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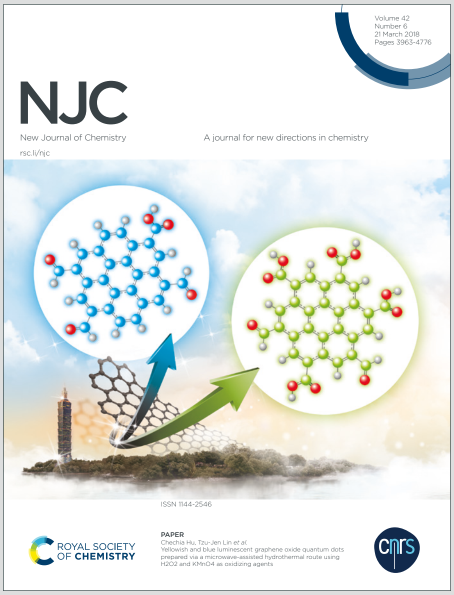

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PAPER
Chechia Hu, Tzu-Jen Lin *et al.*
Yellowish and blue luminescent graphene oxide quantum dots prepared via a microwave-assisted hydrothermal route using H2O2 and KMnO4 as oxidizing agents

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Iron vs Ruthenium: Syntheses, structures and IR spectroelectrochemical characterisation of half-sandwich Group 8 acetylide complexes†

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† Dedicated to Professor Todd B. Marder, colleague, friend, mentor and raconteur, in recognition of his outstanding contributions to chemistry.

Abstract

A convenient modification to the established synthetic routes for the preparation of complexes [M(C≡CR)(dppe)Cp′] (M = Fe, Ru; Cp′ = η^5-C_5H_5 (Cp), η^5-C_5Me_5 (Cp*); R = C_6H_5, C_6H_4OMe, $C_6H_4NO_2$, ^{t}Bu) and [Ru(C≡CR)$(PPh_3)_2$Cp] from the corresponding [MCl(PP)Cp′] complex and the alkyne HC≡CR via an intermediate vinylidene is described. The complexes are generally obtained as high quality crystalline samples directly from the reaction mixture. In agreement with previous studies, the iron complexes undergo a predominantly metal-centred oxidation, whilst there is greater involvement of the acetylide ligand in the oxidation processes associated with the ruthenium analogues. Analysis of the redox properties and spectroelectrochemical investigations reveal limited differences in the gross electronic structures of the Cp vs Cp* derivatives in each of the Fe and Ru series.

Introduction

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The isomerization of alkynes to vinylidenes within the coordination sphere of half-sandwich Group 8 metal acetylide complexes bearing ancillary phosphine ligands has provided access to a range of fascinating stoichiometric and catalytic organometallic chemistry.[1-7] In turn, deprotonation of terminal vinylidene complexes $[M\{C=C(H)R\}(PP)Cp']^+$ (M = Fe, Ru, Os; R = H, alkyl, aryl; PP = bis(mono) or chelating diphosphine; Cp′ = Cp, Cp*) has been identified as the preferred route for the preparation of metal acetylide complexes of general form [M(C≡CR)(PP)Cp′].[8] Complementary to this approach, the in situ desilylation / metallation reactions of [MCl(PP)Cp′] with trimethylsilyl-protected alkynes ($Me_3SiC{\equiv}CR$) in the presence of a fluoride source have also proven immensely useful.[9] In the case of complexes [Fe(C≡CAr)(dppe)Cp*] (Ar = aryl), Sonogashira-style cross-couplings of aryl halides with [Fe(C≡CH)(dppe)Cp*] have also been shown to provide a useful synthetic pathway to these compounds.[10]

The acetylide species [M(C≡CR)(PP)Cp′] are, in general, readily oxidized at modest potentials to the radical cations, $[M(C{\equiv}CR)(PP)Cp']^+$. The characteristic shifts in the ν(C≡C) bands on oxidation provide a clear diagnostic measure for the site of oxidation, with the larger shifts observed in ruthenium[11, 12] and osmium[13] complexes indicating a greater alkynyl ligand based oxidation process than the more metal-centred processes that take place with the iron analogues.[14] These synthetic, electrochemical and spectroscopic properties have made iron and ruthenium {M(C≡CR)(PP)Cp′} fragments exceptionally popular building blocks for the construction and study of ligand-bridged bi- and polymetallic systems, which are ideal for the further study of mixed-valence derivatives and associated investigations of intramolecular electron-transfer processes.[15-21]

In this contribution we describe a simple modification to the preparation of iron and ruthenium acetylide complexes, [M(C≡CR)(PP)Cp′], which allows the one-pot preparation and isolation of pure material, often as single-crystals suitable for X-ray diffraction, directly from the reaction vessel. We have taken advantage of the series so prepared to collect systematic electrochemical, IR spectroelectrochemical and structural benchmarking data to facilitate further studies of mixed-valence complexes based on these fragments that are of contemporary interest.

Results and Discussion

Routes to [Fe(C≡CR)(dppe)Cp] complexes*

The synthetic routes reported to date for complexes [Fe(C≡CR)(dppe)Cp*] from the halide complex [FeCl(dppe)Cp*][22] are illustrative of a range of the potential routes that have been employed in the preparation of half-sandwich acetylide complexes of the Group 8 metals. In an early report, the compound [Fe(C≡CPh)(dppe)Cp*] was prepared in two-steps, with initial reaction of [Fe(NCMe)(dppe)Cp*]PF_6 and HC≡CPh giving the vinylidene [Fe{C=C(H)Ph}(dppe)Cp*]PF_6 which could be isolated (55%) and subsequently deprotonated. Purification of the acetylide complex was achieved by column chromatography and low temperature crystallization gave [Fe(C≡CPh)(dppe)Cp*] in 47% yield.[23] The reaction of [FeCl(dppe)Cp*] with a terminal alkyne, HC≡CR, in a polar medium (e.g. methanol) in the presence of a salt which serves as a halide anion abstractor (e.g. NH_4PF_6) over periods of typically 12

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hours or more also gives the vinylidene complexes [Fe{C=C(H)R}(dppe)Cp*](PF$_6$) (87 – 97%), which can be isolated or deprotonated in situ to give [Fe(C≡CR)(dppe)Cp*] (80 – 98%).[24]

Photochemical ligand exchange reactions have also been demonstrated to give similar complexes from [FeCl(CO)$_2$Cp*], dppe, a terminal aryl alkyne and DBU.[25] The reaction likely proceeds via initial carbonyl dissociation and formation of the carbonyl cation, [Fe(CO)(dppe)Cp*]$^+$ before a second photochemical displacement of the remaining carbonyl ligand to create the vacant coordination site for binding and isomerization of the alkyne ligand to give the vinylidene complexes. Subsequent deprotonation gave the acetylide complexes [Fe(C≡CR)(dppe)Cp*] in moderate to good yield (28 – 79%) in an overall two-step, one pot process; a higher yield (92%) of [Fe(C≡CPh)(dppe)Cp*] was obtained when the reaction with HC≡CPh was carried out in stepwise two-step, two-pot fashion. Alternatively, metalla-Sonogashira reactions[26] of [Fe(C≡CH)(dppe)Cp*] with aryl halides, ArBr, catalyzed by Pd/Cu co-catalysts in amine solvents have also proven useful;[10, 25] indeed many examples of functionalized arylacetylide complexes [Fe(C≡CAr)(dppe)Cp*] have been prepared by this route and isolated in yields from 30 – 71%.[10] Regardless of the method of preparation, the oxidation of [Fe(C≡CR)(dppe)Cp*] complexes at low potentials and the relatively high basicity of the C(β) carbon creates difficulties in isolating pure samples of these compounds, leading to numerous descriptions of purification procedures in the literature.

Routes to [Fe(C≡CR)(dppe)Cp] complexes

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Synthetic routes to Fe(C≡CR)(dppe)Cp complexes have been amply demonstrated from [FeCl(dppe)Cp][27] and [FeI(PP)Cp] (PP = dppe, (*R*)-(+)-1,2-bis(diphenylphosphino)propane ((*R*)-PROPHOS))[28] using a variety of halide abstracting agents, including NH_4PF_6[29] and $AgBF_4$.[30] Astruc has described a simple visible-light driven photolysis reaction of [FeCp(η^6-C_6H_5Me)]PF_6 with terminal alkynes in the presence of dppe to give [Fe(C≡CR)(dppe)Cp] complexes in near quantitative yields,[31] whilst photolysis of [Fe(CO)(dppe)Cp]BF_4 with alkynes gives the corresponding vinylidenes,[32] and photolytic carbonyl-phosphine exchange of [Fe(C≡CR)$(CO)_2$Cp] gives [Fe(C≡CR)(dppe)Cp] complexes (24% in the case of [Fe(C≡CCH_2CH_2CN)(dppe)Cp]).[33] Transmetallation of the alkynyl ligand from [Au(C≡CAr)(PPh_3)] to [FeCl(dppe)Cp] (Ar = Ph, C_6H_5Me) has also provided route to acetylide complexes [Fe(C≡CAr)(dppe)Cp] in moderate (43 – 54%) yield.[34]

Routes to [Ru(C≡CR)(dppe)Cp] complexes*

Although early preparations of complexes [Ru(C≡CR)(dppe)Cp*] described the formation of the intermediate vinylidene from [RuCl(dppe)Cp*] and a terminal alkyne in methanol without any additional halide abstracting agent affording the products in 40 – 64% yield,[23] the great majority of subsequent reports have utilized NH_4PF_6 or similar species as a co-reagent in the preparation of the intermediate vinylidene.[11, 12, 35-48] The effective use of the metallo-Sonogashira reaction in the preparation of such complexes has also been described, giving complexes in 20-80% yield,[11] whilst transmetallation from [Au(C≡CAr)(PPh_3)] to [RuCl(dppe)Cp*] has also been demonstrated giving [Ru(C≡CAr)(dppe)Cp*] (ca. 50%).[34] The in situ desilylation/metallation reaction has also proven to be effective for a wide variety of

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alkynyl ligand substituents,[9] with the complexes often precipitating cleanly as microcrystalline powders during the course of the reaction.[38, 43, 49-60]

Routes to [Ru(C≡CR)(dppe)Cp]

The synthetic chemistry of [Ru(C≡CR)(dppe)Cp] complexes is similar to that of complexes [Ru(C≡CR)(dppe)Cp*]. Many of the examples of complexes [Ru(C≡CR)(dppe)Cp] reported to date have been prepared via deprotonation of the corresponding vinylidene, obtained from [RuCl(dppe)Cp], a halide abstracting agent and the appropriate terminal alkyne.[27, 38, 61, 62] However, the desilylation/metallation route has also proven effective with the complexes precipitating cleanly from the methanol reaction solution, and has become a route of choice in recent times.[38, 63, 64]

Routes to [Ru(C≡CR)($(PPh_3)_2$Cp]

Complexes [Ru(C≡CR)$(PPh_3)_2$Cp] are perhaps the archetypal members of the family of half-sandwich Group 8 metal acetylide complexes. These compounds are almost universally prepared via deprotonation of an intermediate vinylidene complex, formed from [RuCl$(PPh_3)_2$Cp] and the terminal alkyne in a polar solvent such as methanol. The initial report described the preparation of [Ru(C≡CPh)$(PPh_3)_2$Cp], which was isolated in 87% yield, via deprotonation of the vinylidene [Ru{C=C(H)Ph}$(PPh_3)_2$Cp]Cl formed in situ from [RuCl$(PPh_3)_2$Cp] and HC≡CPh in methanol.[65] Analogous procedures were found effective in later studies.[66-70] However, the addition of halide abstracting agents such as NH_4PF_6, $NaBPh_4$, or other similar compound within the reaction mixture has become commonplace in many synthetic schemes.[12, 36, 38, 42, 43, 45, 68, 71-86] Desilylation / metallation strategies have also proven effective[9] the complexes generally being isolated by precipitation from the methanol

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reaction medium and purified by column chromatography. Transmetallation reactions from gold acetylides have also been demonstrated for this metal ligand group.[34]

A simplified synthetic procedure

From the brief summaries above, it is apparent that the rearrangement of terminal alkynes to vinylidenes within the coordination sphere of half-sandwich metal complexes $\{M(PP)Cp'\}^+$ fragments provides a convenient entry to the chemistry of metal acetylide complexes $[M(C{\equiv}CR)(PP)Cp']$. The very early literature indicates that the formation of $[M\{C{=}C(H)R\}(PP)Cp']^+$ complexes can take place directly from $[MCl(PP)Cp']$ and the alkyne in a polar solvent such as methanol,[23, 65] with the ionization of the M-Cl bond apparently sufficient under such conditions to be displaced by the alkyne ligand. Over the intervening years, it has become more common to run these reactions in the presence of a ‘halide abstracting agent’, although the true importance of such co-reagents is perhaps due for re-consideration. Certainly if the vinylidene complex is to be isolated then the metathesis of the smaller chloride counter ion for a larger PF_6^-, BPh_4^- or other example is to be recommended. However, for the formation of the vinylidene and deprotonation in situ it is less clear if the co-reagent is necessary.

Here, we have explored the direct reactions of the half-sandwich chloride complexes $[FeCl(dppe)Cp^*]$, $[FeCl(dppe)Cp]$, $[RuCl(dppe)Cp^*]$, $[RuCl(dppe)Cp]$ and $[RuCl(PPh_3)_2Cp]$ with $HC{\equiv}CPh$, $HC{\equiv}CC_6H_4$-*p*-OMe, $HC{\equiv}CC_6H_4$-*p*-NO_2 and $HC{\equiv}C^tBu$ as representative terminal acetylenes. The reactions are typically carried out in a small volume of laboratory grade methanol, which was degassed by sparging with nitrogen before use, but not specially dried. The reactions proceeded readily

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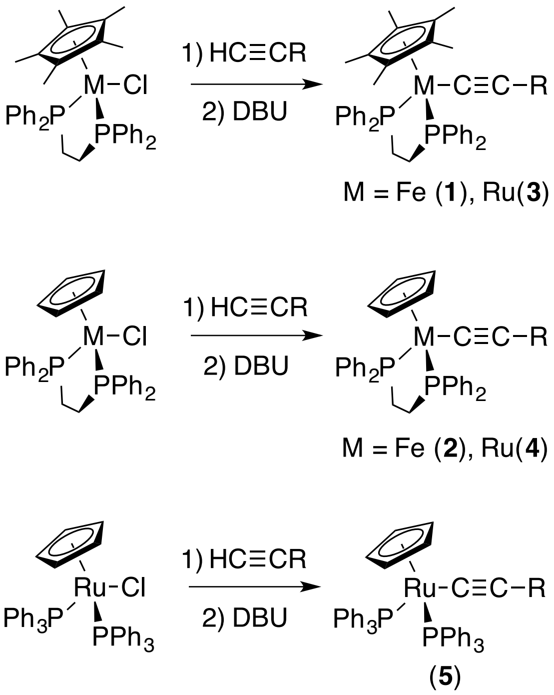
under reflux to give solutions containing the appropriate vinylidene over the course of ca. 1 – 2 hours, with only the formation of [Ru{C=C(H)^{t}Bu}(dppe)Cp] taking somewhat longer (5h) (Scheme 1). The progress of the reaction was followed by the dissolution of the [MCl(PP)Cp′] reagent, the pronounced colour changes accompanying vinylidene formation and in situ $^{31}P\{^1H\}$ NMR monitoring indicating the clean transformation of the chloride [MCl(PP)Cp′] to [M{C=C(H)R}(PP)Cp′]Cl complexes.



	R
a	C_6H_5
b	C_6H_4OMe-4
c	$C_6H_4NO_2$-4
d	Bu^t

Scheme 1. The preparation of complexes [**1a-d**] – [**5a-d**]

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The conversion of the vinylidene to the acetylide and work-up was achieved simply by stopping the stirring and heating of the reaction mixture, and then allowing a drop of 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) to slowly diffuse into the hot solution. As the reaction solution cooled, the acetylide products crystallised, often in a form suitable for single-crystal X-ray diffraction, and were isolated in 50 – 88% yield by simple filtration. However, the complex $[Ru(C{\equiv}CC_6H_4\text{-}p\text{-}NO_2)(dppe)Cp]$ (**4c**) proved to be rather more soluble in methanol and sensitive to methoxide addition at C(α) to give the methoxy carbene $[Ru\{C(OMe)CH_2C_6H_4\text{-}p\text{-}NO_2\}(dppe)Cp]^+$. In this case, work-up necessitated purification by preparative TLC.

Each of the complexes was characterised by the usual array of NMR spectroscopies (^{1}H, ^{13}C{^{1}H}, ^{31}P{^{1}H}), IR spectroscopy and mass spectrometry, with data generally consistent with that available in the literature. The ^{31}P{^{1}H} NMR data were particularly diagnostic of the various metal fragments, falling near 99 (**1**), 106 (**2**), 81 (**3**), 86 (**4**) and 51 (**5**) ppm. Much more subtle variations were observed as a function of the acetylide substituent, with the ^{31}P{^{1}H} NMR resonances of the *t*Bu complexes **d** falling somewhat downfield of the aryl compounds **a** – **c** in each series. The assignments of the ^{13}C{^{1}H} NMR data were made on the basis of ^{1}H-^{13}C{^{1}H} COSY spectra and the J_{CP} coupling constants in the case of C(α) (Table S1). The C(α) resonances of the acetylide ligands in the complexes $[M(C{\equiv}CR)(PP)Cp']$ were more sensitive to the electronic nature of the R group, falling in sequence δ(C(α)) / ppm **c** (R = C_6H_4-*p*-NO_2) > **a** (R = C_6H_5) > **b** (R = C_6H_4-*p*-OMe) > **d** (R = *t*Bu).

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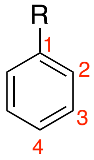
The $^{13}C\{^1H\}$ NMR chemical shift of aromatic hydrocarbons can be estimated from simple additive relationships and well-defined, but empirical, substituent specific parameters, z_i (Equation 1, Table 1)

$$\delta_C = 128.5 + \sum z_i \qquad (1)$$

Table 1. NMR substituent parameters for Equation 1.



R	z_1	z_2	z_3	z_4
H	0	0	0	0
OMe	30.2	-14.7	0.9	-8.1
NO_2	19.6	-5.3	0.8	6.0
*t*Bu	22.1	-3.4	-0.4	-3.1
Cp*(dppe)Fe−C≡C	2.1	3.2	-1.0	-5.3
Cp(dppe)Fe−C≡C	1.5	1.9	-1.0	-5.5
Cp*(dppe)Ru−C≡C	3.0	1.8	-0.9	-5.9
Cp(dppe)Ru−C≡C	1.4	2.0	-1.4	-5.6
$Cp(Ph_3P)_2Ru$−C≡C	2.2	2.1	-0.7	-5.4

From this expression, the associated substituent parameters, z_i, of the metal acetylide fragments were estimated from the $^{13}C\{^1H\}$ chemical shifts of complexes **1a**, **2a**, **3a**, **4a** and **5a** (Table 1). The additive relationship of Equation 1 were found to hold remarkably well for the metal arylacetylide complexes [**1b**,**c**] – [**5b**,**c**] (Table 2), giving further confidence in the assignments proposed (Table S1).

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Table 2. Summary of experimental and estimated $^{13}C\{^{1}H\}$ NMR data (C_1, C_2, C_3, C_4) of compounds [**1b**,**c**] – **5b**,**c**].[a]

	C1		C2		C3		C4	
	Exp	Calc	Exp	Calc	Exp	Calc	Exp	Calc
1b[b]	124.8	122.5	131.5	132.6	114.1	112.8	156.7	153.4
1c[c]	137.7	136.6	129.7	132.5	124.0	122.2	141.8	141.8
2b[c]	124.3	121.9	131.7	131.3	113.6	112.8	156.7	153.2
2c[b]	136.8	136.0	130.3	131.2	123.7	122.2	143.4	142.6
3b[c]	124.5	123.4	131.2	131.2	113.3	112.9	155.7	152.8
3c[c]	138.5	137.5	130.0	131.1	123.6	122.3	142.1	142.2
4b[c]	123.1	121.8	131.7	131.4	113.0	112.4	156.0	153.1
4c[c]	137.4	135.9	130.5	131.3	123.3	121.8	142.7	142.7
5b[c]	123.8	122.6	131.5	131.5	113.4	113.1	156.0	153.4
5c[c]	137.7	136.6	130.5	129.7	123.8	122.2	142.8	142.8

[a] estimated values from Equation 1 and data in Table 1. [b] experimental data in C_6D_6 solution. [b] experimental data in $CDCl_3$ solution.

Molecular Structures

The molecular structures of the compounds **1a-d** – **5a-d** have been determined, here or previously (Table 3, Figures S83 – S91). A survey of the key bond lengths give in Table 1 indicates some important trends across the series and within each sub-group. The {M(dppe)Cp} (M = Fe, Ru) fragments are rather more compact than the {M(dppe)Cp*} analogues, and despite the more electron-donating nature of the Cp* fragment, the average M-P distances are marginally shorter in the Cp systems. This may suggest that intramolecular steric interactions between the Cp* and dppe ligands over-ride any increase in the M-P back-bonding contribution arising from the more electron-rich metal fragment with respect to comparisons of {M(dppe)Cp} and {M(dppe)Cp*} complexes.

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Metal-acetylide back-bonding is thought to play only a small role in the overall electronic structure of metal acetylide complexes,[87] and direct analyses of electronic trends in the π-framework as a simple function of bond lengths can be complicated by underlying effects arising from the σ-system and bond polarization.[88] Within the relatively precise experimental data set in Table 3 (Figure 1), the M-C(α) and C(α)≡C(β) bond lengths are essentially insensitive to the nature of the Cp´ ligand in each pair of complexes [M(C≡CC_6H_4Y)(dppe)Cp´]. Comparisons of the structural data from the Y = OMe and NO_2 series hints at a degree of increased cumulenic character along the M-C≡C-C_6H_4-NO_2 backbone. However, the greatest indication of the variation in electron density at the metal centre induced by the electron-donating (Y = OMe), electron-neutral (Y = H) or electron-withdrawing (Y = NO_2) group comes from the most precisely determined M-P bond lengths.[76] The systematic elongation of these bonds within each sub-set of complexes (e.g. M-P **1b** < **1a** < **1c**) is consistent with the overall decrease in electron density at the metal centre and diminished M-P back-bonding.

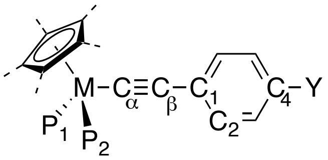

Figure 1. The atom labeling scheme used in Table 3.

Table 3. Selected bond lengths (Å), bond and torsion angles (º) from the crystallographically determined structures of **1a-d** – **5a-d**.

		M-P$_1$	M-P$_2$	M-C(α)	C(α)-C(β)	C(β)-C(1)	C(4)-Y	P$_1$-M-P$_2$	Ref
[Fe(C≡CPh)(dppe)Cp*]	**1a**	2.1857(10)	2.1745(9)	1.894(3)	1.210(4)	1.430(4)		85.92(4)	[10]
[Fe(C≡CPh)(dppe)Cp][a]	**2a**	2.1618(17)	2.1577(16)	1.908(6)	1.205(8)	1.443(8)		86.80(6)	this work
[Ru(C≡CPh)(dppe)Cp*]	**3a**	2.2622(12)	2.2563(12)	2.011(4)	1.215(5)	1.431(5)		83.73(4)	[11]
[Ru(C≡CPh)(dppe)Cp]	**4a**	2.240(1)	2.250(1)	2.009(3)	1.204(5)	1.444(5)		83.3(1)	[89]
[Ru(C≡CPh)(PPh$_3$)$_2$Cp]	**5a**	2.307(1)	2.294(1)	2.017(5)	1.214(7)	1.462(8)		100.9(1)	[89]
[Fe(C≡CC$_6$H$_4$OMe-4)(dppe)Cp*]	**1b**	2.1789(6)	2.1884(6)	1.899(2)	1.215(3)	1.437(3)	1.382(3)	86.50(2)	[90]
[Fe(C≡CC$_6$H$_4$OMe-4)(dppe)Cp]	**2b**	2.1611(11)	2.1752(11)	1.900(4)	1.217(6)	1.446(6)	1.369(5)	86.88(4)	this work
[Ru(C≡CC$_6$H$_4$OMe-4)(dppe)Cp*]	**3b**	2.2652(6)	2.2643(6)	2.015(2)	1.216(3)	1.433(3)	1.379(3)	83.01(2)	[11]
[Ru(C≡CC$_6$H$_4$OMe-4)(dppe)Cp]	**4b**	2.2461(12)	2.2599(12)	2.023(5)	1.203(6)	1.444(6)	1.378(5)	84.03(4)	this work
[Ru(C≡CC$_6$H$_4$OMe-4)(PPh$_3$)$_2$Cp][b]	**5b**	2.2922(6)	2.2902(5)	2.019(2)	1.212(3)	1.442(3)	1.378(3)	99.18(2)	[81]
[Fe(C≡CC$_6$H$_4$NO$_2$-4)(dppe)Cp*]	**1c**	2.1911(8)	2.1857(8)	1.876(3)	1.220(4)	1.419(4)	1.455(4)	86.56(3)	[10]
[Fe(C≡CC$_6$H$_4$NO$_2$-4)(dppe)Cp]	**2c**	2.158(2)	2.157(2)	1.856(8)	1.216(10)	1.442(11)	1.450(13)	85.15(8)	[28]
[Ru(C≡CC$_6$H$_4$NO$_2$-4)(dppe)Cp*]	**3c**	2.2639(6)	2.2721(6)	2.001(3)	1.218(4)	1.424(4)	1.452(3)	83.77(2)	this work
[Ru(C≡CC$_6$H$_4$NO$_2$-4)(dppe)Cp]	**4c**	2.2525(8)	2.2463(8)	1.993(3)	1.214(4)	1.424(4)	1.451(4)	84.91(3)	[61]
[Ru(C≡CC$_6$H$_4$NO$_2$-4)(PPh$_3$)$_2$Cp]	**5c**	2.297(2)	2.301(2)	1.994(5)	1.202(8)	1.432(7)	1.468(6)	101.17(7)	[66]
[Fe(C≡CBu^t)(dppe)Cp*]	**1d**	2.1557(15)	2.1762(15)	1.912(5)	1.208(7)	1.490(7)		85.96(6)	this work
[Fe(C≡CBu^t)(dppe)Cp][b]	**2d**	2.1472(7)	2.1557(7)	1.920(2)	1.123(3)	1.483(3)		86.94(2)	this work
[Ru(C≡CBu^t)(dppe)Cp*]	**3d**	2.2440(9)	2.2527(11)	2.015(4)	1.215(6)	1.482(6)		82.13(4)	this work
[Ru(C≡CBu^t)(dppe)Cp]	**4d**	2.2463(6)	2.2528(6)	2.019(2)	1.198(3)	1.478(3)		83.53(2)	this work
[Ru(C≡CBu^t)(PPh$_3$)$_2$Cp]	**5d**	2.2807(4)	2.2815(4)	2.0224(18)	1.207(2)	1.478(2)		102.57(2)	this work

[a] data from one of four molecules in the unit cell [b] data from one of two molecules in the unit cell

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Electrochemistry and Spectroelectrochemistry

A number of previous studies have explored trends in electrochemical potential of complexes [M(C≡CR)(PP)Cp′] as a function of the alkynyl group substituent, R.[10, 11] However, fewer studies have looked at the comparative redox potentials of such complexes as a function of the different {M(PP)Cp′} fragments. Here, the family of complexes **1a-d** – **5a-d** offer an opportunity to benchmark the electrochemical potentials of the five readily available half-sandwich complex types over a range of alkynyl substituents and permit comparisons of the relative behavior (Table 4)

Table 4. Electrochemical potentials ($E_{1/2}$ / V vs Fc/Fc$^+$) for complexes **1a-d** – **5a-d** (CH_2Cl_2 / 0.1 M NBu_4PF_6)

	^{t}Bu	C_6H_4-*p*-OMe	Ph	C_6H_4-*p*-NO_2
Fe(dppe)Cp*	–0.76	–0.67	–0.63	–0.46
Fe(dppe)Cp	–0.54	–0.46	–0.40	–0.27
Ru(dppe)Cp*	–0.35	–0.31	–0.24	–0.08
Ru(dppe)Cp	–0.19	–0.17	–0.09	+0.08
Ru(PPh_3)$_2$Cp	–0.10	–0.12	–0.03	+0.14

Each complex undergoes a largely electrochemically and chemically reversible one-electron oxidation process in room temperature solution (CH_2Cl_2 / 0.1 M NBu_4PF_6) at moderate potential vs ferrocene/ferricenium [$E_{1/2}$(Fc/Fc$^+$) = 0 V] at a platinum working electrode (Table 2, Figure S1). The anodic and cathodic current ratios of the {Ru(PPh_3)$_2$Cp} series (**5**) indicates some degree of chemical instability in the oxidized products, but linear plots of peak currents against $\nu^{1/2}$ are consistent with the electrochemical reversibility (diffusion controlled) of these processes. The other

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complexes display almost ideal electrochemical behavior. The data in Table 2 also reveals that for both iron and ruthenium examples of {M(dppe)Cp′} complexes, the introduction of a Cp* ligand causes a decrease in oxidation by ca. –0.2 V relative to the Cp analogue. Similarly, the iron examples {Fe(dppe)Cp′} undergo oxidation approximately some 0.3 – 0.4 V lower (less positive) than the isostructural {Ru(dppe)Cp′} examples. Comparisons of the oxidation potentials of complexes [Ru(C≡CR)(dppe)Cp] (**4a-d**) and [Ru(C≡CR)(PPh_3)$_2$Cp] (**5a-d**) clearly indicate the more electron-donating nature of the dppe vs (PPh_3)$_2$ ancillary ligands, with the complexes **4** undergoing oxidation some 0.05 – 0.09 V lower (less positive) than the analogous compounds **5** (Table 4).

The characteristic shifts in the ν(C≡C) frequencies of metal acetylide complexes on oxidation have proven useful as indirect reporters on the nature of the redox processes in such systems (i.e. ligand vs metal character),[11, 12, 15, 91-97] and in this regard spectroelectrochemistry has proven to be an especially useful technique to assess such changes.[98] Although the complex types described here are well-known, there have been few direct comparisons of the spectroscopic behavior of the [M(C≡CC_6H_4Y)(dppe)Cp] complexes with their better investigated Cp* analogues.

Infra-red spectoelectrochemical data from the complexes in sub-series **b** – **d** are given in Table 5, and spectra illustrated in Figure S2. Given the propensity for phenylacetylide complexes to dimerize on oxidation,[97] the series of complexes [M(C≡CPh)(PP)Cp′] (**a**) were not investigated within the spectroelectrochemical cell.

Table 5. Summary of IR spectroelectrochemical data (from 0.1 M NBu_4PF_6 / CH_2Cl_2 solutions) for complexes [**1b-d**] – [**5b-d**].

		$E_{1/2}$ / V[a]	ν(C≡C) / cm^{-1}		ν(C≡C) / cm^{-1}	Δν(C≡C) / cm^{-1}
[Fe(C≡CC$_6$H$_4$OMe-4)(dppe)Cp*]	**1b**	–0.67	2059 *ATR 2059*	[**1b**]$^+$	1988	–71
[Fe(C≡CC$_6$H$_4$OMe-4)(dppe)Cp]	**2b**	–0.46	2065 *ATR 2064*	[**2b**]$^+$	1978	–87
[Ru(C≡CC$_6$H$_4$OMe-4)(dppe)Cp*]	**3b**	–0.31	2074 *ATR 2074*	[**3b**]$^+$	1929	–145
[Ru(C≡CC$_6$H$_4$OMe-4)(dppe)Cp]	**4b**	–0.17	2079 *ATR 2080*	[**4b**]$^+$	1938	–141
[Ru(C≡CC$_6$H$_4$OMe-4)(PPh$_3$)$_2$Cp]	**5b**	–0.12	2072 *ATR 2065*	[**5b**]$^+$	1930	–142
[Fe(C≡CC$_6$H$_4$NO$_2$-4)(dppe)Cp*]	**1c**	–0.46	2036s, 2008s *ATR 2026, 1999*	[**1c**]$^+$	N/A[c]	
[Fe(C≡CC$_6$H$_4$NO$_2$-4)(dppe)Cp]	**2c**	–0.27	2044s, 2010w *ATR 2042, 2010*	[**2c**]$^+$	N/A [e]	
[Ru(C≡CC$_6$H$_4$NO$_2$-4)(dppe)Cp*]	**3c**	–0.08	2047s, 2015m *ATR 2044, 2003*	[**3c**]$^+$	N/A	
[Ru(C≡CC$_6$H$_4$NO$_2$-4)(dppe)Cp]	**4c**	+0.08	2056s, 2014w *ATR 2053, 2017*	[**4c**]$^+$	N/A	
[Ru(C≡CC$_6$H$_4$NO$_2$-4)(PPh$_3$)$_2$Cp]	**5c**	+0.14	2052s, 2011w *ATR 2031, 2004*	[**5c**]$^+$	N/A	
[Fe(C≡CBu^t)(dppe)Cp*]	**1d**	–0.76	2069 *ATR 2062*	[**1d**]$^+$	2034	–35
[Fe(C≡CBu^t)(dppe)Cp]	**2d**	–0.54	2069 *ATR 2078*	[**2d**]$^+$	2025	–44
[Ru(C≡CBu^t)(dppe)Cp*]	**3d**	–0.35	2087 *ATR 2083*	[**3d**]$^+$	1984, 1967	–103, –120
[Ru(C≡CBu^t)(dppe)Cp]	**4d**	–0.19	2084 *ATR 2084*	[**4d**]$^+$	1982, 1963	–102, –121
[Ru(C≡CBu^t)(PPh$_3$)$_2$Cp]	**5d**	–0.10	2089 *ATR 2081*	[**5d**]$^+$	1977, 1957	–112, –132

[a] vs ferrocene / ferricenium

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The smaller shift in the ν(C≡C) band (Δν(C≡C)) of the iron complexes **1b** and **2b** on oxidation in comparison with the ruthenium examples **3b**, **4b** and **5b** is consistent with the greater metal character in the iron oxidation events,[14, 90, 99] and the more ligand-centred oxidation of the ruthenium compounds (Table 3).[11, 12, 43] However, for each metal, the spectroelectrochemical response is almost independent of the nature of the ancillary ligands.

The IR spectra of the nitro-substituted complexes **c** present a range of features worthy of comment. The neutral complexes **1c – 5c** are characterized by two ν(C≡C) bands separated by ca. 30 – 40 cm^{-1} in both the solid state and CH_2Cl_2 solution (Table 3). These features arise from the stabilization of two conformers of the nitroaromatic moiety with respect to the {M(PP)Cp′} fragment stabilized by the enhanced donor-acceptor interaction through the alkynyl moiety. These conclusions are readily mapped to the results of frequency calculations carried out on DFT optimized geometries (BLYP35, LANL2DZ (Ru) / 6-31G** (all other atoms), CPCM(CH_2Cl_2)) chosen to sample two points on the ground-state potential energy surfaces of **4c** and [**4c**]$^+$, as representative examples. The geometries of the neutral system were optimized from initial structures in which the nitrobenzene ring was positioned approximately bisecting the P-Ru-P angle (**4c′**) or rotated around the Ru-C≡C axis by ca. 90º (**4c′′**) (Figure 2). These two representative geometries, which differ in energy only by ca. 2 kJ/mol (**4c′** being more stable at this level of theory), give rise to ν(C≡C) bands at 2028 cm^{-1} (**4c′**) and 2043 cm^{-1} (**4c′′**), in good agreement with the two band envelopes observed in the experimental spectrum (2014, 2056 cm^{-1}; Table 3).

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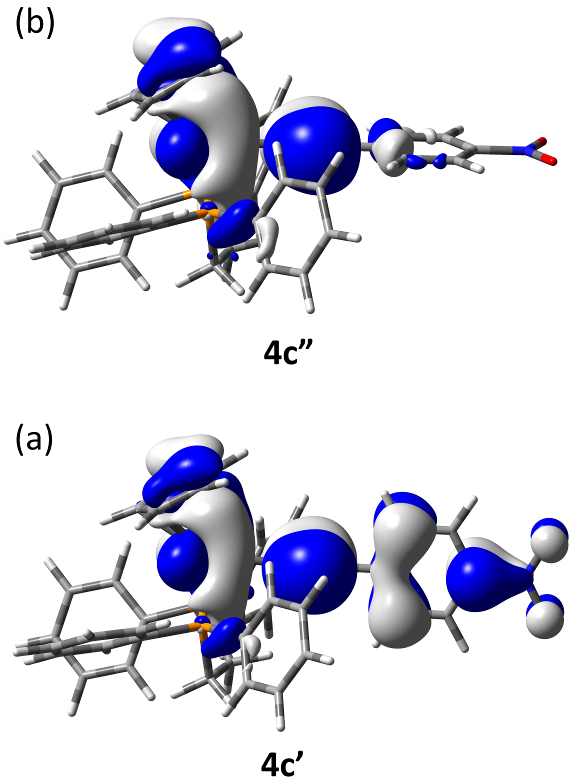

Figure 2. Plots of the computational model complexes **4c´** and **4c´´**, illustrating the different conformation of the aryl ring and the associated distribution of the HOMO in each case (HOMO % composition Ru / C≡C / C_6H_4-*p*-NO_2: **4c´** 36/28/20; **4c´´** 46/29/2)

In contrast, the one-electron oxidised complexes [**1c** – **5c**]$^+$ do not display an IR active ν(C≡C) band; this is likely due the diminished dipole moment over the alkynyl moiety and reflects a degree of metal character in the oxidation event for both the iron and ruthenium systems.

In the case of the *t*Bu terminated complexes **1d** – **5d** the average shift in the ν(C≡C) band was smaller than the aryl-capped complexes. This reflects the diminished delocalization of the radical cation and the greater metal character in the oxidation

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event for both iron and ruthenium complexes. The IR spectra of the ruthenium complexes [**3d**]$^+$, [**4d**]$^+$ and [**5d**]$^+$ were characterized by two distinct ν(C≡C) bands separated by ca. 20 cm^{-1}, in this case likely due to Fermi coupling.

Conclusions

A convenient one-pot procedure for the preparation of the half-sandwich metal acetylide complexes [M(C≡CR)(dppe)Cp′] (M = Fe, Ru; Cp′ = Cp, Cp*; R = C_6H_5, C_6H_4OMe, $C_6H_4NO_2$, ^{t}Bu) and [Ru(C≡CR)$(PPh_3)_2$Cp] has been described. These complexes, which are usually obtained as high-quality crystalline samples directly from the reaction vessel, have been characterized by a combination of spectroscopic, spectrometric and electrochemical methods. Whilst electrochemical and IR spectroelectrochemical studies confirm the anticipated distinction in the predominant redox character of the iron (more metal centred) and ruthenium (more acetylide ligand centred), the systematic study also reveals little change in the nature of these processes as a function of the Cp vs Cp* ancillary ligand. The relative expense of pentamethylcyclopentadiene vs cyclopentadiene and the lower computational expense involved in DFT investigations of the Cp derivatives, suggests that {M(dppe)Cp} based complexes are viable substitutes for the more thoroughly investigated {M(dppe)Cp*} systems in future studies.

Experimental

General information

All reactions were carried out under nitrogen using standard Schlenk procedures, but no special methods were used during work up. Reaction solvents were used as received, and degassed by sparging with nitrogen before use. The compounds [FeCl(dppe)Cp*],[22] [FeCl(dppe)Cp],[22] [RuCl(dppe)Cp*],[22] [RuCl(dppe)Cp],[22] and [RuCl(PPh_3)$_2$Cp],[8] and the alkynes 4-ethynyl anisole ($HC\equiv CC_6H_4$-*p*-OMe)[100] and 4-ethynyl nitrobenzene ($HC\equiv CC_6H_4NO_2$)[100] were prepared by literature routes. Other compounds were purchased and used as received.

NMR data were collected on 400 MHz Varian, 500 MHz Bruker and 600 MHz Bruker machines. ^1H and $^{13}C\{^1H\}$ NMR spectra were referenced to $CDCl_3$ solvent signals (δ 7.26 ppm and δ 77.16 ppm respectively) and C_6D_6 solvent signals (δ 7.16 ppm and δ 128.06 ppm respectively). A summary of $^{13}C\{^1H\}$ NMR data is given in Table S1. IR spectra were recorded on a Cary 630 FTIR Spectrometer with an ATR method. Electrospray Ionisation, positive mode (ESI+) Mass Spectra were collected on a Waters Liquid Chromatograph Premier Mass Spectrometer.

Cyclic voltammetry was conducted in a standard three-electrode cell, with Pt disc working electrode, Pt wire counter and Pt wire pseudo-reference electrodes, from solutions in 0.1 M NBu_4PF_6 / CH_2Cl_2, with data collected from an EmStat3+ potentiostat. The decamethylferrocene/decamethylferrocinium or ferrocene/ferrocinium couples were used as internal references for potential measurements ($Fc^*H/Fc^*H^+ = -0.48$ V; $FcH/FcH^+ = 0.00$ V). Spectroelectrochemical studies were conducted in a transmission cell of Hartl design fitted with CaF_2 widows,[101] and controlled by the EmStat3+ from solutions of the analyte (ca. 1 mM) in 0.1 M NBu_4PF_6 / CH_2Cl_2. Data were recorded on Cary 5000 UV-vis-NIR and Cary 660 FT-IR/NIR spectrometers.

Synthetic details

Preparation of [Fe(C≡CC_6H_5)(dppe)Cp*] (1a) [23]

A solution of [FeCl(dppe)Cp*] (0.100 g, 0.160 mmol) and HC≡CC_6H_5 (19.4 μL, 0.177 mmol) in MeOH (5 mL) was heated at reflux for 1.25h to give a red-brown coloured solution of the vinylidene [Fe{C=C(H)C_6H_5}(dppe)Cp*]Cl. After this time, heating and stirring were discontinued and DBU (1 drop) was carefully added to the hot solution by allowing the base to run along the inner wall of the Schlenk flask. Slow cooling upon standing gave **1a** as red crystals (0.056 g, 0.081 mmol, 51 %; lit. 47%). ^{1}H NMR ($CDCl_3$): *δ*/ppm 7.88, 7.27-7.38 (m, 20H, PPh_2), 7.14, 6.74 (m, 5H, Ph), 2.73 (bs, 2H, CH_2 (dppe)), 1.88 (bs, 2H, CH_2 (dppe)), 1.54 (s, 15H, Cp*). ^{31}P{^{1}H} NMR (C_6D_6): *δ*/ppm 100.39 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2048s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M]^+$ ($[C_{44}H_{44}P_2Fe]^+$) 691.2272 amu; Observed: 691.2274 amu.

Preparation of [Fe(C≡CC_6H_5-*p*-OMe)(dppe)Cp*] (1b) [25]

A solution of [FeCl(dppe)Cp*] (0.102 g, 0.163 mmol) and HC≡CC_6H_4-*p*-OMe (22.8 μL, 0.176 mmol) in MeOH (5 mL) was heated at reflux for 1.25h to give a dark green coloured solution of the vinylidene [Fe(C=C(H)C_6H_4-*p*-OMe)(dppe)Cp*]Cl. Heating and stirring were discontinued before careful addition of 1 drop of DBU to the hot solution via the inside wall of the reaction vessel. On slow cooling, crimson coloured crystals of **1b** were deposited (0.078 g, 0.108 mmol, 66 %; lit 56%). ^{1}H NMR (C_6D_6):

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δ/ppm 8.06, (m, 4H, Ph), 6.80-7.32 (m, 20H, PPh_2), 3.34 (s, 3H, OMe), 2.67 (bs, 2H, CH_2 (dppe)), 1.84 (bs, 2H, CH_2 (dppe)), 1.56 (s, 15H, Cp*). $^{31}P\{^1H\}$ NMR (C_6D_6): δ/ppm 100.53 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2059s cm^{-1}. Calculated for $[M]^+$ ($[C_{45}H_{46}OP_2Fe]^+$) 721.2378 amu; Observed: 721.2375 amu.

Preparation of [Fe(C≡CC$_6$H$_4$-*p*-NO$_2$)(dppe)Cp*] (1c) [10]

A solution of [FeCl(dppe)Cp*] (0.102 g, 0.163 mmol) and HC≡CC$_6$H$_4$-*p*-NO$_2$ (0.031 g, 0.211 mmol) in MeOH (10 mL) was heated at reflux for 50min to give a green coloured solution of the vinylidene [Fe{C=C(H)C$_6$H$_4$-*p*-NO$_2$}(dppe)Cp*]Cl. Heating and stirring were discontinued before a drop of DBU was added to the hot reaction solution via the inside wall of the reaction vessel. Upon slow cooling the solution deposited **1c** as a purple powder (0.069 g, 0.094 mmol, 57 %; lit. 64%). ^1H NMR ($CDCl_3$): δ/ppm 7.93, 6.73 (d, J_{HH} = 8.8 Hz, 4H, Ph), 7.77, 7.26 (m, 20H, PPh_2), 2.60 (m, 2H, CH_2 (dppe)), 2.01 (m, 2H, CH_2 (dppe)), 1.42 (s, 15H, Cp*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm 99.13 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2026s, 1999s; ν(NO_2) 1569s, 1312s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M]^+$ ($[C_{44}H_{43}FeNO_2P_2Fe]^+$) 736.2123 amu; Observed: 736.2112 amu.

Preparation of [Fe(C≡C^{t}Bu)(dppe)Cp*] (1d) [24]

A solution of [FeCl(dppe)Cp*] (0.102 g, 0.163 mmol) and HC≡C^{t}Bu (100 μL, 0.812 mmol) in MeOH (5 mL) was heated at reflux for 1h to give a red coloured solution of the vinylidene [Fe{C=C(H)^{t}Bu}(dppe)Cp*]Cl. Heating and stirring were ceased, and addition of a drop of DBU to the reaction mixture via the inside wall of the reaction

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vessel and slow cooling gave **1d** as crimson crystals (0.055 g, 0.0813 mmol, 50 %; lit. 80 – 87%). ^{1}H NMR (C_6D_6): δ/ppm 8.09, 7.0-7.30 (m, 20H, PPh_2), 2.77 (bs, 2H, CH_2 (dppe)), 1.94 (bs, 2H, CH_2 (dppe)), 1.54 (s, 15H, Cp*), 1.31 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR (C_6D_6): δ/ppm 101.07 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2062s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{42}H_{49}FeP_2]^+$) 671.2659 amu; Observed: 671.2653 amu.

Preparation of [Fe(C≡CC$_6$H$_5$)(dppe)Cp] (2a)[34]

A solution of [FeCl(dppe)Cp] (0.102 g, 0.183 mmol) and $HC{\equiv}CC_6H_5$ (30.2 μL, 0.275 mmol) in MeOH (5 mL) was heated at reflux for 1h to give a red-brown coloured solution of the vinylidene $[Fe\{C{=}C(H)C_6H_5\}(dppe)Cp]Cl$. Heating and stirring was discontinued, and a drop of DBU introduced to the hot solution via the inner wall of the flask. On standing and slow cooling, maroon coloured crystals of **2a** were deposited (0.057 g, 0.092 mmol, 50 %; lit. 43%). ^{1}H NMR ($CDCl_3$): δ/ppm 7.94, 7.41-7.30, 6.92-6.48 (m, 25H, PPh_2, Ph), 4.25 (s, 5H, Cp), 2.61 (m, 2H, CH_2 (dppe)), 2.22 (m, 2H, CH_2 (dppe)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm 106.45 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2057s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M]^+$ ($[C_{39}H_{34}P_2Fe]^+$) 621.1490 amu; Observed: 621.1488 amu.

Preparation of [Fe(C≡CC$_6$H$_4$-p-OMe)(dppe)Cp] (2b)

A solution of [FeCl(dppe)Cp] (0.104 g, 0.188 mmol) and $HC{\equiv}CC_6H_4$-p-OMe (100 μL 0.910 mmol) in MeOH (5 mL) was heated at reflux for 1.5h to give a brown-red coloured solution of the vinylidene $[Fe(C{=}C(H)C_6H_4$-*p*-OMe)(dppe)Cp]Cl, which was treated with 1 drop of DBU in the manner described before. The solution was allowed to cool to room temperature and then chilled to give red crystals of **2b**

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(0.0824 g, 0.126 mmol, 67 %). ^{1}H NMR (C_6D_6): δ/ppm 8.04 (m, 4H, H_o), 7.41 (m, 6H, $H_{m,\ para}$), 7.32 (m, 2H, $H_{para'}$), 7.26 (bs, 4H, $H_{m'}$), 7.21 (m, 4H, $H_{o'}$), 6.9, 6.6 (d, J_{HH} = 7.8 Hz, 4H, Ph), 4.31 (s, 5H, Cp), 3.25 (s, 3H, OMe), 2.57 (bs, 2H, CH_2 (dppe)), 1.97 (bs, 2H, CH_2 (dppe)). ^{31}P{^{1}H} NMR (C_6D_6): δ/ppm 106.75 (s, PPh_2). IR (solid, ATR): ν(C≡C): 2064s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M]^+$ ($[C_{40}H_{36}OP_2Fe]^+$) *m/z* 651.1595 amu; Observed: 650.1600 amu

Preparation of [Fe(C≡C$_6$H$_4$-*p*-NO$_2$)(dppe)Cp] (2c) [28, 102]

A solution of [FeCl(dppe)Cp] (0.104 g, 0.181 mmol) and HC≡CC_6H_4-*p*-NO_2 (0.0647 g, 0.439 mmol) in MeOH (5 mL) was heated at reflux for 2h to give a ruby-purple coloured solution of the vinylidene [Fe{C=C(H)C_6H_4-*p*-NO_2}(dppe)Cp]Cl. After heating was stopped, addition of a drop of DBU via the inside wall of the reaction vessel and slow cooling resulted in formation of dark purple crystals of **2c** (0.0580 g, 0.087 mmol, 48 %; lit. 68, 31%). ^{1}H NMR (C_6D_6): δ/ppm 7.86-6.97 (m, 20H, PPh_2), 7.0, 6.5 (d, J_{HH} = 8.7 Hz, 4H, Ph), 4.25 (s, 5H, Cp), 2.40 (m, 2H, CH_2 (dppe)), 1.95 (m, 2H, CH_2 (dppe)). ^{31}P{^{1}H} NMR (C_6D_6): δ/ppm 105.77 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2042s, 2010m; ν(NO_2) 1573s, 1303s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M]^+$ ($[C_{39}H_{33}FeNO_2P_2Fe]^+$) 666.1341 amu; Observed: 666.1342 amu.

Preparation of [Fe(C≡C^{t}Bu)(dppe)Cp] (2d)[23]

A solution of [FeCl(dppe)Cp] (0.105 g, 0.189 mmol) and HC≡C^{t}Bu (100 µL, 0.812 mmol) in MeOH (5 mL) was heated at reflux for 1h to give a red-orange coloured solution of the vinylidene [Fe{C=C(H)^{t}Bu}(dppe)Cp]Cl. After heating and stirring was ceased, addition of DBU and slow cooling in the manner described above gave gave **2d** as red crystals (0.047 g, 0.078 mmol, 41 %; lit. 23%). ^{1}H NMR (C_6D_6):

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δ/ppm 8.15-7.05 (m, 20H, PPh_2), 4.32 (s, 5H, Cp), 2.71 (m, 2H, CH_2 (dppe)), 2.18 (m, 2H, CH_2 (dppe)), 1.08 (s, 9H, H_4). $^{31}P\{^1H\}$ NMR (C_6D_6): *δ*/ppm 107.85 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2078s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M]^+$ ($[C_{37}H_{38}FeP_2]^+$) 601.1803 amu; Observed: 601.1797 amu.

Preparation of [Ru(C≡CC_6H_5)(dppe)Cp*] (3a)[23]

A solution of [RuCl(dppe)Cp*] (0.101 g, 0.151 mmol) and HC≡CC_6H_5 (18 μL, 0.164 mmol) was allowed to react in refluxing MeOH (10 mL) for 1h to give a pink-orange solution of the vinylidene [Ru{C=C(H)C_6H_5}(dppe)Cp*]Cl. After this time, heating and stirring was discontinued, and a drop of DBU introduced to the hot solution via the inner wall of the flask. On standing and slow cooling, yellow crystals of **3a** were deposited (0.073 g, 0.099 mmol, 66 %; lit. 40%). ^1H NMR ($CDCl_3$): *δ*/ppm 7.61-7.82, 6.78-7.35 (m, 25H, PPh_2, Ph), 2.68 (m, 2H, CH_2 (dppe)), 2.05 (m, 2H, CH_2 (dppe)), 1.56 (s, 15H, Cp*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ*/ppm 81.45 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2064s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{44}H_{45}P_2Ru]^+$) 737.2040 amu; Observed: 737.2040 amu.

Preparation of [Ru(C≡CC_6H_4-p-OMe)(dppe)Cp*] (3b)[11]

A solution of [RuCl(dppe)Cp*] (0.101 g, 0.151 mmol) and HC≡CC_6H_4-*p*-OMe (100 μL, 0.771 mmol) in MeOH (5 mL) was heated at reflux for 2h to give a pink-red solution of the vinylidene [Ru{C=C(H)C_6H_4-*p*-OMe}(dppe)Cp*]Cl. Heating was stopped and a drop of DBU added via the inside wall of the Schlenk flask and the solution allowed to stand. On slow cooling, yellow crystals of **3b** were deposited (0.0831 g, 0.108 mmol, 72 %; lit. 68%). ^1H NMR ($CDCl_3$): *δ*/ppm 7.77-7.81, 7.05-7.19 (m, 20H, PPh_2), 6.61, 6.72 (d, J_{HH} = 8.8 Hz, 4H, Ph), 3.73 (s, 3H, OMe), 2.68

(m, 2H, CH_2 (dppe)), 2.04 (m, 2H, CH_2 (dppe)), 1.56 (s, 15H, Cp*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ*/ppm 80.99 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2074s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{45}H_{47}OP_2Ru]^+$) 767.2146 amu; Observed: 767.2145 amu.

Preparation of [Ru(C≡CC_6H_4-*p*-NO_2)(dppe)Cp*] (3c)[11]

A solution of [RuCl(dppe)Cp*] (0.109 g, 0.163 mmol) and HC≡CC_6H_4-*p*-NO_2 (0.026 g, 0.183 mmol) in MeOH (5 mL) was heated at reflux for 1h to give a red coloured solution of the vinylidene [Ru{C=C(H)C_6H_4-*p*-NO_2}(dppe)Cp*]Cl. After heating was stopped, a drop of DBU was allowed to run into the hot solution via the inside wall of the reaction vessel. On slow cooling, purple crystals of **3c** were deposited (0.09 g, 0.115 mmol, 71 %; lit. 80%). ^1H NMR ($CDCl_3$): *δ*/ppm 7.88, 6.65 (d, J_{HH} = 9 Hz, 4H, Ph), 7.15-7.40, 7.67-7.70 (m, 20H, PPh_2), 2.63 (m, 2H, CH_2 (dppe)), 2.07 (m, 2H, CH_2 (dppe)), 1.56 (s, 15H, Cp*). $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ*/ppm 80.42 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2044s, 2003m; ν(NO_2) 1573s, 1318s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{44}H_{44}NO_2P_2Ru]^+$) 782.1891 amu; Observed 782.1894 amu.

Preparation of [Ru(C≡C^{t}Bu)(dppe)Cp*] (3d)[23]

A solution of [RuCl(dppe)Cp*] (0.102 g, 0.152 mmol) and HC≡C^{t}Bu (20.2 μL, 0.164 mmol) in MeOH (5 mL) was heated at reflux for 50 min to give an orange coloured solution of the vinylidene [Ru{C=C(H)^{t}Bu}(dppe)Cp*]Cl. After heating and stirring were ceased, addition of DBU and slow cooling in the manner described above gave **2d** as a yellow powder (0.076 g, 0.106 mmol, 65 %; lit. 64%). ^1H NMR ($CDCl_3$): *δ*/ppm 7.13-7.82 (m, 20H, PPh_2), 2.73 (m, 2H, CH_2 (dppe)), 2.08 (m, 2H, CH_2 (dppe)), 1.53 (s, 15H, Cp*), 0.89 (s, 9H, ^{t}Bu). $^{31}P\{^1H\}$ NMR ($CDCl_3$): *δ*/ppm 81.20

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(s, PPh_2). IR (solid, ATR): ν(C≡C) 2083s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{42}H_{49}RuP_2]^+$) 717.2353 amu; Observed: 717.2371 amu.

Preparation of [Ru(C≡CC$_6$H$_5$)(dppe)Cp] (4a)[65]

A solution of [RuCl(dppe)Cp] (0.11 g, 0.18 mmol) in methanol (5 ml) was treated with phenylacetylene (100 µL, 0.91 mmol) and the mixture heated at reflux for 2 h to give a cherry-red solution of the vinylidene [Ru{C=C(H)C_6H_5}(dppe)Cp]Cl. The solution volume was reduced to ca. 2 ml in vacuo before a drop of DBU was added via the inside wall of the reaction vessel and allowed to stand to afford **4a** as a yellow microcrystalline solid which was collected by filtration, washed with hexanes and dried (0.060 g, 0.090 mmol, 50 %; lit. 75%). ^1H NMR ($CDCl_3$): δ/ppm 7.93 (m, 4H, H_o), 7.40 (m, 6H, $H_{para/m}$), 7.27 (m, 10H, $H_{o/para/m}$), 6.88 (dd, J_{HH} = 7.1 Hz, 2H, H_5), 6.80 (t, J_{HH} = 7.1 Hz, 1H, H_6), 6.41 (d, J_{HH} = 7.5 Hz, 2H, H_4), 4.78 (s, 5H, Cp), 2.66 (m, 2H, CH_2 (dppe)), 2.29 (m, 2H, CH_2 (dppe)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ /ppm 86.14 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2076s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{39}H_{35}RuP_2]^+$) 667.1258 amu; Observed: 667.1265 amu.

Preparation of [Ru(C≡CC$_6$H$_4$-*p*-OMe)(dppe)Cp] (4b)

A solution of [RuCl(dppe)Cp] (0.11 g, 0.18 mmol) and 4-ethynylanisole (100 µL, 0.77 mmol) was heated at reflux in 5 ml of methanol for 1hr to give a dark-red coloured solution of the vinylidene [Ru{C=C(H)C_6H_4-*p*-OMe}(dppe)Cp]Cl. The solvent volume was reduced and DBU added in the manner described for **4a** above to give a yellow crystalline sample of **4b** (0.077 g, 0.11 mmol, 61 %). ^1H NMR ($CDCl_3$) δ/ppm 7.92 (m, 4H, H_o), 7.40 (m, 6H, $H_{para/m}$), 7.26-7.24 (m, 10H, $H_{o/para/m}$), 6.45 (d, J_{HH} = 8.8 Hz, 2H, H_5), 6.32 (d, J_{HH} = 8.8 Hz, 2H, H_4), 4.77 (s, 5H, Cp), 3.65 (s, 3H,

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H_7), 2.66 (m, 2H, CH_2 (dppe)), 2.26 (m, 2H, CH_2 (dppe)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm 86.20 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2080s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{40}H_{37}OP_2Ru]^+$) 697.1363 amu; Observed: 697.1375 amu.

Preparation of [Ru(C≡CC$_6$H$_4$-*p*-NO$_2$)(dppe)Cp] (4c) [61]

The reaction of [RuCl(dppe)Cp] (0.11 g, 0.18 mmol) with 4-ethynylnitrobenzene (0.030, 0.21 mmol) in dry, degassed methanol (5 ml) was allowed to proceed at reflux for 3 h to give a dark-red coloured solution of the vinylidene [Ru{C=C(H)C_6H_4-*p*-NO_2}(dppe)Cp]Cl. After this time, a solution of DBU (1 drop) in 1 mL of dry methanol was added to the stirred reaction mixture. The resulting precipitate was purified by preparative TLC (3:7 acetone: hexanes) to afford **7c** as a dark red solid (0.060 g, 0.084 mmol, 77 %; lit. 30%). ^1H NMR ($CDCl_3$): δ/ppm 7.87 (m, 4H, H_o), 7.75 (d, J_{HH} = 8.8 Hz, 2H, H_5), 7.40 (m, 6H, $H_{para/m}$), 7.29 (m, 10H, $H_{o/p/m}$), 6.33 (d, J_{HH} = 8.8 Hz, 2H, H_4), 4.81 (s, 5H, Cp), 2.61 (m, 2H, CH_2 (dppe)), 2.32 (m, 2H, CH_2 (dppe)). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm 85.39 (s, PPh_2). IR (solid, ATR): ν(C≡C) 2053s, 2017m; ν(NO_2) 1580s, 1306s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{39}H_{34}NO_2P_2Ru]^+$) 712.1108 amu; Observed: 712.1144 amu.

Preparation of [Ru(C≡C^{t}Bu)(dppe)Cp] (4d)

A solution of [RuCl(dppe)Cp] (0.12, 0.19 mmol) and 3,3-dimethylbut-1-yne (100 μL, 0.81 mmol) was allowed to react in refluxing methanol (5 ml) for 5h to give a red-orange solution of the vinylidene [Ru{C=C(H)^{t}Bu}(dppe)Cp]Cl. Reduction of the solvent volume to ca. 2 ml and addition of DBU to the standing solution resulted in the crystallisation of **4d**, with further reduction of solvent volume yielding additional product as a yellow precipitate (total yield 0.065 g, 0.10 mmol, 53 %). ^1H NMR

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($CDCl_3$): δ /ppm 7.92 (m, 4H, H_o), 7.34 (m, 6H, $H_{para/m}$), 7.22 (m, 10H, $H_{o/p/m}$), 4.67 (s, 5H, Cp), 2.72 (m, 2H, CH_2 (dppe)), 2.31 (m, 2H, CH_2 (dppe)), 0.53 (s, 9H, H_4). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm 87.36 (s, PPh_2). IR (solid ATR): ν(C≡C) 2084s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{37}H_{39}RuP_2]^+$) 647.1571 amu; Observed: 647.1577 amu.

Preparation of [Ru(C≡CC_6H_5)(PPh_3)$_2$Cp] (5a) [8]

A solution of [RuCl(PPh_3)$_2$Cp] (0.101 g, 0.139 mmol) and HC≡CC_6H_5 (24 µL, 0.219 mmol) was heated in refluxing MeOH (5 mL) for 1h to give a cherry red solution of the vinylidene [Ru{C=C(H)C_6H_5}(PPh_3)$_2$Cp]Cl. After this time, heating and stirring were discontinued and DBU (1 drop) was carefully added to the hot solution by allowing the base to run along the inner wall of the Schlenk flask. Slow cooling gave **1a** as yellow crystals (0.097 g, 0.123 mmol, 88 %; lit. 96%), which could be collected via vacuum filtration, washed with MeOH (2 × 5 mL) and air-dried. ^1H NMR ($CDCl_3$): δ/ppm 7.52-7.47, 7.21-7.06 (m, 35H, PPh_3, Ph), 4.32 (s, 5H, Cp). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ/ppm 50.38 (s, PPh_3). IR (solid, ATR): ν(C≡C) 2064s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{49}H_{41}P_2Ru]^+$) 793.1727 amu; Observed: 793.1721 amu.

Preparation of [Ru(C≡CC_6H_4-*p*-OMe)(PPh_3)$_2$Cp] (5b) [81]

A solution of [RuCl(PPh_3)$_2$Cp] (0.106 g, 0.146 mmol) and HC≡CC_6H_4-*p*-OMe (20 µL, 0.154 mmol) in MeOH (10 mL) was heated at reflux for 1h to give a dark red coloured solution of the vinylidene [Ru{C=C(H)C_6H_4-*p*-OMe}(PPh_3)$_2$Cp]Cl. Heating and stirring was discontinued, a drop of DBU added via the inside wall of the Schlenk flask and the solution allowed to stand where upon yellow crystals of **5b** were

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deposited on slow cooling (0.092 g, 0.112 mmol, 77%; lit. 57%). ^{1}H NMR (CDCl$_3$): δ/ppm 7.48-7.51, 7.06-7.20, 6.70-6.72 (m, 34H, PPh$_3$, Ph), 4.30 (s, 5H, Cp), 3.78 (s, 3H, OMe). ^{31}P{^{1}H} NMR (CDCl$_3$): δ/ppm 50.33 (s, PPh$_3$). IR (solid, ATR): ν(C≡C) 2065s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{50}H_{42}OP_2Ru]^+$) 823.1833 amu; Observed: 823.1833 amu.

Preparation of [Ru(C≡CC$_6$H$_4$-*p*-NO$_2$)(PPh$_3$)$_2$Cp] (5c) [66]

A solution of [RuCl(PPh$_3$)$_2$Cp] (0.103 g, 0.142 mmol) and HC≡CC$_6$H$_4$-*p*-NO$_2$ (0.046 g, 0.142 mmol) in MeOH (5 mL) was heated at reflux for 1h to give a dark red coloured solution of the vinylidene [Ru{C=C(H)C$_6$H$_4$-*p*-NO$_2$}(PPh$_3$)$_2$Cp]Cl. After heating was stopped, the solution was treated with a drop of DBU in the manner described above and allowed to slowly cool to give **5c** as a dark purple crystals (0.077 g, 0.092 mmol, 65 %; lit. 74%). ^{1}H NMR (CDCl$_3$): δ/ppm 8.00-8.03, 7.09-7.44 (m, 34H, PPh$_3$, Ph), 4.37 (s, 5H, Cp). ^{31}P{^{1}H} NMR (CDCl$_3$): δ/ppm 50.68 (s, PPh$_3$). IR (solid, ATR): ν(C≡C) 2031s, 2004m; ν(NO$_2$) 1569s, 1303s cm^{-1}. ESI(+)-MS (*m/z*): Calculated for $[M+H]^+$ ($[C_{49}H_{40}NO_2P_2Ru]^+$) 838.1578 amu; Observed 838.1573 amu.

Preparation of [Ru(C≡C^{t}Bu)(PPh$_3$)$_2$Cp] (5d) [103]

A solution of [RuCl(PPh$_3$)$_2$Cp] (0.1076 g, 0.148 mmol) and HC≡C^{t}Bu (100 μL, 0.812 mmol) in MeOH (5 mL) was heated at reflux for 2h to give a red-orange coloured solution of the vinylidene [Ru{C=C(H)Bu^t}(PPh$_3$)$_2$Cp]Cl. After heating and stirring were stopped, deprotonation and slow cooling in the manner described above gave yellow crystals of **5d** (0.0705 g, 0.091 mmol, 62 %; lit. 86%). ^{1}H NMR (CDCl$_3$): δ/ppm 7.53-7.07 (m, 30H, PPh$_3$), 4.30 (s, 5H, Cp), 1.31 (s, 9H, ^{t}Bu). ^{31}P{^{1}H} NMR (CDCl$_3$): δ/ppm 50.52 (s, PPh$_3$). IR (solid, ATR): ν(C≡C) 2081s cm^{-1}. ESI(+)-MS

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(*m/z*): Calculated for $[M+H]^+$ ($[C_{47}H_{45}RuP_2]^+$) 773.2040 amu; Observed: 773.2059 amu.

Crystallography

Experimental data are summarised in Table S2. All crystallographic data have been deposited with the CCDC (CCDC 2009973-2009981) and can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.KCB21EZ, UK (fax +441223336033; email deposit@ccdc.cam.ac.uk).

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View Article Online
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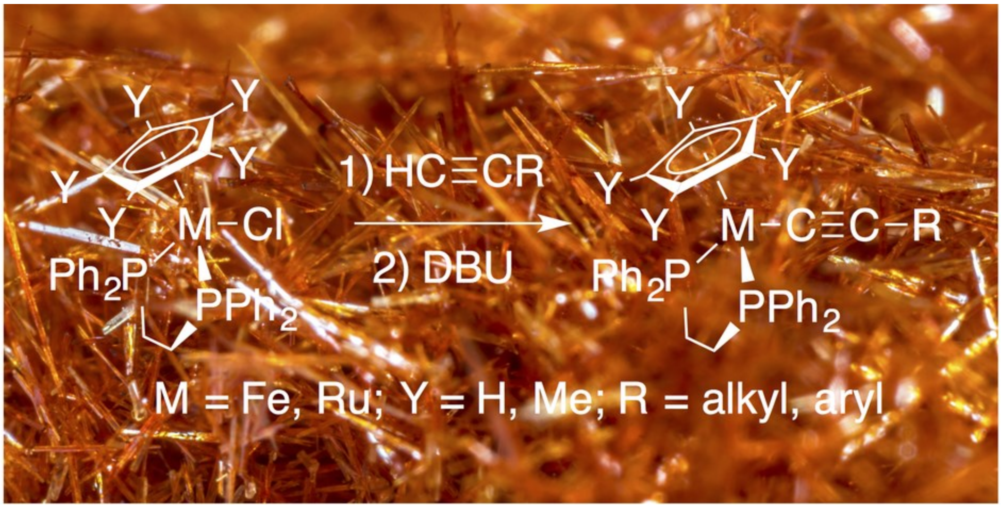

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Table of contents text

A synthetic ‘trick’ affording complexes [M(C≡CR)(dppe)Cp′] (M = Fe, Ru) in high purity directly from the reaction vessel is described.