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Heteroleptic dirhodium(II) complexes with redox-active ferrocenyl ligands: synthesis, electrochemical properties and redox-responsive chemoselectivity in carbene C-H insertion

Illia Ruzhlyo,^[a] Alix Sournia-Saquet,^[a] Alain Moreau,^[a] Tom Delord,^[a] Eric Manoury,^[a] Rinaldo Poli^{[a],[b]} and Agnès Labande*^[a]

[a] I. Ruzhlyo, Dr. A. Sournia-Saquet, A. Moreau, Dr. E. Manoury, Pr R. Poli, Dr. A. Labande
LCC-CNRS, Université de Toulouse, CNRS, INPT, 205 route de Narbonne, 31077 Toulouse, France
E-mail: agnes.labande@lcc-toulouse.fr

[b] Pr R. Poli
Institut Universitaire de France, 1, rue Descartes, 75231 Paris, France.

Abstract: A series of original heteroleptic dirhodium(II) complexes (**4a-j**) of formula $Rh_2(OAc)_3(L)$, where L is a redox-active ferrocenecarboxylate ligand, has been prepared. These dirhodium(II) complexes have been characterised by NMR, mass spectrometry and cyclic voltammetry. All complexes show a quasi-reversible redox behaviour for the ferrocenyl unit. The latter can be selectively oxidised by $[N(4-C_6H_4Br)_3]^+ \cdot BF_4^-$. Four selected heteroleptic complexes **4a**, **4b**, **4f** and **4i**, have been evaluated as catalysts for the intramolecular decomposition of a diazo compound. The ratio between the aromatic substitution product **6** and the aliphatic C-H insertion product **7** increases (up to 19% increase) when using the *in situ* generated oxidised form of the dirhodium(II) complexes (**4a**⁺**BF**₄⁻ to **4i**⁺**BF**₄⁻). This shows that the oxidation of the ferrocenecarboxylate ligand has an effect on the chemoselectivity of the dirhodium-catalysed diazo decomposition, and thus that the electronic properties of a complex can be tuned without exchanging ligands.

Keywords: ferrocene • dirhodium • diazo compounds • oxidation • electrochemistry

Introduction

Paddlewheel dirhodium(II) complexes are powerful catalysts, particularly useful for the decomposition of diazo compounds (e.g. C-H functionalization, cyclopropanation, [3+2]-cycloadditions of carbonyl ylides), which are widely used for the preparation of complex organic molecules.^[1] Compared to catalysts based on other metals, dirhodium(II) complexes offer the greatest diversity in terms of ligands, the most commonly used ones being carboxylates, carboxamides and to a lesser extent phosphates.^[2] The strong influence of the bridging ligand nature on the chemo-, regio- and stereoselectivity of diazo-based reactions is well-established.^[1c, 3] For example, the electrophilicity of the rhodium centre, which can be correlated to the value of its oxidation potential, increases dramatically from a carboxamide to a carboxylate ligand or from an acetate to a trifluoroacetate.^[3a, 4] The selectivity also depends on many other factors, such as the ligand sterics,^[5] the diazo substrate nature,^[6] etc. More recently, the influence of axial ligands has been increasingly investigated.^[7] These selectivity issues were the subject of many reports. However, it is difficult to evaluate the contribution of electronic effects alone, since a change of ligand almost always implies a simultaneous change in sterics. Interestingly, Doyle *et al.* demonstrated that the chemical oxidation of a dirhodium(II,II) complex bearing carboxamide ligands into a dirhodium(II,III) complex enhances its Lewis acidity and makes it a much better catalyst for [3+2]-cycloadditions and hetero-Diels-Alder reactions.^[8] However, stable, oxidized dirhodium(II,III) complexes bearing carboxylate ligands have not yet been reported.

On the other hand, in a seminal 1994 report, Wrighton showed that, by controlling the oxidation state of a redox-active ligand in a rhenium complex, it is possible to finely tune the electron density at the metal centre and thus change the reactivity of the complex toward nucleophiles.^[9] Since this pioneering work, many elegant studies have made use of redox-active ligands to alter a catalyst reactivity (redox-switchable catalysis).^[10] Most examples rely on the exceptional properties of ferrocene, the redox behaviour of which is well-known and which offers a wide range of possibilities for functionalization.^[11] In a seminal 2006 example, Gibson and Long demonstrated that the change in redox state of ferrocene moieties on a substitutionally inert ligand allows to tune the activity of a lactide titanium polymerization catalyst.^[10b] Later in 2013, Plenio *et al.* oxidized a ferrocenyl ligand on a ruthenium metathesis catalyst to make it labile and thus initiate the ring-opening metathesis polymerization of *cis*-cyclooctene.^[10h] More recently, Sarkar *et al.* demonstrated that an enhanced Lewis acidity through oxidation of a ferrocene-containing ligand can promote the catalytic activity of a gold(I) complex.^[10i] Hey-Hawkins *et al.* also reported tris(ferrocenyl)arene-based gold(I) complexes for redox-switchable catalysis.^[10r] They very elegantly demonstrated that it is possible to access four different oxidation states via sequential oxidation of the ferrocenyl

units, and to consequently fine-tune the catalytic activity of the related gold(I) complex toward the ring-closing isomerisation of N-(2-propyn-1-yl)benzamide.

Rhodium(II) complexes bearing ferrocenyl ligands have been reported as early as 1982, when the Noels group used $\text{Rh}_2(\text{FcCO}_2)_4$ as catalyst for the decomposition of a diazo compound and subsequent carbene insertion into an O-H bond (FcCO_2H = ferrocenecarboxylic acid).^[12] Since then, various ferrocenecarboxylic acids or other ferrocene-based ligands have been introduced, either as bridging ligands^[7c, 13] or as axial ligands,^[14] on dirhodium(II) structures. However, surprisingly, the redox-active character of ferrocene has never been exploited in this chemistry. Given our long-standing interest in the redox chemistry of ferrocene and its implications in organometallic chemistry,^[15] we wondered whether this concept could be applied to dirhodium catalysis. We describe here the synthesis of several ferrocene-based carboxylic acids and of the corresponding heteroleptic $\text{Rh}_2(\text{OAc})_3(\text{L})$ complexes, where L is the ferrocenyl-functionalised ligand. Their electrochemical properties have been systematically investigated and a few selected dirhodium(II) complexes have been used in the catalysed decomposition of a diazo substrate.

Results and Discussion

Synthesis of ferrocenecarboxylic acids

A series of ferrocenyl-based carboxylic acids **1a-k** was prepared according to previously published procedures.^[16] The different electronic contributions of the various selected substitution patterns (Figure 1) were aimed at evaluating their impact on the stability of oxidized species and on the reactivity of the dirhodium(II) complexes.

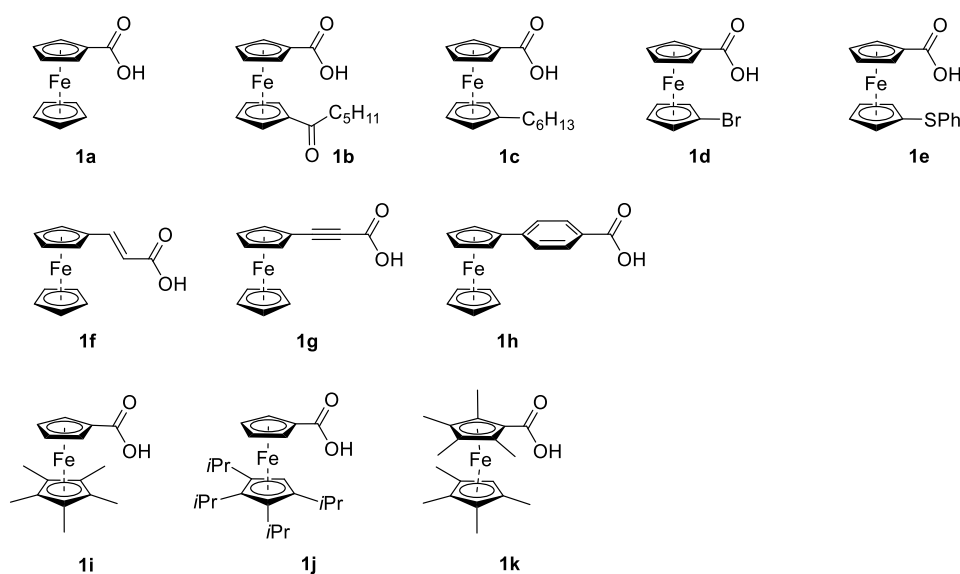


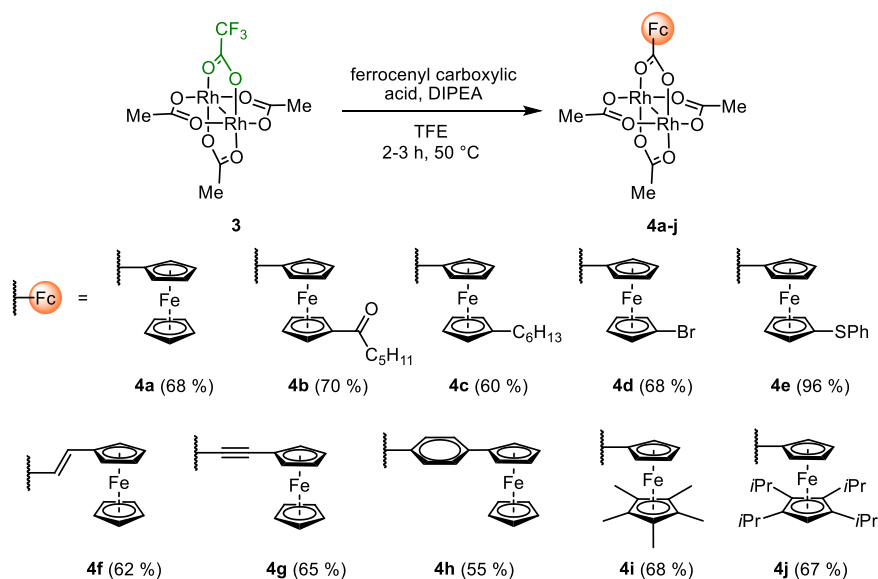
Figure 1. Ferrocenecarboxylic acids used in this study.

Thus, apart from commercially available ferrocenecarboxylic acid **1a**, the ferrocenyl acid **1b** possessing an electron-withdrawing keto group on the 1' position was prepared by a Friedel-Crafts reaction on methyl ferrocenecarboxylate and further saponification.^[16h] Reduction of the keto functionality of **1b** by triethylsilane in TFA gave acid **1c**,^[16e] now possessing an electron-donating, lipophilic alkyl chain. Ferrocenecarboxylic acid **1d**, bearing an electron-withdrawing bromo substituent in the 1' position, was obtained from 1,1'-dibromoferrrocene^[16c] and the thioether-substituted acid **1e** was prepared from 1-bromo-1'-phenylthioferrocene.^[16b] Several permethylated ferrocenecarboxylic acids were also prepared, such as pentamethylferrocene carboxylic acid **1i**,^[16d] the bulky tetraisopropylferrocenecarboxylic acid **1j** and the most electron-rich of the series, octamethylferrocenecarboxylic acid **1k**.^[16i] The effect of electronic communication and proximity between ferrocene and the dirhodium centre through a conjugated linker was also of interest. This was probed by introduction of ethenyl (**1f**), ethynyl (**1g**) and phenyl (**1h**) spacers. Carboxylic acid **1f** was prepared in two steps from readily available

ferrocenecarboxaldehyde,^[16f] whereas the synthesis of **1g** required an adaptation of literature procedures and was realised in three steps from ferrocenecarboxaldehyde.^[16a] Finally, **1h** was obtained by the reaction of ferrocene with 4-(methoxycarbonyl)benzenediazonium and subsequent saponification of the methyl ester.^[16g] All acids were obtained in reasonable to good yields and characterized by NMR and mass spectrometry, particularly for **1b**, **1e** and **1j**, which have not been previously characterized (**1b**) or reported.

Synthesis of heteroleptic dirhodium(II) complexes

Classical methods for ligand exchange reactions on dirhodium(II),^[1b, 2] which involve heating a mixture of $\text{Rh}_2(\text{OAc})_4$ **2** and the carboxylic acid ligand in refluxing chlorobenzene using a Soxhlet extraction apparatus, can be applied to prepare homoleptic complexes $\text{Rh}_2[\mathbf{1x}^{(-H)}]_4$. However, such a straightforward synthesis raises two issues: on one hand, the resulting complexes could be very poorly soluble, as it has been observed with the species derived from the simple ferrocenyl carboxylic acid ligand. On the other hand, since electronic communication between the ferrocene unit and the rhodium centres is anticipated, the oxidation of one ferrocenyl unit should affect the oxidation of the three other ferrocenes and make the latter more difficult. We therefore chose to prepare heteroleptic complexes of type $\text{Rh}_2(\text{OAc})_3[\mathbf{1x}^{(-H)}]$. By carefully optimizing the conditions, particularly by tuning the ligand amount, we found that we could generate the desired heteroleptic complexes from $\text{Rh}_2(\text{OAc})_3(\text{tfa})$ **3**,^[17] which possesses a more labile trifluoroacetate ligand. Depending on the electronic properties of the incoming ferrocenyl ligand, a mixture of several heteroleptic complexes $\text{Rh}_2(\text{OAc})_{4-x}[\mathbf{1x}^{(-H)}]_x$ was obtained and had to be separated by column chromatography on silicagel. The more donating the substituent, the lower the ligand exchange selectivity. After purification, heteroleptic complexes **4a-j** were obtained as air-stable, green solids (except **4f**, which is brown) in reasonable to good yields. The solubility of these heteroleptic complexes varies significantly according to the ligand nature. Thus, whereas complexes **4b-c** and **4i-j** bearing alkyl substituents are well soluble in acetone, sonication was necessary with **4a**, **4d** and **4f-g** to dissolve them in the same solvent. Only **4i** is readily soluble in dichloromethane and the other ones only quite moderately. **4e** and **4h** are the least soluble compounds of the series and only dissolve in DMSO. ¹H NMR spectra showed the characteristic signals of the ferrocenyl protons between 3.8 and 5 ppm and two different signals around 1.7-1.9 ppm, corresponding to the three remaining acetate ligands and integrating for 3H (*trans* to ferrocenyl ligand) and 6H (*cis* to ferrocenyl ligand), respectively. ESI and HR-MS ESI mass spectrometry also confirmed the sole presence of the expected monosubstituted complexes **4a-j**, of formula $\text{Rh}_2(\text{OAc})_3[\mathbf{1a-j}^{(-H)}]$. Unfortunately, complex **4k** possessing the most electron-rich carboxylate ligand could not be obtained, probably for steric reasons because of the two methyl groups situated in *ortho* to the carboxylic acid.



Scheme 1. Synthesis of heteroleptic dirhodium(II) complexes **4a-j** of formula $\text{Rh}_2(\text{OAc})_3[\mathbf{1a-j}^{(-H)}]$.

Electrochemistry

The ferrocenecarboxylic acids **1a-k** and the heteroleptic dirhodium(II) complexes **4a-j** were studied by cyclic voltammetry (Table 1 and Supp. Info).

Table 1. Half-wave potentials (V) and peak-to-peak separation (mV) for the oxidation of carboxylic acids **1a-k** in CH₂Cl₂.

Carboxylic acid ^[a]	E _{1/2} (V) ^[b]	ΔE _p (mV) ^[b]
1a	0.24	88
1b	0.46	83
1c	0.18	81
1d	0.39	81
1e	0.29	83
1f	0.12	88
1g	0.22	93
1h	0.06	85
1i	-0.06	78
1j	0.04	76
1k	-0.22	76

[a] Cyclic voltammograms were recorded on a Pt microelectrode. 1 mM of **1x** in CH₂Cl₂ with *n*Bu₄NBF₄ (0.1 M) at a scan rate of 0.2 V.s⁻¹.
[b] All potentials are reported versus [FcH/FcH⁺] (0.56 V vs. SCE).

By cyclic voltammetry at a scan rate of 0.2 V.s⁻¹, most carboxylic acids display a quasi-reversible redox wave for the ferrocene moiety (ΔE_p, or E_{pa}-E_{pc} ca. 88 mV). As expected, the introduction of electron-donating substituents on the Cp ring makes the ferrocene easier to oxidize, with E_{1/2} ranging from 0.18 to -0.22 V for acids **1c** and **1i-k**, respectively. On the contrary, the presence of a carbonyl group on the Cp ring in **1b** raises the redox potential to 0.46 V, making this carboxylic acid the most difficult to oxidize in the series. The nature of the linker also has its importance, since the acid having an ethynyl linker (**1h**) is oxidized at a ca. 80 mV more positive potential than **1g** with its double bond.

Cyclic voltammograms of the heteroleptic dirhodium(II) complexes **4a-j** also showed a quasi-reversible redox wave for ferrocene, situated between E_{1/2}^{Fc} = -0.08 V (**4i**) and 0.45 V (**4b**) (Table 2 and Supp. Info). The second redox wave at more positive potentials (0.77 to 0.88 V) corresponds to the Rh₂⁴⁺/Rh₂⁵⁺ couple and displays a quasi-reversible behaviour. Logically, the ferrocene oxidation in complex **4i**, possessing five electron-donating methyl groups, occurs at the lowest potential (-0.08 V) for the series, while the most difficult oxidation was observed for the ferrocenyl group in complex **4b** (+0.45 V). However, the oxidation potential of the rhodium centre does not correlate with that of the ferrocenyl ligand: the easiest dirhodium centre to oxidize is that in complex **4f**, with a E_{1/2}^{Rh} of 0.78 V, versus 0.88 V for complex **4g**. Both complexes possess a non-substituted ferrocenyl unit, but the former has an ethenyl spacer, and the latter an ethynyl spacer. The redox potentials of the ferrocenyl unit do not change upon coordination of the carboxylates on rhodium, which can be seen on the cyclic voltammograms of selected carboxylic acids and complexes (Figure 2).

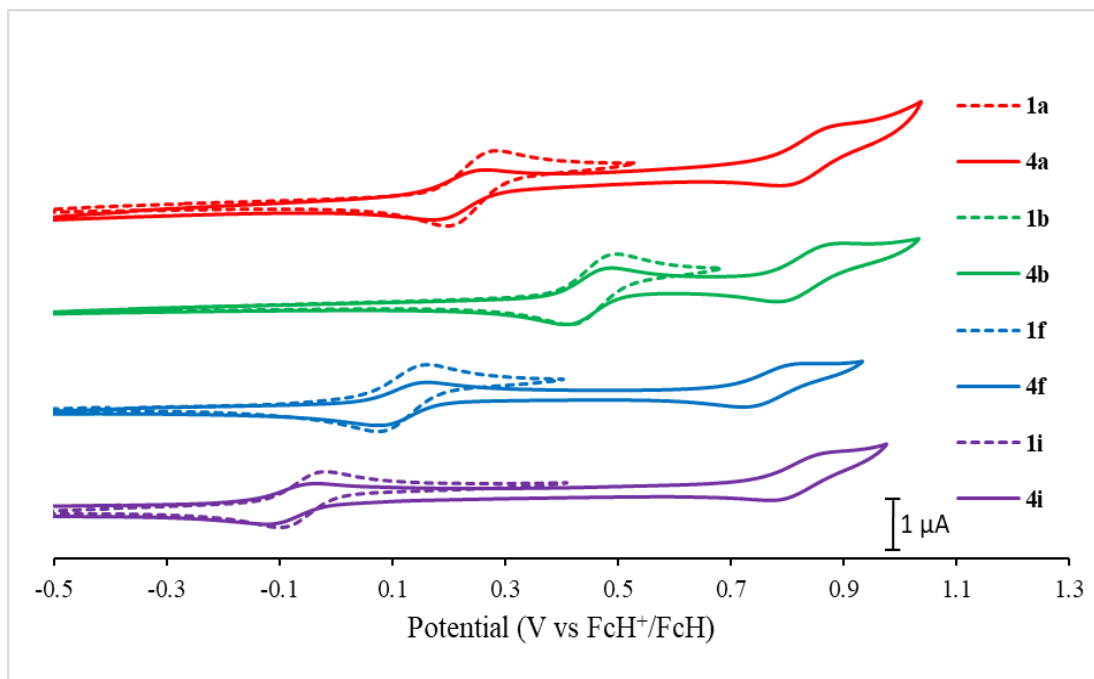


Figure 2. Cyclic voltammograms of selected ferrocenecarboxylic acids **1a-b**, **1f** and **1i** (dashed curves) and heteroleptic dirhodium(II) complexes **4a-b**, **4f** and **4i** (solid curves) on a Pt microelectrode, 1 mM in CH₂Cl₂ with *n*Bu₄NBF₄ (0.1 M) at a scan rate of 0.2 V s⁻¹.

Table 2. Half-wave potentials (V) and peak-to-peak separation (mV) for the oxidation of heteroleptic dirhodium(II) complexes **4a-j** in CH₂Cl₂.

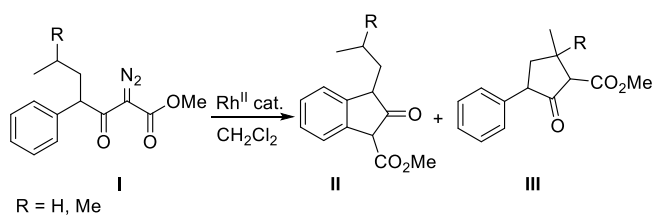
Rh ^{II} complex ^[a]	$E_{1/2}^{Fc}$ (V) ^[b]	ΔE_p^{Fc} (mV) ^[b]	$E_{1/2}^{Rh}$ (V) ^[b]	ΔE_p^{Rh} (mV) ^[b]	ΔE^{Fc-Rh} (V)
2	-	-	0.72	53	-
3	-	-	0.93	68	-
4a	0.22	95	0.84	73	0.62
4b	0.45	81	0.84	122	0.39
4c	0.16	88	0.84	117	0.68
4d	0.36	85	0.83	103	0.47
4e	0.35	93	0.82	78	0.47
4f	0.12	88	0.78	107	0.66
4g	0.23	90	0.88	112	0.65
4h ^[c]	0.06	93	0.82	137	0.76
4i	-0.08	88	0.83	115	0.91
4j	-0.04	88	0.83	112	0.87

[a] Cyclic voltammograms were recorded on a Pt microelectrode. 1 mM of **4x** in CH₂Cl₂ with *n*Bu₄NBF₄ (0.1M) at a scan rate of 0.2 V.s⁻¹. [b] All potentials are reported versus [FcH/FcH⁺] (0.56 V vs. SCE). [c] Measured on a glassy carbon electrode

The oxidation product of the ferrocenyl unit into ferrocenium could not be obtained by electrolysis at controlled potential: either the oxidized species precipitated on the electrode surface and passivated it during the process, or it was impossible to separate it from the supporting electrolyte. We therefore turned to chemical oxidants to generate the oxidized species $4x^+BF_4^-$. Relatively strong oxidants were considered, so that they could be used with all our complexes, whatever the redox potential of the ferrocenyl unit. $[N(4-C_6H_4Br)_3]^+ \cdot BF_4^-$ ($E_{1/2} = 0.70$ V vs. $[FcH/FcH^+]$ in CH_2Cl_2) is a selective, one-electron oxidant the by-product of which can easily be removed by Et_2O washing. It was therefore chosen for the oxidation of complexes **4a-j** in dichloromethane. In all cases its redox potential was lower than that of the rhodium oxidation, but it was nevertheless used in strictly stoichiometric amount to avoid the presence of unreacted oxidant during the subsequent catalytic tests. The oxidation reaction was almost instantaneous, as the intense blue colour of the oxidant solution in DCM disappeared very quickly upon addition to the dirhodium complex solution. Most complexes showed a more intense blue-green colour after oxidation and a reduced solubility, which is expected upon formation of a cationic species.

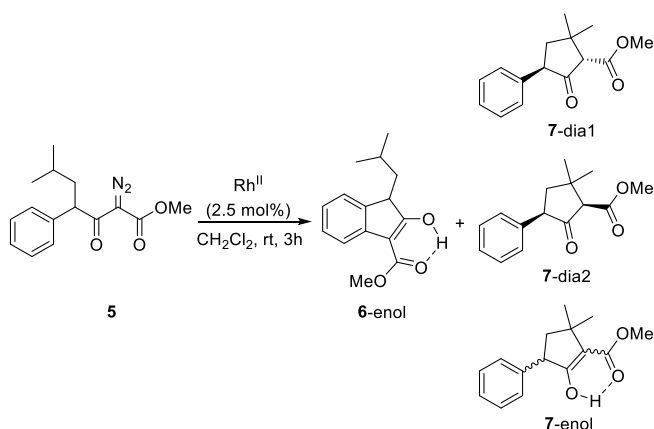
Catalysed decomposition of a diazo substrate

As mentioned above, site selectivity in dirhodium(II)-catalysed reactions of diazo compounds depends on many factors, among which the nature of the ligands present on rhodium. As an example, after an early report by Taber *et al.*,^[18] Ikegami *et al.*^[19] demonstrated that the catalysed decomposition of diazo compounds **I** could proceed intramolecularly to give a mixture of aromatic substitution (**II**) and aliphatic C-H insertion (**III**) products (Scheme 2). It was shown that the ratio between the different products changes dramatically depending on the ligand present on the catalyst: with $R = H$, the **II**:**III** selectivity changed from 54:46 to 79:21 from benchmark $Rh_2(OAc)_4$ **2** to more electron-deficient $Rh_2(tfa)_4$. On the other hand, the highest selectivity for the aromatic substitution product **II** was obtained with $Rh_2(tpa)_4$ bearing a bulky ligand with electronic properties similar to that of $Rh_2(OAc)_4$. Even more marked differences were obtained with the diazo substrate with $R = Me$, with a selectivity switch from 38:62 to 93:7 using respectively $Rh_2(OAc)_4$ and $Rh_2(tpa)_4$.



Scheme 2. Ligand-induced chemoselectivity in the dirhodium(II)-catalyzed decomposition of diazo compounds (Ikegami *et al.*).^[19]

However, it seems difficult to evaluate the effect of electronics or sterics alone when changing the ligand. Testing the same reaction with the **4a-j** catalysts as a function of the ferrocene oxidation state should allow us to study the influence of electronics only on the reaction selectivity. The decomposition of diazo substrate **5** was chosen as a model reaction.



Scheme 3. Intramolecular reaction of diazo substrate **5** catalysed by heteroleptic ferrocenyl dirhodium(II) complexes **4a-b**, **4f** and **4i** (for **6**: only the major enol form is represented).

Table 3. Decomposition of diazo compound **5** catalysed by dirhodium(II) complexes.

Entry ^[a]	Rh complex	6 : 7 (%) ^[b]	6 : 7 ^[c]
1	2	86	34:66
2	3	83	63:37
3	4a	87	37:63
4	4a *BF ₄ ⁻	94	49:51
5	4b	84	42:58
6	4b ^[d]	90	43:57
7	4b *BF ₄ ⁻	87	51:49
8	4f	88	30:70
9	4f *BF ₄ ⁻	91	48:52
10	4i	90	41:59
11	4i *BF ₄ ⁻	93	60:40

[a] Reagents and conditions: diazo substrate **5** (0.2 mmol), Rh^{II} cat. (2.5 mol%), CH₂Cl₂ (1.5 + 1.5 mL). [b] Global isolated yield. [c] Determined by integration of characteristic ¹H NMR signals (CDCl₃). [d] 1 equivalent of reduced (4-BrC₆H₄)₃N added relative to dirhodium complex **4b**.

The synthesis of diazo substrate **5** was realised using modified procedures from analogous compounds.^[18] The characteristic ¹H NMR signals of both compounds **6** and **7** produced by the catalysed transformation, *i.e.* the methyl groups of the ester functionalities, are well separated and thus the **6**:**7** ratio was easily determined. In CDCl₃, **6** appears to be present almost exclusively in its enol form (**6**-enol, see Scheme 3), with a characteristic chemical shift of 11.13 ppm for the O-H proton. In the ¹³C NMR spectrum, the chemical shift of the carbonyl group concerned with the tautomerism shifts from 198.3 to 184.8 ppm, and that of the C=C-OH carbon to 103.6 ppm: these shifts are also very typical of the presence of an enol form. The NMR of compound **7** proved more complex to analyse, since it was not only concerned with the same keto-enol equilibrium, but the keto form also exists as a mixture of two diastereoisomers. This results in the presence of three ¹H NMR signals for the methyl ester, at 3.84 ppm (**7**-enol), 3.78 ppm (**7**-dia1) and 3.74 ppm (**7**-dia2). Similarly, four signals were observed in the ¹³C NMR spectrum for the keto-ester carbonyl groups, respectively at 210.09 ppm (**7**-dia1) and 213.02 ppm (**7**-dia2), and 168.94 ppm (**7**-dia1) and 169.70 ppm (**7**-dia2); a pair of signals characteristic of the enol form (**7**-enol) can be seen at 175.46 ppm (C=C-OH) and 170.82 ppm (CO₂Me). As each diastereoisomer is in equilibrium with its enol form, it was not possible to determine the diastereomeric ratio for **7**. The relative configuration of each diastereoisomer was tentatively assigned from analysis of the 2D-NMR data.

The salient results of the catalytic tests are collected in Table 3. The benchmark catalyst Rh₂(OAc)₄ **2** allowed the total conversion of **5** in 3 h at room temperature in DCM and afforded the products **6** and **7** in a 34:66 ratio, in agreement with the result reported by Ikegami *et al.*^[19] The reaction was then carried out with the heteroleptic complex Rh₂(OAc)₃(tfa) **3**, bearing a more electron-withdrawing tfa ligand ($E_{1/2}^{\text{Rh}} = 0.72 \text{ V} / [\text{FcH}/\text{FcH}^+]$, see Table 2). Again, the total conversion of **5** was observed after 3 h (TLC monitoring), along with a marked selectivity change in favour of the aromatic substitution product **6**. This first result shows that it is not always necessary to change all four ligands around rhodium to observe a noticeable selectivity change. Then a few selected heteroleptic complexes, with the ferrocenyl unit in its reduced state, were evaluated: complex **4a** with unsubstituted ferrocene was chosen as reference, **4b** for its electron-withdrawing ligand coupled with a good solubility in organic solvents, **4i** bearing the most electron-donating ferrocenyl ligand of the series, and **4f** to assess the influence of a spacer. Moreover, **4f** shows the lowest oxidation potential of the series for the rhodium centre. All complexes showed a good activity, as the reactions were complete after 3 h at room temperature. At this stage, only negligible selectivity differences were observed when varying the nature of the ligand: a slightly higher proportion of aliphatic C-H activation product **7** was obtained with electron-rich ligands. Thus, the **6**:**7** ratio changed from 37:63 with complex **4a** to 42:58 with complex **4b**. On the other hand, a 30:70 ratio was observed with complex **4f** bearing an ethenyl spacer between the carboxylate and ferrocenyl groups and which, remarkably, also possesses the lowest oxidation potential for the rhodium centre ($E_{1/2}^{\text{Rh}} = 0.78 \text{ V} / [\text{FcH}/\text{FcH}^+]$, vs 0.83 V on average for other complexes). These first results confirm the relationships

between the redox potential of the rhodium centre (and not of the ferrocenyl centre), the electrophilicity of the catalyst, and the chemoselectivity. The ferrocenyl unit was then oxidized by addition of 1.0 equivalent of $[N(4-C_6H_4Br)_3]^+ \cdot BF_4^-$ oxidant in dichloromethane, and the diazo substrate **5** was added after 30 min under the same reaction conditions. Although the solubility of some oxidized complexes was limited, the addition of **5** and subsequent formation of the rhodium carbenoid improved the solubility in dichloromethane. Again, good reactivity was observed in all cases and the global yields were satisfying. Gratifyingly, a significant difference in chemoselectivity was observed in all cases with the oxidized form of the complexes, with a 9 to 19% increase in aromatic substitution product **6** compared to the reduced form. The first striking observation is that the difference becomes more important as the electron-donating character of the ferrocenyl unit increases, from complex **4b** with its electron-withdrawing keto group to complex **4i** bearing the Cp* moiety. This trend is rather accurately related to the redox potential of the ferrocenyl unit, less so to the difference between the ferrocenyl oxidation and the dirhodium oxidation (ΔE^{Fc-Rh} , see Table 2). One of the most important difference was obtained with complex **4f**·BF₄⁻ bearing the ethenyl spacer, confirming an efficient electronic communication between the ferrocenyl moiety and the rhodium centre. As the oxidized species are generated, an equimolar amount of N(4-C₆H₄Br)₃ is produced. In order to check whether the amine itself could interact with the rhodium complexes and thus influence the course of the reaction, one equivalent of N(4-C₆H₄Br)₃ (relative to the rhodium complex) was added to complex **4b** before addition of diazo compound **5**. However, no variation of the **6**:**7** ratio was observed, which confirms that N(4-C₆H₄Br)₃ is not implicated in the process. The addition of $[N(4-C_6H_4Br)_3]^+ \cdot BF_4^-$ oxidant to the diazo compound **5**, without dirhodium catalyst, did not furnish **6** or **7** under identical conditions. From all this data we can conclude that ferrocene oxidation in our heteroleptic complexes induces a selectivity change and that the sole influence of electronic factors on catalysis can be evaluated in a dirhodium(II) complex. The extent of the chemoselectivity change is similar to (albeit slightly lower than) that observed when one acetate ligand is replaced by a more electron-withdrawing trifluoroacetate ligand.

Conclusion

We have shown that the chemoselectivity of the dirhodium-catalysed intramolecular decomposition of a diazo compound could be tuned without changing the ligand on rhodium, by simple oxidation of the ferrocene moiety of the ligand. This has been realised by introducing only one ferrocenyl ligand in the complex, and we surmise that the replacement of more acetates by these redox-active ligands on rhodium could enhance this behaviour. Thanks to the low oxidation potential of the ferrocenyl moiety in complex **4i**, a much weaker oxidant could also be considered to affect catalysis. These parameters, as well as the scope of diazo substrates, will be studied in due course.

Experimental Section

All manipulations were performed under an inert atmosphere of dry argon by using vacuum line and Schlenk tube techniques. Solvents for all syntheses were either dried by standard methods and distilled under argon before use, or purified on an Innovative PURE SOLV Solvent Purification System equipped with 4 Å MS columns, unless otherwise stated. Ferrocenecarboxylic acid **1a** was purchased from Sigma-Aldrich and used without further purification. Other known ferrocenyl compounds were prepared according to previously reported procedures. The syntheses of ferrocenecarboxylic acids **1b** to **1k**, as well as Rh₂(OAc)₃(tfa) **3** and diazo substrate **5**, are described in the Supporting Information. Cp always refers to the ring that possesses the CO₂H or CO₂- substituent, and Cp' to the other ring.

General methodology for the synthesis of heteroleptic ferrocenyl dirhodium(II) complexes (**4a-j**):

To a suspension of Rh₂(OAc)₃(tfa) **3** (1 equiv.) and carboxylic acid (1.1 equiv.) in trifluoroethanol (0.02 M solution of dirhodium precursor), *N,N*-diisopropylethylamine (2 equiv.) was added and the resulting mixture was stirred at 50 °C for 2 h, at which time TLC analysis showed full consumption of Rh₂(OAc)₃(tfa). Then, a spatula of Celite® was added, the solvent was removed *in vacuo* and the solid residue was purified by column chromatography (flash silica gel, EtOAc/hexane = 1/1 or EtOAc/hexane = 2/1).

Dirhodium(II) tris[μ-(acetato-κO:κO')][μ-(ferrocenecarboxylato-κO:κO')] (**4a**)

Starting from 50 mg of **3**, dirhodium complex **4a** was obtained as a green solid (41.6 mg, 68% yield).

HRMS (ESI, pos.) *m/z*: [M+H]⁺ calcd for C₁₇H₁₈FeO₈Rh₂ 611.8461, found: 611.8469 ¹H NMR (400 MHz, *d*₆-acetone) δ 4.57 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp), 4.22 (t, *J* = 1.9 Hz, 2H, 2 x CH Cp), 4.00 (s, 5H, 5 x CH Cp'), 1.80 (s, 3H, *trans*-CH₃CO₂), 1.78 (s, 6H, 2 x *cis*-CH₃CO₂). ¹³C NMR (101 MHz, *d*₆-acetone) δ 190.57 (*trans*-CH₃CO₂), 190.49 (2 x *cis*-CH₃CO₂), 189.48 (C₅H₄CO₂), 75.03 (C_{quat} Cp), 71.05 (2 x CH Cp), 70.34 (5 x CH Cp'), 70.07 (2 x CH Cp), 23.58 (2 x *cis*-CH₃CO₂), 23.25 (*trans*-CH₃CO₂).

Dirhodium(II) tris[μ-(acetato-κO:κO')][μ-(1'-(1-oxohexyl)-ferrocene-1-carboxylato-κO:κO')] (**4b**)

Starting from 50 mg of **3**, dirhodium complex **4b** was obtained as a green solid (49.7 mg, 70% yield).

HRMS (ESI, pos.) m/z : $[M+H]^+$ calcd for $C_{23}H_{29}FeO_9Rh_2$ 710.9271, found: 710.9268. 1H NMR (400 MHz, d_6 -acetone) δ 4.56 (t, $J = 1.9$ Hz, 2x2H, 2 x CH Cp + 2 x CH Cp'), 4.29-4.27 (m, 2x2H, 2 x CH Cp + 2 x CH Cp'), 2.70 (t, $J = 7.1$ Hz, 2H, Cp'C(O)CH₂), 1.813 (s, 6H, 2 x *cis*-CH₃CO₂), 1.807 (s, 3H, *trans*-CH₃CO₂), 1.66-1.62 (m, 2H, Cp'C(O)CH₂CH₂), 1.39-1.34 (m, 4H, 2 x CH₂), 0.94-0.90 (m, 3H, CH₂CH₃). ^{13}C NMR (101 MHz, d_6 -acetone) δ 203.37 (C(O)CH₂), 190.74 (2 x *cis*-CH₃CO₂), 190.63 (*trans*-CH₃CO₂), 188.39 (C₅H₄CO₂), 81.53 (C_{quat} Cp or Cp'), 76.17 (C_{quat} Cp or Cp'), 74.29 (2 x CH Cp or Cp'), 72.79 (2 x CH Cp or Cp'), 71.40 (2 x CH Cp or Cp'), 71.22 (2 x CH Cp or Cp'), 39.95 (C(O)CH₂), 32.25 (CH₂CH₂CH₃), 24.81 (COCH₂CH₂), 23.63 (2 x *cis*-CH₃CO₂), 23.40 (CH₂CH₃), 23.26 (*trans*-CH₃CO₂), 14.32 (CH₂CH₃).

Dirhodium(II) tris[μ -(acetato- $\kappa O:\kappa O'$)] [μ -(1'-hexylferrocene-1-carboxylato- $\kappa O:\kappa O'$)] (4c)

Starting from 50 mg of **3**, dirhodium complex **4c** was obtained as a green solid (42.3 mg, 60% yield).

HRMS (ESI, pos.) m/z : $[M]^+$ calcd for $C_{23}H_{30}FeO_8Rh_2$ 695.9400, found: 695.9413. 1H NMR (400 MHz, d_6 -acetone) δ 4.46 (s, 2H, 2 x CH Cp), 4.17 (s, 2H, 2 x CH Cp), 3.86 (m, 4H, 4 x CH Cp'), 2.24 (t, $J = 7.6$ Hz, 2H, C₅H₄CH₂), 1.79 (m, 9H, 3 x CH₃COO), 1.41 (s, 2H, C₅H₄CH₂CH₂), 1.30 (m, 6H, CH₂(CH₂)₃CH₃), 0.88 (t, $J = 6.5$ Hz, 3H, CH₃). ^{13}C NMR (101 MHz, d_6 -acetone) δ 190.50 (*trans*-CH₃CO₂), 190.41 (2 x *cis*-CH₃CO₂), 189.61 (C₅H₄CO₂), 91.45 (C_{quat} Cp'), 75.13 (C_{quat} Cp) 71.64 (2 x CH Cp), 70.72 (2 x CH Cp), 70.53 (2 x CH Cp'), 69.68 (2 x CH Cp'), 32.47 (one of CH₂(CH₂)₃CH₃), 32.07 (C₅H₄CH₂CH₂), 29.93 (one of CH₂(CH₂)₃CH₃), 29.58 (C₅H₄CH₂), 23.62 (one of CH₂(CH₂)₃CH₃), 23.32 (2 x *cis*-CH₃CO₂), 23.26 (*trans*-CH₃CO₂), 14.36 (CH₃).

Dirhodium(II) tris[μ -(acetato- $\kappa O:\kappa O'$)] [μ -(1-bromoferrocene-1'-carboxylato- $\kappa O:\kappa O'$)] (4d)

Starting from 50 mg of **3**, dirhodium complex **4d** was obtained as a green solid (46.3 mg, 68% yield).

HRMS (ESI, pos.) m/z : $[M]^+$ calcd for $C_{17}H_{17}BrFeO_8Rh_2$ 689.7566, found: 689.7579. 1H NMR (400 MHz, CDCl₃) δ 4.58 (t, $J = 2.0$ Hz, 2H, 2 x CH Cp or Cp'), 4.29 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp or Cp'), 4.25 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp or Cp'), 3.96 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp or Cp'), 1.81 (s, 3H, *trans*-CH₃CO₂), 1.79 (s, 6H, 2 x *cis*-CH₃CO₂). ^{13}C NMR (101 MHz, CDCl₃) δ 190.67 (*trans*-CH₃CO₂), 190.55 (2 x *cis*-CH₃CO₂), 188.51 (C₅H₄CO₂), 78.53 (C_{quat} Cp or Cp'), 76.60 (C_{quat} Cp or Cp'), 74.03 (2 x CH Cp or Cp'), 72.48 (2 x CH Cp or Cp'), 72.33 (2 x CH Cp or Cp'), 70.03 (2 x CH Cp or Cp'), 23.62 (2 x *cis*-CH₃CO₂), 23.25 (*trans*-CH₃CO₂).

Dirhodium(II) tris[μ -(acetato- $\kappa O:\kappa O'$)] [μ -(1'-(phenylthio)ferrocene-1-carboxylato- $\kappa O:\kappa O'$)] (4e)

Starting from 50 mg of **3**, dirhodium complex **4e** was obtained as a green solid (69.3 mg, 96% yield).

HRMS (ESI, pos.) m/z : $[M]^+$ calcd for $C_{23}H_{22}FeO_8Rh_2S$ 719.8495, found: 719.8506. 1H NMR (400 MHz, d_6 -DMSO) δ 7.20 (t, $J = 7.6$ Hz, 2H, 2 x CH Ph), 7.07 (t, $J = 7.3$ Hz, 1H, CH Ph), 6.96 (d, $J = 7.8$ Hz, 2H, 2 x CH Ph), 4.65 (m, 2H, 2 x CH Cp or Cp'), 4.42 (m, 2H, 2 x CH Cp or Cp'), 4.24 (m, 2H, 2 x CH Cp or Cp'), 4.15 (m, 2H, 2 x CH Cp or Cp'), 1.82 (s, 3H, *trans*-CH₃CO₂), 1.74 (s, 6H, 2 x *cis*-CH₃CO₂). ^{13}C NMR (101 MHz, d_6 -DMSO) δ 191.33 (*trans*-CH₃CO₂), 191.26 (2 x *cis*-CH₃CO₂), 189.05 (C₅H₄CO₂), 139.55 (C_{quat} Ph), 128.91 (2 x *o*- or *m*-CH Ph), 125.65 (2 x *o*- or *m*-CH Ph), 125.24 (*p*-CH Ph), 76.76 (C_{quat} Cp or Cp'), 76.09 (2 x CH Cp or Cp'), 74.29 (C_{quat} Cp or Cp'), 72.17 (2 x CH Cp or Cp'), 71.79 (2 x CH Cp or Cp'), 70.85 (2 x CH Cp or Cp'), 23.84 (2 x *cis*-CH₃CO₂), 23.67 (*trans*-CH₃CO₂).

Dirhodium(II) tris[μ -(acetato- $\kappa O:\kappa O'$)] [μ -[2-(carboxy- $\kappa O:\kappa O'$)ethenyl]ferrocenato]] (4f)

Starting from 50 mg of **3**, dirhodium complex **4f** was obtained as a brown solid (39.6 mg, 62% yield).

HRMS (ESI, pos.) m/z : $[M+H]^+$ calcd for $C_{19}H_{21}FeO_8Rh_2$ 638.8696, found: 638.8707. 1H NMR (400 MHz, d_6 -acetone) δ 7.17 (d, $J_{HH} = 15.8$ Hz, 1H, FcCH=CH), 5.81 (d, $J_{HH} = 15.7$ Hz, 1H, FcCH=CH), 4.50 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 4.35 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 4.09 (s, 5H, 5 x CH Cp'), 1.78 (s, 3H, *trans*-CH₃CO₂), 1.76 (s, 6H, 2 x *cis*-CH₃CO₂). ^{13}C NMR (101 MHz, d_6 -acetone) δ 190.39 (*trans*-CH₃CO₂ + 2 x *cis*-CH₃CO₂), 185.78 (C₅H₄CO₂), 141.82 (FcCH=CH), 118.62 (FcCH=CH), 80.20 (C_{quat} Cp), 71.09 (2 x CH Cp), 70.18 (5 x CH Cp'), 69.04 (2 x CH Cp). 23.23 (*trans*-CH₃CO₂ + 2 x *cis*-CH₃CO₂).

Dirhodium(II) tris[μ -(acetato- $\kappa O:\kappa O'$)] [μ -[2-(carboxy- $\kappa O:\kappa O'$)ethynyl]ferrocenato]] (4g)

Starting from 50 mg of **3**, dirhodium complex **4g** was obtained as an olive-green solid (41.4 mg, 65% yield).

HRMS (ESI, pos.) m/z : $[M]^+$ calcd for $C_{19}H_{19}FeO_8Rh_2$ 636.8538, found: 636.8533. 1H NMR (400 MHz, d_6 -acetone) δ 4.52 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 4.36 (t, $J = 1.9$ Hz, 2H, 2 x CH Cp), 4.23 (s, 5H, 5 x CH Cp'), 1.81 (s, 6H, 2 x *cis*-CH₃CO₂), 1.79 (s, 3H, *trans*-CH₃CO₂). ^{13}C NMR (101 MHz, d_6 -acetone) δ 190.97 (*trans*-CH₃CO₂), 190.87 (2 x *cis*-CH₃CO₂), 170.77 (C₅H₄CO₂), 82.48 (FcC \equiv C), 79.67 (FcC \equiv C), 73.03 (2 x CH Cp), 70.90 (5 x CH Cp'), 70.85 (2 x CH Cp), 61.93 (C_{quat} Cp), 23.27 (2 x *cis*-CH₃CO₂), 23.22 (*trans*-CH₃CO₂).

Dirhodium(II) tris[μ -(acetato- $\kappa O:\kappa O'$)] [μ -(4-ferrocenylbenzoato- $\kappa O:\kappa O'$)] (4h)

Starting from 50 mg of **3**, dirhodium complex **4h** was obtained as a green solid (38.0 mg, 55% yield).

HRMS (ESI, pos.) m/z : $[M]^+$ calcd for $C_{23}H_{22}FeO_8Rh_2$ 687.8774, found: 687.8770. 1H NMR (300 MHz, d_6 -DMSO) δ 7.69-7.66 (m, 2H, 2 x CH Ph), 7.52-7.49 (m, 2H, 2 x CH Ph), 4.81 (br s, 2H, 2 x CH Cp), 4.39 (br s, 2H, 2 x CH Cp), 3.97 (s, 5H, 5 x CH Cp'), 1.84 (s, 3H, *trans*-CH₃CO₂), 1.78 (s, 6H, 2 x *cis*-CH₃CO₂). ^{13}C NMR (101 MHz, d_6 -DMSO) δ 191.44 (*trans*-CH₃CO₂), 191.32 (2 x *cis*-CH₃CO₂), 184.65 (PhCO₂), 144.21 (C_{quat}Fc Ph), 128.52 (2 x CH Ph), 128.19 (C_{quat}CO₂ Ph), 125.17 (2 x CH Ph), 82.81 (C_{quat} Cp), 69.69 (2 x CH Cp), 69.53 (5 x CH Cp'), 66.73 (2 x CH Cp), 23.68 (2 x *cis*-CH₃CO₂ + *trans*-CH₃CO₂).

Dirhodium(II) tris[μ -(acetato- $\kappa O:\kappa O'$)] [μ -(1',2',3',4',5'-pentamethylferrocene-1-carboxylato- $\kappa O:\kappa O'$)] (4i)

Starting from 25 mg of **3**, dirhodium complex **4i** was obtained as a green solid (23.3 mg, 68% yield).

HRMS (ESI, pos.) m/z : $[M]^+$ calcd for $C_{22}H_{28}FeO_8Rh_2$ 681.9244, found: 681.9253. 1H NMR (400 MHz, d_6 -acetone) δ 4.01 (t, $J = 1.8$ Hz, 2H, 2 x CH Cp), 3.78 (t, $J = 1.8$ Hz, 2H, 2 x CH Cp), 1.81 (s, 3H, *trans*-CH₃COO), 1.76 (s, 6H, *cis*-CH₃COO), 1.71 (s, 15H, 5 x CH₃ Cp*). ^{13}C NMR (101 MHz, d_6 -acetone) δ 189.48 (*cis*- and *trans*-CH₃CO₂), 188.25 (C₅H₄CO₂), 80.59 (5 x C_{quat} Cp*), 77.02 (C_{quat} Cp), 73.60 (2 x CH Cp), 71.60 (2 x CH Cp), 22.52 (2 x *cis*-CH₃CO₂), 22.32 (*trans*-CH₃CO₂), 9.84 (5 x CH₃ Cp*).

Dirhodium(II) tris[μ -(acetato- $\kappa O:\kappa O'$)] [μ -(1',2',3',4'-tetraisopropylferrocene-1-carboxylato- $\kappa O:\kappa O'$)] (4j)

Starting from 25 mg of **3**, dirhodium complex **4j** was obtained as a green solid (26.1 mg, 67% yield).

HRMS (ESI, pos.) m/z : $[M]^+$ calcd for $C_{29}H_{42}FeO_8Rh_2$ 780.0339, found: 780.0345. 1H NMR (400 MHz, d_6 -acetone) δ 4.44 (s, 2H, 2 x CH Cp), 4.24 (s, 2H, 2 x CH Cp), 3.72 (s, 1H, CH Cp'), 2.73-2.58 (m, 4H, 4 x CH(CH₃)₂), 1.80 (m, 9H, 3 x CH₃COO), 1.35 (d, $J = 7.0$ Hz, 6H, CH(CH₃)₂), 1.26-1.19 (m, 12H, 2 x CH(CH₃)₂), 0.96 (d, $J = 6.7$ Hz, 6H, CH(CH₃)₂). ^{13}C NMR (101 MHz, d_6 -acetone) δ 189.27 (CH₃CO₂ or C₅H₄CO₂), 93.38 (2

x C_{quat} Cp'), 91.70 (2 x C_{quat} Cp'), 71.97 (2 x CH Cp), 70.93 (2 x CH Cp), 61.18 (CH Cp'), 25.56 (*trans*-CH₃CO₂ + 2 x *cis*-CH₃CO₂), 23.62, 23.49, 22.76, 22.61, 22.35 (CH(CH₃)₂ + CH(CH₃)₂). C_{quat} Cp not found.

General methodology for the dirhodium(II)-catalyzed decomposition of diazo substrate **5**:

An oven-dried Schlenk flask was charged with the dirhodium(II) catalyst (0.005 mmol, 2.5 mol%) under argon. Dry CH₂Cl₂ (1.5 mL) was added and a solution of the diazo substrate **5** (54.8 mg, 0.2 mmol) in dry CH₂Cl₂ (1.5 mL) was added dropwise over 1 h via a syringe pump. The TLC analysis showed that the reaction was over after 3 h. The reaction mixture was filtered through a short pad of silica, extensively washed with 10 mL of CH₂Cl₂. The solvent was evaporated *in vacuo* and the crude residue was weighed to determine the (**6+7**) yield and analysed by ¹H NMR to determine the (**6:7**) ratio.

Catalytic reactions with the oxidized dirhodium(II) complexes **4a-b***, **4f*** and **4i***:

An oven-dried Schlenk flask was charged with the dirhodium(II) catalyst (0.005 mmol, 2.5 mol%) under argon. A solution of the [N(4-C₆H₄Br)₃]⁺.BF₄⁻ oxidant in dry CH₂Cl₂ (1.5 mL) was added and the reaction mixture was stirred for 30 min. A solution of the diazo substrate **5** (54.8 mg, 0.2 mmol) in dry CH₂Cl₂ (1.5 mL) was then added dropwise to the mixture over 1 h via a syringe pump. The TLC analysis showed that the reaction was over after 3 h. The reaction mixture was filtered through a short pad of silica, extensively washed with 10 mL CH₂Cl₂. The solvent was evaporated *in vacuo* and the crude residue was weighed to determine the (**6+7**) yield and analysed by ¹H NMR to determine the (**6:7**) ratio.

Aromatic substitution product 6: HRMS (DCI-CH₄) *m/z*: [M+H]⁺ calcd for C₁₅H₂₀O₃ 247.1334, found: 247.1339. ¹H NMR (400 MHz, CDCl₃), enol form: δ 11.13 (s, 1H, C=C-OH), 7.62 (app.d, *J* = 7.5 Hz, 1H, CH Ph), 7.31-7.26 (m, 2H, CH Ph), 7.13 (td, *J* = 7.5, 1.2 Hz, 1H, CH Ph), 3.98 (s, 3H, CO₂CH₃), 3.62 (t, *J* = 6.9 Hz, 1H, CHC(OH)=C), 2.05 (app. hept., *J* = 7.1 Hz, 1H, CH₂CH(CH₃)₂), 1.81 (ddd, *J* = 13.9, 7.0, 7.0 Hz, 1H, CH₂CH(CH₃)₂), 1.69 (ddd, *J* = 13.8, 7.2, 7.2 Hz, 1H, CH₂CH(CH₃)₂), 1.0 (d, *J* = 6.6 Hz, 3H, CH(CH₃)₂), 0.99 (d, *J* = 6.6 Hz, 3H, CH(CH₃)₂); ¹³C NMR (101 MHz, CDCl₃), δ 184.75 (C=C-OH), 169.55 (CO₂Me), 138.60, 138.43 (2 x C_{quat} , Ph), 127.08, 123.62, 123.15, 123.14 (4 x CH Ph), 103.62 (C=C-OH), 51.47 (CO₂CH₃), 46.35 (CHC(OH)=C), 39.72 (CH₂CH(CH₃)₂), 25.56 (CH₂CH(CH₃)₂), 22.90, 22.79 (2 x CH₂CH(CH₃)₂).

Aliphatic C-H activation product 7: HRMS (DCI-CH₄) *m/z*: [M+H]⁺ calcd for C₁₅H₂₀O₃ 247.1334, found: 247.1338. ¹H NMR (400 MHz, CDCl₃), **dia 1**: δ 7.38-7.21 (m, 5H, CH Ph), 3.78 (s, 3H, CO₂CH₃), 3.71 (m, 1H, CH₂CHPh), 3.16 (s, C(CH₃)₂CHCO₂Me), 2.36 (dd, *J* = 12.8 Hz, 8.6 Hz, 1H, CH₂), 2.05 (app. t, *J* = 12.7 Hz, 1H, CH₂), 1.40 (s, 3H, CH₃), 1.21 (s, 3H, CH₃); **dia 2**: δ 7.35-7.23 (m, 5H, CH Ph), 3.75 (s, 3H, CO₂CH₃), 3.68 (m, 1H, CH₂CHC(O)), 3.13 (app. s, C(CH₃)₂CHC(O)), 2.51 (t, *J* = 12.7 Hz, 1H, CH₂), 2.25 (dd, *J* = 13.0 Hz, 9.0 Hz, 1H, CH₂), 1.29 (s, 3H, CH₃), 1.25 (s, 3H, CH₃); **enol form**: δ 7.38-7.21 (m, 5H, CH Ph), 4.05 (t, *J* = 8.8 Hz, 1H, CH₂CHPh), 3.84 (s, 3H, CO₂CH₃), 2.25 (dd, *J* = 12.8 Hz, 8.6 Hz, 1H, CH₂), 1.76 (dd, *J* = 13.0 Hz, 8.7 Hz, 1H, CH₂), 1.34 (s, 3H, CH₃), 1.26 (s, 3H, CH₃). ¹³C NMR (101 MHz, CDCl₃), **dia 1**: δ 210.09 (C(O), ketone), 168.94 (CO₂Me), 137.71 (C_{quat} Ph), 128.6, 128.1, 127.13 (5 x CH Ph), 66.03 (C(CH₃)₂CHCO₂Me), 53.49 (CH₂CHPh), 51.98 (CO₂CH₃), 45.09 (CH₂CHPh), 38.25 (C(CH₃)₂), 29.46 (C(CH₃)₂), 23.74 (C(CH₃)₂); **dia 2**: δ 210.09 (C(O), ketone), 168.94 (CO₂Me), 137.71 (C_{quat} Ph), 128.6, 128.1, 127.13 (5 x CH Ph), 66.03 (C(CH₃)₂CHCO₂Me), 53.49 (CH₂CHPh), 51.98 (CO₂CH₃), 45.09 (CH₂CHPh), 38.25 (C(CH₃)₂), 29.46 (C(CH₃)₂), 23.74 (C(CH₃)₂); **dia 2**: δ 213.02 (C(O), ketone), 169.70 (CO₂Me), 138.14 (C_{quat} , Ph), 128.6, 128.1, 127.08 (5 x CH Ph), 65.32 (C(CH₃)₂CHCO₂Me), 54.55 (CH₂CHPh), 51.98 (CO₂CH₃), 44.71 (CH₂CHPh), 38.29 (C(CH₃)₂), 29.40 (C(CH₃)₂), 25.13 (C(CH₃)₂); **enol form**: δ 175.46 (C=C-OH), 170.82 (CO₂Me), 141.31 (C_{quat} , Ph), 128.6, 127.96, 126.86 (5 x CH Ph), 109.91 (C=C-CO₂Me), 51.07 (CO₂CH₃), 48.99 (CH₂CHPh), 48.10 (CH₂CHPh), 40.22 (C(CH₃)₂), 29.32 (C(CH₃)₂), 27.67 (C(CH₃)₂).

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