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Mendeleev Commun., 2021, **31**, 620–623

Mendeleev Communications

Oxidation-promoted synthesis of ferrocenyl planar chiral rhodium(III) complexes for C–H functionalization catalysis

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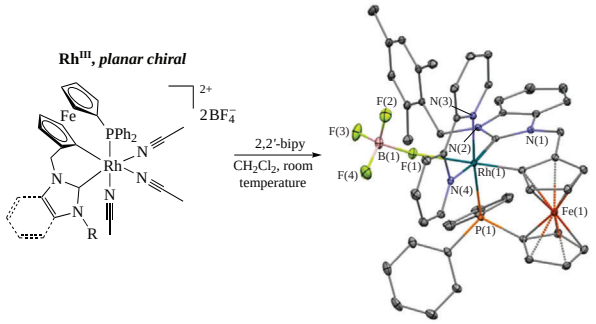
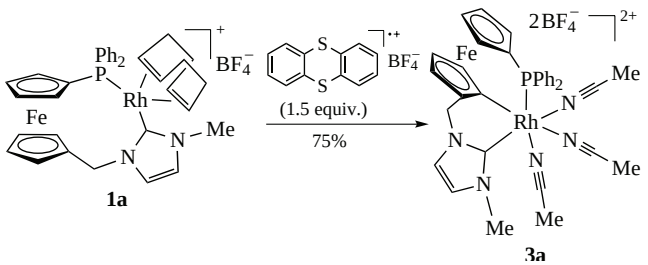
DOI: 10.1016/j.mencom.2021.09.010

The chemical oxidation of rhodium(I) complexes [Rh(L)(COD)][BF_4], where L is a ferrocenyl phosphine/N-heterocyclic carbene ligand, with 2 equiv. of a triarylaminium salt [(4-BrC_6H_4)$_3$N][BF_4] in acetonitrile gave planar chiral, air-stable [Rh(L^{-H})($MeCN$)$_3$][BF_4]$_2$ complexes where the ferrocene ($C_5H_4CH_2Im^R$ or $C_5H_4CH_2BIm^{CH_2Mes}$) ring has been C–H activated at the position 2 in good to excellent yields. An important reactivity difference between our complexes and the ubiquitous [Cp*Rh($MeCN$)$_3$]X_2 complex has been observed in the Grignard-type arylation of 4-nitrobenzaldehyde.



Keywords: rhodium, N-heterocyclic carbenes, ferrocene, redox active ligands, catalysis.

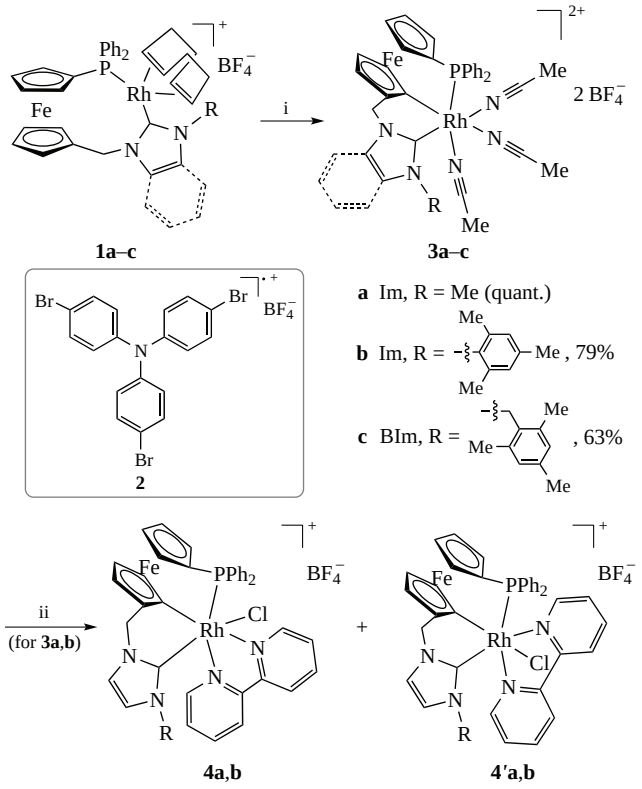
The rhodium-catalyzed functionalization of C(sp^2)–H bonds has become intensely studied as an atom-economical reaction that allows one to obtain poorly accessible compounds.[1–10] In this context, [Cp*$RhCl_2$]$_2$ and [Cp*Rh($MeCN$)$_3$]X_2 have been privileged catalysts for this reaction and to our knowledge, there is only one example reporting catalytic C–H activation with a non-half-sandwich complex.[11] As three coordination sites are required for the reaction to proceed, it is very difficult to design new ligands that allow improving activities and selectivities, and developing asymmetric versions.[12–20] In this context, new rhodium(III) complexes bearing planar chiral ferrocenyl N-heterocyclic carbene (NHC)/phosphine ligands were obtained by oxidation of the corresponding rhodium(I) complexes, followed by activation of a ferrocene C–H bond. In this work, an optimized synthesis of the original complex[21,22] (Scheme 1) is described, and various imidazolylidene substituents are introduced on the NHC moiety in order to study the stereoelectronic effects on the catalytic activity in the Grignard-type arylation of 4-nitrobenzaldehyde. The synthesis of rhodium(III) complex **3a** was previously carried out starting either from rhodium(I) complex **1a**, bearing a COD ligand,[21] or from the corresponding dicarbonyl rhodium(I) complex.[22] Both methods have disadvantages: the reaction was easily performed using the mild oxidant $AgBF_4$ from the dicarbonyl complex, but the latter is moderately bench-stable and has to be prepared from **1a**; on the other hand, a stronger and moderately stable oxidant, thianthrenium tetrafluoroborate [Th][BF_4], was necessary to drive the reaction to completion with complex **1a**, which bears the more strongly coordinated COD ligand (see Scheme 1).



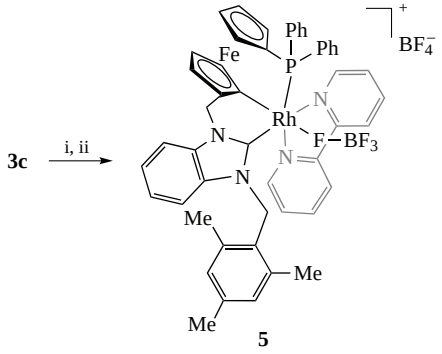
Scheme 1 *Reagents and conditions*: [Th][BF_4], MeCN, room temperature, 24 to 48 h.

We therefore focused our efforts on finding new efficient yet stable oxidants to optimize the synthesis of **3a** directly from **1a** and opted for the triarylaminium salt [(4-BrC_6H_4)$_3$N][BF_4] **2** (Scheme 2).[23] The latter is a weaker oxidant compared to [Th][BF_4] ($E°_{1/2}$ = 0.67 and 0.86 V *vs.* [FcH/FcH^+] in MeCN, respectively), but is more stable and therefore easier to handle and store. The reaction of complex **1a** with 1.9 equiv. of salt **2** went smoothly at 50 °C, the driving force being the precipitation of (4-BrC_6H_4)$_3$N from acetonitrile. Complex **3a** was easily retrieved in quantitative yield. With the aim of studying the influence of the stereoelectronic properties on the catalytic activity, we applied the new synthetic conditions to other rhodium(I) complexes.[24,25] Thus, compound **1b** was chosen for its bulky mesityl substituent on the imidazol-2-ylidene (Im) moiety, whereas analogue **1c** possesses a more flexible CH_2-mesityl substitutent on the nitrogen atom but a bulkier and slightly less donating benzimidazol-2-ylidene (BIm) unit. The expected rhodium(III) complexes **3b**,**c** were obtained as deep red, air-stable solids in 79 and 63% yields, respectively (see Scheme 2).

All rhodium(III) complexes were characterized by multinuclear NMR and HR-MS (see Online Supplementary Materials). The NMR data unambiguously shows the C–H activation of the ferrocene C–H bond: only seven proton resonances for the ferrocenyl unit are present in the ^{1}H NMR



Scheme 2 *Reagents and conditions*: i, $[(4\text{-}BrC_6H_4)_3N][BF_4]$ **2** (1.9 equiv., MeCN, 50 °C, 16 h; ii, 2,2′-bipyridine, CH_2Cl_2, room temperature.



Scheme 3 *Reagents and conditions*: i, 2,2′-bipyridine, CH_2Cl_2, room temperature; ii, $MeOBu^t$/acetone-d_6, crystallization.

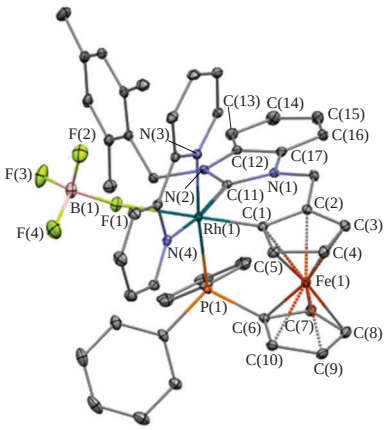


Figure 1 Mercury view of compound **5**. Ellipsoids are shown at the 30% probability level. All hydrogens are omitted for clarity. Selected bond lengths (Å) and angles (°): Rh(1)–P(1) 2.3711(3), Rh(1)–C(1) 1.9912(12), Rh(1)–C(11) 2.0330(12), Rh(1)–N(3) 2.0808(10), Rh(1)–N(4) 2.1291(10), Rh(1)–F(1) 2.3500(7), B(1)–F(1) 1.4512(17); P(1)–Rh(1)–C(1) 90.06(3), P(1)–Rh(1)–C(11) 85.92(3), C(1)–Rh(1)–C(11) 91.62(5), P(1)–Rh(1)–N(3) 174.70(3), C(1)–Rh(1)–N(3) 84.73(4), C(11)–Rh(1)–N(3) 93.26(4), P(1)–Rh(1)–N(4) 102.67(3), C(1)–Rh(1)–N(4) 88.90(4), C(11)–Rh(1)–N(4) 171.40(4), N(3)–Rh(1)–N(4) 78.23(4), P(1)–Rh(1)–F(1) 98.50(2), C(1)–Rh(1)–F(1) 165.42(4), C(11)–Rh(1)–F(1) 100.71(4), N(3)–Rh(1)–F(1) 86.80(3), N(4)–Rh(1)–F(1) 77.75(3).

spectra, as well as three resonances for quaternary carbons in the ferrocene region of the ^{13}C NMR spectra. A characteristic signal was observed for the carbenic carbon as a doublet of doublets at 147.6 for **3b**, and at 161.4 ppm (app. doublet of doublets) for **3c**. These values are in the range of those expected for similar rhodium(III) complexes (*e.g.*, complex **3a**).[21,26,27] Finally, the ^{31}P NMR shows a doublet at 41.2 for **3b** and 40.9 ppm for **3c**, typical of a phosphorus linked to a rhodium(III) center.

Since complexes **3b**,**c** could not be crystallized, they were reacted with 1.5 equiv. of 2,2′-bipyridine (bipy) in CH_2Cl_2 to yield orange-red solids (see Scheme 2), however their ^1H and ^{13}C NMR spectra were too complex for interpretation. The ^{31}P NMR spectrum of **4b** in acetone-d_6 displays only two doublets at 32.2 (J_{RhP} = 120.5 Hz) and 29.9 ppm (J_{RhP} = 124.5 Hz) in a 1 : 1 ratio, similar to what was observed with **4a**.[21] This may indicate the formation of the expected compounds, with the bipy and one chloride occupying the previous acetonitrile positions, as a mixture of diastereomers (**4b** + **4′b**). The ^{31}P NMR spectrum of the **3c** + bipy reaction products shows a more complex picture, namely, three doublets of varying intensity according to the reaction batch at 36.3 (J_{RhP} = 119.6 Hz), 35.8 (J_{RhP} = 129.7 Hz) and 32.8 ppm (J_{RhP} = 123.6 Hz). These values are difficult for unambiguous assignment to any particular species.

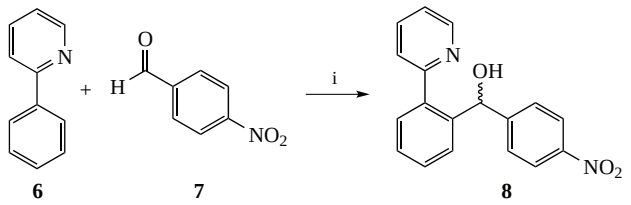
Pleasingly, careful layering of methyl *tert*-butyl ether on a solution of **3c** in acetone-d_6 provided deep red X-ray quality crystals of **5** (Scheme 3).† The crystal structure confirmed the presence of a σ bond between the NHC-functionalized Cp ring and the rhodium center. As in the case of $[Rh(L)Cl(bipy)][BF_4]$ **4a**, one bipy occupies two of the three MeCN coordination positions in **5**. However, instead of a chloride abstracted from the solvent as in the case of **4a**, the last position in **5** was surprisingly occupied by a κ^1:F-coordinated BF_4 ligand. Crystal structures containing Rh–FBF_3 bonds are quite unusual and only five other examples with rhodium(III) have been reported so far by Milstein[28–31] and Breit.[32] The BF_4^- anion is coordinated *trans* to the Rh–C bond at ferrocene, with a Rh(1)–F(1) distance of 2.3500(7) Å, which is in the range of previously reported Rh–F bond distances. This structure confirms the presence of the Rh–C bond at ferrocene with a *fac* arrangement of the tridentate ligand. The bipy ligand is situated *trans* to the NHC and phosphine ligands. All other distances are within the expected range for this

† *Crystal data for* **5**. Crystals of $C_{53}H_{50}B_2F_8FeN_4OPRh$ (M = 1122.32) are triclinic, space group $P\bar{1}$, at 100 K: a = 11.4449(8), b = 11.8714(8) and c = 19.9736(15) Å, α = 97.060(2)°, β = 94.539(2)°, γ = 116.821(2)°, V = 2375.54(18) Å^3, Z = 2, d_{calc} = 1.569, μ(MoKα) = 0.763 mm^{-1}, F(000) = 1144. 93547 reflections were measured and 8402 independent reflections (R_{int} = 0.0322) were used in a further refinement. The refinement converged to wR_2(all data) = 0.027 and GOF = 1.006 for all independent reflections [R_1 = 0.021 was calculated against F for 8141 observed reflections with $I > 3\sigma(I)$]. The measurements were made on a Bruker Apex Smart CCD diffractometer with graphite-monochromated MoKα radiation (λ = 0.71073 Å). The structure was solved using SUPERFLIP. All non-hydrogen atoms were refined anisotropically using CRYSTALS. The H atoms were located in a difference map, but those attached to carbon atoms were repositioned geometrically. The H atoms were initially refined with soft restraints on the bond lengths and angles to regularize their geometry and U[iso](H) (in the range 1.2−1.5 times U[eq] of the parent atom), after which the positions were refined with riding constraints.

CCDC 1848989 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

type of complex, and most are similar to those observed for **4a**, with the noticeable exception of the Rh(1)–P(1) distance, which is longer in **5**; this may be accounted for by the high strain exerted on the ligand to keep the tridentate coordination: the latter adopts a severely distorted geometry to accommodate the octahedral coordination of rhodium. Indeed, the metal coordination forces the phosphorus atom to deviate significantly from the plane of the Cp ring to which it is attached by 0.350(1) Å, and tilts the two ferrocene cyclopentadienyl units to a dihedral angle of 10.01(5)°. In the same way as for **4a**, both planar chirality at ferrocene and central chirality at the metal are now present, hence the potential production of up to three diastereoisomers (given the imposed *fac* stereochemistry of the tridentate ligand). However, in the present case a different diastereoisomer crystallized (the bipy ligand was situated *trans* to the phosphine and to the Rh–C bond at ferrocene in the case of **4a**). For the latter, DFT calculations carried out on the three possible isomers had shown that the calculated electronic energies of two isomers were relatively close (ΔG of 3.7 kcal mol^{-1}), whereas the third one – with the bipy ligand *trans* to the NHC ligand and the Rh–C bond at ferrocene, not observed experimentally – had a much higher energy minimum (8.4 kcal mol^{-1} relative to the most stable isomer), which was explained by severe steric constraints.[21] The same limitations seem to apply here.

Complexes **3a**–**c** were then evaluated as catalysts in the Grignard-type arylation of 4-nitrobenzaldehyde **7** with 2-phenylpyridine **6** (Scheme 4, Table 1).[33] Indeed, Rh^{III} complexes bearing three coordination sites available for C(sp^2)–H functionalization catalysis are very often restrained to Cp-based architectures,[7–9] and our system seemed interesting in that regard. The reaction worked well with anhydrous THF but an optimum was found with 1.5 equiv. of H_2O relative to 2-phenylpyridine (51% conversion, entry 3). Average conversions were obtained after 24 h and increasing the reaction time did not allow us to improve significantly the conversion (58% after 48 h, see entry 3). Unfortunately, complexes **3b,c** gave none of the expected product and only starting materials were detected (entry 6). With more sterically hindered 1-(2-methylphenyl)isoquinoline no reaction did occur (entry 7).



6 **7** **8**

Scheme 4 *Reagents and conditions*: i, [Rh] (5 mol%), THF, H_2O, 65 °C, 24 h.

Table 1 Grignard-type arylation of 4-nitrobenzaldehyde **7**.[a]

Entry	[Rh]	H_2O (equiv. *vs.* **6**)	Conversion[b] (%)
1	**3a**	–	43
2	**3a**	1	50
3	**3a**	1.5	51 (58[c])
4	**3a**	3	36
5	**3a**	10	33
6	**3b**,**c**	1.5	n.r.
7[d]	**3a**	1.5	n.r.
8	**1a**–**c**	1.5	n.r.

[a] Conditions: 2-phenylpyridine **6** (1.0 equiv.), 4-nitrobenzaldehyde **7** (2.0 equiv.), [Rh] (5 mol%), H_2O, THF (0.5 ml, 0.4 M), 65 °C, 24 h. [b] From characteristic ^{1}H NMR signals of **6** and **8**. [c] Reaction time 48 h. [d] 1-(2-Methylphenyl)isoquinoline was tested instead of 2-phenylpyridine.

In recent years, it has been shown that M–NHC bonds, although very strong, could cleave under chosen catalytic conditions and lead to active metallic species without NHC stabilizing ligand.[34] Whereas the cleavage of the Rh–NHC bond in **3a**–**c** seems unlikely, due to the tridentate nature of the ligand that stabilizes the structure, Rh^I precursors **1a**–**c** may behave differently. However, the latter proved completely inactive for this reaction under identical conditions: after 24 h at 65 °C, no trace of the expected product **8** was observed and only starting materials were detected by ^{1}H NMR (see Table 1, entry 8). ^{31}P NMR analysis of the crude mixture confirmed the integrity of the structure in **1a**, as the typical doublet at *ca*. 20 ppm was observed. Only traces of unidentified by-products were characterized by singlets at *ca*. 23 and 39 ppm, and can explain the slightly brown aspect of the catalyst after reaction. This confirms the very high stability of rhodium(I) complexes **1a**–**c** under reaction conditions,[25] and the efficiency of the redox strategy described earlier to promote COD departure in the presence of MeCN (no COD hydrogenation was observed for **1a** under 3 bar H_2 in THF for 16 h). As in rhodium(III) complexes **3a**–**c**, the bidentate nature of the ligand, bearing strongly coordinating phosphine and NHC ligands, does not seem to favor the cleavage of the Rh–NHC bond.

Unfortunately, complexes **3a**–**c** also proved inactive as catalysts for the synthesis of 3,4-dihydroisoquinolones, whatever the conditions used.[12,13,35] These results are rather surprising since our rhodium(III) complexes easily lose an acetonitrile ligand and either react with dichloromethane to coordinate a chloride (**3a**)[21] or a BF_4^- anion (**3c**). It seems that the tridentate (NHC,P,C) ligands may be too sterically crowded and may prevent the approach of bulkier substrates, contrary to the ubiquitous $[Cp^*Rh(MeCN)_3]^{2+}$ complex.[33]

In conclusion, the synthesis of several planar chiral rhodium(III) complexes has been carried out by oxidation of rhodium(I) complexes containing an electroactive ferrocenyl unit. Optimized conditions have been developed with the use of a relatively mild, stable oxidant. Although the least sterically crowded complex allows the functionalization of 2-phenylpyridine with 4-nitrobenzaldehyde, no reaction occurred with complexes bearing bulkier ligands, pointing to an important reactivity difference between our complexes and the ubiquitous $[Cp^*RhCl_2]_2$ and $[Cp^*Rh(MeCN)_3]X_2$ complexes. Mechanistic studies are in progress to better understand the reasons of this low reactivity in C–H functionalization reactions.

The authors thank the Centre National de la Recherche Scientifique (CNRS) for financial support.

Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.1016/j.mencom.2021.09.010.

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Received: 26th April 2021; Com. 21/6544