyridine with \([\text{RuCl}_2(p\text{-cymene})_2]\) : preparation of complex 9,\(^{113, 18b}\)

This compound was prepared from 2-phenylpyridine 8 (0.2 mmol, 29 µL). The desired complex 9 was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (30:70) as the eluent, and isolated as a dark green solid (81 mg, 94 %). \(R_f\) (petroleum ether/EtOAc 30:70) = 0.35.

\(^1\text{H} \text{NMR}\) (400 MHz, CDCl\(_3\)): \(\delta = 9.16\) (d, 1H, \(J = 5.2\) Hz, H\(_{12}\)), 8.09 (d, 1H, \(J = 7.6\) Hz, H\(_3\)), 7.65-7.53 (m, 3H, H\(_9\), H\(_{10}\), H\(_6\)), 7.11 (t, 1H, \(J = 7.2\) Hz, \(J = 7.2\) Hz, H\(_4\)), 6.99-6.94 (m, 2H, H\(_5\), H\(_{11}\)), 5.52-5.48 (m, 2H, cymene), 5.10 (d, 1H, \(J = 5.6\) Hz, cymene), 4.91 (d, 1H, \(J = 5.6\) Hz, cymene), 2.37 (sept, 1H, \(J = 6.8\) Hz, C\(_H\)MeMe’), 1.98 (s, 3H, Me cymene), 0.91 (d, 3H, \(J = 6.8\) Hz, CHMeMe’), 0.81 (d, 3H, \(J = 6.8\) Hz, CHMeMe’). \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (100 MHz, CDCl\(_3\)): \(\delta = 181.5\) (C-Ru), 165.4, 154.7, 143.5, 139.7, 136.7, 129.5, 124.0, 122.6, 121.5, 118.9, 100.8, 100.6, 90.9, 89.7, 84.3, 82.3, 30.9, 22.6, 21.8, 18.9.

### 2.6 Reaction of 1-phenyl-1\(H\)-pyrazole with \([\text{RuCl}_2(p\text{-cymene})_2]\) : preparation of complex 11,\(^{18d}\)

This compound was prepared from 1-phenyl-1\(H\)-pyrazole (0.2 mmol, 26.4 µL). The desired complex 10 was purified by chromatography column on silica gel with a mixture of petroleum ether/ethyl acetate (30:70) as the eluent, and was isolated as a greenish solid (65.0 mg, 79 %) \(R_f\) (petroleum ether/EtOAc 30:70) = 0.40.

\(^1\text{H} \text{NMR}\) (300 MHz, CDCl\(_3\)): \(\delta = 8.15\) (d, 1H, \(J = 7.2\) Hz, H\(_6\)), 8.06 (d, 1H, \(J = 2.1\) Hz, H\(_{11}\)), 7.91 (d, 1H, \(J = 2.7\) Hz, H\(_3\)), 7.19-7.01 (m, 3H, H\(_3\), H\(_4\), H\(_5\)), 6.47 (t, 1H, \(J = 2.7\) Hz, H\(_{10}\)), 5.57 (d, 2H, \(J = 6.0\) Hz, cymene), 5.30 (d, 1H, \(J = 6.0\) Hz, cymene), 5.09 (d, 1H, \(J = 6.0\) Hz, cymene), 2.47-2.44 (sept, 1H, \(J = 6.9\) Hz, CHMeMe’), 2.47 (s, 3H, Me cymene), 0.97 (d, 3H, \(J = 6.9\) Hz, CHMeMe’), 0.93 (d, 3H, \(J = 6.9\) Hz, CHMeMe’). \(^{13}\text{C}\{^1\text{H}\} \text{NMR}\) (75 MHz, CDCl\(_3\)): \(\delta = 161.9\) (C-Ru), 142.2, 141.9, 140.2, 126.1, 125.0, 123.2, 113.5, 108.4, 100.09, 100.08, 88.7, 88.2, 84.2, 82.2, 30.7, 22.5, 22.0, 18.9.

### 2.7 Preparation of complex 12

\([\text{RuCl}_2(p\text{-cymene})_2]\) (0.1 mmol, 61.2 mg), 1-phenyl-1\(H\)-pyrazole (0.2 mmol, 26.4 µL), diphenylacetylene (0.2 mmol, 35.6 mg), KOAc (0.4 mmol, 40 mg) and methanol (5 mL) were...
introduced in a dried Schlenck tube under Argon, equipped with magnetic stirring bar and was stirred at ambient temperature for 20 h. The solvent was then evaporated under vacuum and the desired product was purified by chromatography column on silica gel with a mixture of petrol ether/ethyl acetate (1:1) as the eluent. The complex \(12^{18e}\) was isolated as a dark green solid in 67% (79.3 mg).

\[\text{\textsuperscript{1}H NMR (300 MHz, CDCl}_3\): } \delta = 8.59 (d, 1H, \textit{J} = 1.5 \text{ Hz, H}_{11}), 7.88 (d, 1H, \textit{J} = 1.5 \text{ Hz, H}_5), 7.39-7.14 (m, 7H), 6.97-6.87 (m, 4H), 6.81-6.74 (m, 3H), 6.52 (t, 1H, \textit{J} = 2.4 \text{ Hz, H}_{10}), 5.57 (d, 1H, \textit{J} = 5.1 \text{ Hz, cymene}), 4.66 (d, 1H, \textit{J} = 5.1 \text{ Hz, cymene}), 4.52 (d, 1H, \textit{J} = 5.1 \text{ Hz, cymene}), 3.51 (d, 1H, \textit{J} = 5.1 \text{ Hz, cymene}), 2.83 (sept, \textit{J} = 6.9 \text{ Hz, CHMeMe'}, 2.47 (s, 3H, \text{ Me cymene}), 1.25 (d, 3H, \textit{J} = 6.9 \text{ Hz, CHMeMe').} \]

\[\text{\textsuperscript{13}C\{\textsuperscript{1}H\} NMR (75 MHz, CDCl}_3\): } \delta = 183.3 (C-Ru), 152.5, 146.7, 146.0, 144.1, 137.7, 137.5, 133.4, 131.6, 128.5, 128.2, 127.2, 126.3, 125.9, 125.5, 124.7, 123.1, 110.3, 107.8, 103.8, 96.4, 81.1, 78.9, 75.3, 31.4, 23.6, 23.2, 19.6.\]

2.8 Catalytic arylation of imine 2a with Ru(II)-OAc catalytic system in NMP

[RuCl\(_2\)(p-cymene)]\(_2\) (0.025 mmol, 15.3 mg), KOAc (0.1 mmol, 10 mg) and K\(_2\)CO\(_3\) (1.5 mmol, 208 mg) were introduced in a dried Schlenck tube under argon, equipped with magnetic stirring bar. Imine 2a (0.5 mmol), phenylbromide (1.25 mmol), NMP (2 mL) and tetradecane (10 \(\mu\)L) as the internal standard for gas chromatography, were added in the Schlenck tube which was then placed in the oil bath at 160 \(^\circ\)C. The reaction mixture was stirred for the specified time. Then, the conversion of the reaction was analyzed by gas chromatography. The reaction mixture was diluted with 30 mL of diethyl ether, washed with water (20 mL \(\times\) 3), and dried over MgSO\(_4\). The solvent was then evaporated under vacuum and the desired product was purified by chromatography using a silica gel column. The solvent was then evaporated under vacuum and the product was purified by chromatography using a silica gel column. The silica gel was previously stirred for 1h in 200 mL of petroleum ether containing 1 mol% Et\(_3\)N (99:1). The products were eluted with a mixture of petroleum ether/ethyl acetate. The product was thus obtained and the mono and diarylated products ratio was determined by \(\text{\textsuperscript{1}H NMR}.\]

\[\text{N-[(o,o'}'-\text{Diphenyl)benzylidene]-p-toluidine (14)\]}

Green solid, yield = 75%, \[\text{\textsuperscript{1}H NMR (200 MHz, CDCl}_3\): } \delta = 8.36 (s, 1H), 7.61-7.40 (m, 13H), 7.10 (d, 2H, \textit{J} = 8.2 \text{ Hz}), 6.62 (d, 2H, \textit{J} = 8.1 \text{ Hz}), 2.33 (s, 3H). \]

\[\text{\textsuperscript{13}C NMR (50 MHz, CDCl}_3\): } \delta = 161.0, 150.0, 143.0, 141.5, 135.7, 134.3, 130.5, 130.15, 129.9, 129.5, 128.5, 127.5, 120.60, 21.38. \]

GC: \(t_R = 30.5 \text{ min. MS (EI): } m/z: 346 (100, M^+ - H), 254 (16), 241 (15), 91 (10), 65 (11); HRMS (ESI): m/z calcd for C\(_{28}\)H\(_{21}\)N (M+ H\(^+\)) 348.1746, found 348.1742.\]
2.8 X-ray crystallography

Crystals of complexes 3a, 3b and 7 were mounted on Bruker APEX2 single crystal X-ray diffractometer using monochromated Mo Kα radiation (λ = 0.71073Å). The structures were solved by direct methods using the program SHELXS-97. Refinement and all further calculations were carried out using SHELXL-97. The H-atoms were included in calculated positions and treated as riding atoms using the SHELXL default parameters. The non H atoms were refined anisotropically, using weighted full-matrix least-square on F². Figures of complexes 3a, 3b and 7 were drawn with ORTEP.

3 Results and discussion

3.1 Synthesis of [RuCl(aryl imine)(p-cymene)] complexes 3a-3d

The reaction of the [RuCl₂(p-cymene)]₂ complex 1 was first performed with 2 equivalents of aldimine 2a in the presence of various amounts of KOAc and K₂CO₃ in THF or methanol as an attempt to produce cyclometallated complex 3a. The choice of solvent is crucial as with 2 equiv. of KOAc no transformation was observed in THF, but in methanol at room temperature 36% of complex 3a were formed. The increase to 4 equiv of KOAc led to the complete formation of the orange complex 3a which was isolated in 90% yield after 20h at room temperature (Scheme 1). It is noteworthy that the addition of K₂CO₃ disfavoured the formation of 3a and this is consistent with the kinetic studies of the reaction of Ru(OAc)₂(arene) with 2-phenylpyridine and 1-phenylpyrazole showing that the reaction was autocatalysed by the freed AcOH, and thus that the rate of ortho C-H bond activation was decreased by K₂CO₃. Only 10% yield of complex 3a was obtained in water as solvent likely due to the low solubility of the ruthenium complex 1 and substrates in water. The cycloruthenation of substituted aryl imines 2b-d with [RuCl₂(p-cymene)]₂ 1 in methanol in the presence of 4 equiv. of KOAc at room temperature for 20 h led to the isolation of red complexes 3b (77%), 3c (52%), and 3d in 73% isolated yields (Scheme 1). The structure of 3a-3d was based on ¹H, ¹³C NMR and the X-ray struture analysis of compounds 3a and 3b.
The ruthenium complex 3a, or its analogous derivative with a Ru-OAc bond instead of a Ru-Cl bond, was not detected in the reaction of Ru(OAc)$_2$(p-cymene) and aryl imine 2a. However the unstable cyclometallate arising from the interaction of 2-phenyl pyridine with Ru(OAc)$_2$(p-cymene) at 27°C in acetonitrile was observed. Thus the aryl imine 2a was reacted with Ru(OAc)$_2$(p-cymene) in methanol but in the presence of one equiv. of KCl and then 66% yield of the complex 3a was isolated (Scheme 2). This result shows that the complex 3a containing a Ru–Cl bond is more stable than its parent compound containing the Ru–OAc bond.

This result, along with the formation of complexes 3a–3d from complex 1 or in situ formed Ru(OAc)$_2$(p-cymene) complex, also shows that the Ru(II)-OAc bonds easily dissociate leading to free external anion OAc$^-$ which is able to deprotonate, on cooperative action of the Ru(II) centre, the neighbour ortho C-H bond of the substrate coordinated to this Ru(II) centre.\textsuperscript{13,14}
3.2 Synthesis of \([\text{RuCl}(\text{N-containing heterocycle})(\text{p-cymene})]\) complexes 5, 7, 9 and 11.

The previous mild conditions for cyclometallation of aryl imines, with \([\text{RuCl}_2(\text{p-cymene})]_2\) in the presence of excess KOAc at room temperature, led us to apply this method for the synthesis and isolation of cycloruthenate complexes from arenes possessing a nitrogen containing heterocycle as directing group. Thus the heterocycle 2-phenyloxazoline 4 was reacted with \([\text{RuCl}_2(\text{p-cymene})]_2\) in the presence of 4 equiv. of KOAc in methanol at room temperature and led to the formation of the green complex \([\text{RuCl}(\text{o-C}_6\text{H}_4-2\text{-oxazoline})(\text{p-cymene})]_5\), which was isolated in 40% (Scheme 3).

The related complex with Ru-OAc bond was observed during the kinetic study of Ru(OAc)\(_2\)(p-cymene) with the same oxazoline derivative 4 in acetonitrile,\(^{14}\) which was shown not to be stable as it readily led to the dissociation of the Ru-OAc bond and to the formation of the complex \([\text{Ru(NCCD}_3)(\text{o-C}_6\text{H}_4-2\text{-oxazoline})(\text{p-cymene})]^+\)(AcO\(^-\)) in the absence of chloride anion and then to \([\text{Ru(NCCD}_3)_4(\text{o-C}_6\text{H}_4-2\text{-oxazoline})]^+\)(AcO\(^-\)) by displacement of the arene.

The heterocycle benzo[h]quinoline 6 was also reacted with \([\text{RuCl}_2(\text{p-cymene})]_2\) \(1\) in methanol under the same conditions and afforded to the green cyclometallated complex 7 isolated in 47% (Scheme 3).

We applied the above conditions to the synthesis of the known dark green cycloruthenate complex 9 arising from 2-phenyl pyridine 8. Indeed 2-phenyl pyridine 8 readily reacts in methanol with \([\text{RuCl}_2(\text{p-cymene})]_2\) \(1\) to afford the dark green complex 9 isolated in 94% yield.
This cyclometallate complex 9 was previously prepared by A. Jutand et al. via the cyclometallation of 2-phenylpyridine with \([\text{RuCl}_2(p\text{-cymene})]_2\) in the presence of KOAc in CH\(_3\)CN,\(^\text{13}\) and by Davies et al. with an excess of NaOAc in dichloromethane (61%).\(^\text{18b}\) This complex 9 is very stable with respect to its analogous complex containing a Ru-OAc bond.

\[
\text{Scheme 3 Cycloruthenation of aryl N-containing heterocycles with } [\text{RuCl}_2(p\text{-cymene})]_2
\]

The reaction of 1-phenylpyrazole 10 with Ru(OAc)\(_2\)(p-cymene) was studied in details in acetonitrile and shown to give at 27°C the orthometallate \([\text{Ru(OAc)}(o\text{-C}_6\text{H}_4\text{-2-NNC}_3\text{H}_3)(p\text{-cymene})]\).\(^\text{14}\) Thus 1-phenylpyrazole 10 was also reacted with \([\text{RuCl}_2(p\text{-cymene})]_2\) with 4 equiv. KOAc in methanol and the green cyclometallated ruthenium(II) complex 11 was formed and isolated in 79% yields (Scheme 3). The complex 11 was previously prepared by Davies et al. from the reaction of \([\text{RuCl}_2(p\text{-cymene})]_2\) and 1-phenylpyrazole in the presence of an excess of NaOAc in dichloromethane (64%).\(^\text{18d}\)

Thus the above results show that arenes containing a functional imine group and a
nitrogen functional group easily react with [RuCl₂(p-cymene)]₂ in methanol with 4 equiv of KOAc at room temperature to produce isolable cycloruthenate [RuCl(o-C₆H₄-N-heterocycle)(p-cymene)] in a good yield. It contrasts with their ready reaction with Ru(OAc)₂(p-cymene) which leads to unstable [Ru(OAc)(o-C₆H₄-N-heterocycle)(p-cymene)] complex with labile Ru-OAc bond. These reactions definitely point out the key role of acetate or carboxylate in general for the deprotonation of ortho arene C-H bonds.

### 3.3 Characterization of the Ru(II)-cyclometallated complexes
The ¹H NMR spectrum of 3a shows the cyclometallated phenyl H⁶ and H³ protons as two inequivalent doublets at δ = 8.20 ppm and δ = 7.54 ppm, respectively, and that the CH=N proton gives a singlet at δ = 8.10 ppm. (Fig. 1) The isopropyl group of the p-cymene is observed as two inequivalent doublets at δ = 0.85 ppm and at δ = 0.99 ppm, and the four aromatic protons of the p-cymene are observed as inequivalent doublets between δ = 4.83 and 5.49 ppm as expected for a p-cymene ligand in a chiral-at-metal Ru-(II) complex centre.

![Fig. 1. Labeling of complexes 3a protons](image)

The ¹H NMR spectra of ruthenium complexes 3b and 3c are similar to that of 3a except that the phenyl H⁶ proton was observed as a doublet at δ = 7.71 ppm or δ = 8.15 ppm for 3b or 3c, respectively. The H⁴ and H³ protons were observed as two doublets at δ = 6.54 ppm and δ = 7.46 ppm for 3b, at δ = 7.21 ppm and δ = 7.43 ppm for 3c. The ¹H NMR spectrum of ruthenium complex 3d is similar to that of 3a except that the C-CH₃ protons in p-cymene were observed as a singlet at δ = 2.27 ppm.
The $^1$H NMR spectrum of complex 5 clearly shows that coordination and cyclometallation of the ligand has occurred. The CH$_2$-N protons and CH$_2$-O protons were observed as multiplets between $\delta = 4.08$ and $\delta = 4.78$ ppm. The H$_2$ proton was observed as a doublet at $\delta = 8.14$ ppm. The $^1$H NMR spectrum of complex 7 shows for the H$_2$ proton a doublet at $\delta = 9.46$ ppm. The $^1$H NMR spectrum of complex 9 showed that the CH=N proton is shifted to a lower field at $\delta = 9.20$ ppm as compared to that of the free ligand $\delta = 8.72$ ppm. The signals for the $p$-cymene ligand in complexes 5, 7, 9, and 11 revealed that they are coordinated in a chiral ruthenium complex.

In the $^{13}$C NMR spectra, the expected number of carbons can be seen and the metallated carbon atoms of cyclometallated ruthenium(II) imine complexes 3a-3d are observed at 189.2, 191.5, 190.5 and 188.3 ppm, respectively, at more lower field than that of cyclometallated ruthenium(II) heterocycle complexes 5, 7, 9 and 11 (182.7, 178.4, 181.5 and 161.9 ppm). The CH=N carbon of complexes 3a, 3b, 3c are observed at 8.10, 7.97 and 8.06 pm, respectively. The $\nu$(C=N) free imine of 2a absorption at 1621 cm$^{-1}$ decreases to 1579 cm$^{-1}$ as expected by coordination of the aryl aldimine nitrogen in complex 3a.

3.4 X-ray structure analysis of complexes 3a, 3b and 7.

Crystal of 3a, 3b and 7, obtained from EtOH/EtOAc solvents, were suitable for X-ray diffraction. The ORTEP view of complexes 3a, 3b and 7 are shown in Fig. 2.

The summary of the data collection and refinement parameters are given in Table 1 whereas selected bond lengths and bond angles are given in Table 2. Each of the structure of 3a, 3b and 7 shows the expected piano stool geometry. As to be seen in Table 1, the Ru-Cl bond lengths of imine complexes 3a and 3b (2.4161(4) Å and 2.4183(6) Å) appeared slightly longer than that of benzo[h]quinoline complex 7 (2.3999(11) Å), and the same observation was made for the Ru-C bond lengths. However the Ru-N bonds of imine complexes 3a and 3b (2.1115(15) Å and 2.0966(19) Å) are longer than that of complex 7 (2.0883(3) Å). On the other hand, the chelate bite angles C-Ru-Cl and Cl-Ru-N appear slightly larger in more flexible arylimine cyclometallated ruthenium(II) complexes 3a and 3b than for the rigid cyclometallated benzo[h]quinoline in complex 7 (Table 1).
Fig. 2 Molecular structure and atom numbering scheme for 3a, 3b and 7 with 50% displacement ellipsoids, all H atoms are omitted for clarity.

Table 1. Selected bond distances and angles of complexes 3a, 3b and 7

<table>
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<th>Complex</th>
<th>bond distances (Å)</th>
<th>angles (°)</th>
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<td>Ru-C</td>
<td>Ru-N</td>
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<tr>
<td>3a</td>
<td>2.0463(17)</td>
<td>2.1115(15)</td>
</tr>
<tr>
<td>3b</td>
<td>2.048(2)</td>
<td>2.0966(19)</td>
</tr>
<tr>
<td>7</td>
<td>2.054(4)</td>
<td>2.088(3)</td>
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Table 2. Crystallographic data for 3a, 3b and 7

<table>
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<tr>
<th>Complex</th>
<th>3a</th>
<th>3b</th>
<th>7</th>
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<tbody>
<tr>
<td>Empirical formula</td>
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<td>C_{25}H_{28}CINORu</td>
<td>C_{23}H_{22}CINRu</td>
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<td>Formula weight</td>
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<td>150(2)</td>
<td>150(2)</td>
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<tr>
<td>λ(Å)</td>
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<td>0.71073</td>
<td>0.71073</td>
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<td>Crystal system</td>
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<td>Orthorhombic</td>
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### Crystallographic Data

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<td>Orange, prism</td>
<td>Orange, prism</td>
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<td>Crystal size (mm)</td>
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<td>0.47 × 0.43 × 0.26</td>
<td>0.43 × 0.15 × 0.08</td>
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<td>P 2₁/n</td>
<td>P c a b</td>
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<td>a (Å)</td>
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<td>11.7681(12)</td>
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<tr>
<td>b (Å)</td>
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<td>7.7852(9)</td>
<td>14.829(2)</td>
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<tr>
<td>c (Å)</td>
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<td>90</td>
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<tr>
<td>β (°)</td>
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<td>γ (°)</td>
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<td>90</td>
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<tr>
<td>V (Å³)</td>
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<td>2265.6(4)</td>
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<td>4</td>
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<td>5114 (0.0520)</td>
<td>4167 (0.0478)</td>
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<td>5114 / 0 / 267</td>
<td>4167 / 0 / 238</td>
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<td>Goodness-of-fit on F²</td>
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<tr>
<td>Final R indices</td>
<td>R₁=0.0230, wR₁=0.0538</td>
<td>R₁=0.0291, wR₁=0.0715</td>
<td>R₁=0.0584, wR₁=0.0974</td>
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<td>[I&gt;2σ(I)]</td>
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<td></td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R₁=0.0262, wR₁=0.0553</td>
<td>R₁=0.0324, wR₁=0.0735</td>
<td>R₁=0.0584, wR₁=0.1023</td>
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<td>Largest diff. peak and hole (e. Å³)</td>
<td>0.451 and -0.399</td>
<td>0.416 and -0.581</td>
<td>2.024 and -1.231</td>
</tr>
</tbody>
</table>

### 3.5 One pot Ru(II) cyclometallation of 1-phenylpyrazole and alkyne insertion

The insertion of an alkyne into a cycloruthenate Ru-C bond is not straightforward,¹⁸ᵃ thus we attempted the direct reaction of the heterocycle 10 with complex 1 and KOAc, under the cyclometallation formation conditions but in the presence of one equivalent of diphenylacetylene in methanol. This reaction led directly to the formation of the complex 12, which was isolated in 67% yield after 20 h at room temperature, and corresponds to the insertion product of the alkyne into the cyclometallated C-Ru bond of intermediate 11, (Scheme 4). This complex was previously obtained by Davies by insertion of diphenylacetylene into the complex 11 and obtained in 42%.¹⁸ᵃ Our results in Scheme 4 show that alkyne insertion complex can be synthesized more efficiently directly from...
phenylpyrazole, alkyne and ruthenium complex 1 than via two steps: the cyclometallation followed by the alkyne insertion.\textsuperscript{18a} Whereas in \textsuperscript{13}C NMR the (C\textsubscript{1}-Ru) carbon singlet of 11 is at $\delta$ 161.9 ppm, for the new cyclometallated complex 12 the =C(Ph)-Ru carbon atom appears as a singlet at $\delta$ = 183.3 ppm. It is suggested that the alkyne insertion takes place on reaction with the in situ generated Ru-OAc containing intermediate, analogous to 11, instead of insertion into the Ru-C bond of the 18 electrons complex 11. The easy Ru-OAc bond dissociation should allow the alkyne coordination and insertion, before final exchange of the acetate by chloride leading to the stable Ru-Cl bond and complex 12.

![Scheme 4. Ruthenium(II) cyclometallation of 1-phenylpyrazole with diphenylacetylene](image)

### 3.6 From stoichiometric to catalytic diarylation of aryl imines

The synthesis of cyclometallated ruthenium(II) imine complexes 3 after ortho C-H bond activation via C-H deprotonation led us to search for the functionalization of the (Ru-C) carbon of a cyclometallated aryl imine with aryl halide. First we showed that the reaction of cyclometallated ruthenium(II) complex 3a with 2 equiv. of arylbromide required the presence of acetate and thus the reaction was performed in the presence of 2 equiv. of KOAc, 2 equiv. of K\textsubscript{2}CO\textsubscript{3} in NMP at 130°C for 24 h. Under these conditions 85% GC-yield of mixed-arylated imines were formed with the ratio of mono-/di- arylated compound of 60:40. (Scheme 5)

![Scheme 5. Catalytic diarylation of aryl imines](image)
Scheme 5 Reaction of cyclometallated complex 3a with phenyl bromide

Based on this result, we have searched for the direct catalytic diarylation of imine 2a with phenyl bromide by using in situ generated ruthenium(II)-carboxylate catalyst (Table 3). Whereas [RuCl₂(p-cymene)]₂ 1 alone in NMP at 120 °C for 48 h gives as expected a low conversion of 45%, the ruthenium complex 1 with 2 equiv. KOAc per Ru atom leads to 85 % conversion (Table 3, entries 1, 2). With in situ prepared Ru(OAc)₂(p-cymene) in NMP the reaction needed to be performed at 160 °C for 48 h to reach complete diarylation (entry 3, 4, 5) and the diarylated imine 14 was isolated in 75 % yield (entry 4). NMP appeared to be the best solvent for this transformation as DMAc and DCE could not improve the conversion into diarylated imine 14 under similar conditions (entries 6, 7). The above observations led us to explore favourable conditions and scope for catalytic diarylation of arylimines.

Table 3 Optimisation for the direct arylation of aldimine 2a with Ru(II)/KOAc catalytic system.[a]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Additives (mol%)</th>
<th>Time (h)</th>
<th>Temp (°C)</th>
<th>Conv. (%)</th>
<th>Mono/di 13/14</th>
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</thead>
<tbody>
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<td>1</td>
<td>NMP</td>
<td>-</td>
<td>48</td>
<td>120</td>
<td>45</td>
<td>14:86</td>
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<tr>
<td>2</td>
<td>NMP</td>
<td>KOAc(20)</td>
<td>48</td>
<td>120</td>
<td>85</td>
<td>15:85</td>
</tr>
<tr>
<td>3</td>
<td>NMP</td>
<td>KOAc(20)</td>
<td>48</td>
<td>140</td>
<td>90</td>
<td>10:90</td>
</tr>
<tr>
<td>4</td>
<td>NMP</td>
<td>KOAc(20)</td>
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<td>160</td>
<td>100(75)²</td>
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<tr>
<td>5</td>
<td>NMP</td>
<td>KOAc(20)</td>
<td>24</td>
<td>160</td>
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<td>6</td>
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<td>KOAc(20)</td>
<td>48</td>
<td>160</td>
<td>88</td>
<td>15:85</td>
</tr>
<tr>
<td>7</td>
<td>DCE</td>
<td>KOAc(20)</td>
<td>48</td>
<td>120</td>
<td>20</td>
<td>40:60</td>
</tr>
</tbody>
</table>

[a] Imine (0.5 mmol), PhBr (1.25 mmol), [RuCl₂(p-cymene)]₂ (5 mol%), additives, 3 equiv K₂CO₃, solvent (2 mL), 10 µL of tetradecane as the internal standard. [b] Conversion of imine. [c] in parenthesis, isolated yields of purified purified diarylated product 14.
4 Conclusion
We have described the easy preparation of new cyclometallated N-containing ruthenium(II) complexes especially derivatives of aryl imines, 2-phenyl oxazoline, benzo[h]quinoline and the improved synthesis of cycloruthenate derivatives of 2-phenylpyridine and 1-phenylpyrazole via C-H bond activation via deprotonation simply with KOAc at room temperature in methanol. X-ray struture analysis of complexes 3a, 3b and 7 confirmed the struture of the cyclic N-Ru-C complexes and show the expected piano stool geometry and chirality-at-metal of the complexes. We have shown the efficient diect catalytic diarylation of an arylimine by arylbromide promoted by the association of [RuCl₂(p-cymene)]₂ with 4 equiv. of KOAc, shown before to afford the Ru(OAc)₂(p-cymene) catalyst.

5 Acknowledgements
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Appendix A. Supplementary material
CCDC 891360 for 3a, 1039989 for 3b, 1039990 for 7 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

6 references


Highlights

Room temperature (N-Ru-C)-cycloruthenation of arylimines.

Key role of acetate for C-H bond activation/deprotonation.

Ru-Cl remaining bond is crucial for cycloruthenate isolation.