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Synthetic and electrochemical studies on alkynyl complexes of iron and ruthenium

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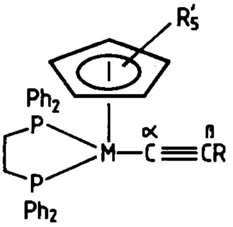
Abstract

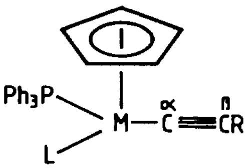
Cyclic voltammetric studies on a series of alkynyl complexes $[M(C{\equiv}CR)L_2(\eta\text{-}C_5R'_5)]$ (M = Fe or Ru; R = Ph, Bu^n or Bu^t; L = CO or P-donor ligand; R′ = H or Me) reveal a one-electron oxidation at a glassy carbon electrode in dichloromethane. The chemical reversibility of the oxidation process is dependent upon all four variables (M, L, R and R′) considered in this investigation.

Introduction

We have previously reported on the cyclic voltammetry and reversible one-electron oxidation of the alkynyl complexes $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]$ (R = Ph, Bu^t;



	R′	M	R
(1a)	Me	Fe	Ph
(1b)	Me	Ru	Ph
(1c)	Me	Ru	Bu^t
(2a)	H	Fe	Ph
(2b)	H	Ru	Ph
(2c)	H	Fe	Bu^t



	L	M	R
(3a)	PPh_3	Ru	Ph
(3b)	PPh_3	Ru	Bu^n
(3c)	PPh_3	Ru	Bu^t
(4a)	CO	Fe	Ph
(4b)	CO	Fe	Bu^n
(4c)	CO	Fe	Bu^t

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C_7H_7 = cycloheptatrienyl) together with the chemical isolation of the corresponding stable radical cations [Mo(C≡CR)(dppe)(η-C_7H_7)][BF_4] [1]. Our studies on cycloheptatrienyl complexes of Group VI transition metals have, in part, been motivated by the formally isoelectronic nature of the fragments Mo(η-C_7H_7) and Ru(η-Cp) which results in a series of analogous complexes such as [MoCl$(CO)_2$(η-C_7H_7)] and [RuCl$(CO)_2$(η-Cp)]. Electrochemical studies on complexes of the type [MXL_2(η-Cp)] (M = Fe or Ru; X = halide, alkyl etc., L = CO, PPh_3; L_2 = dppe) are numerous [2,3] but we are unaware of any such investigations on alkynyl derivatives [M(C≡CR)L_2(η-$C_5R'_5$)] (1–4). Therefore, to further our work on the comparative chemistry of Mo(η-C_7H_7) and M(η-$C_5R'_5$) (M = Fe, Ru; R' = H or Me), we have prepared and carried out electrochemical studies on twelve alkynyl complexes of Fe and Ru including, to our knowledge, the first reported examples of pentamethylcyclopentadienyl derivatives. In addition to redox properties we also consider ^{13}C NMR data which amplify the rather limited data available for alkynyl-carbon chemical shifts in cyclopentadienyl complexes of iron and ruthenium.

Results and discussion

Four discrete complex types [M(C≡CR)(dppe)(η-C_5Me_5)] (**1**) (M = Fe, Ru), [M(C≡CR)(dppe)(η-Cp)] (**2**) (M = Fe, Ru), [Ru(C≡CR)$(PPh_3)_2$(η-Cp)] (**3**) and [Fe(C≡CR)(CO)(PPh_3)(η-Cp)] (**4**), with the substituents R on the alkynyl group selected from Ph, Bu^n or Bu^t, have been investigated. Established methods were employed for synthesis of complexes **2**, **3** and **4** [4,5]; **1a** was obtained by treatment of the acetonitrile cation [Fe(NCMe)(dppe)(η-C_5Me_5)]$^+$ [6] with HC≡CPh in refluxing 1,2-dichloroethane and subsequent deprotonation of the resulting vinylidene [Fe(C=CHPh)(dppe)(η-C_5Me_5)]$^+$ (**5**). Details of the characterisation of new complexes, by infrared spectroscopy, mass spectrometry and microanalysis (Table 1), and ^1H NMR (Table 2) and ^{13}C NMR spectroscopy (Table 3) are given in the appropriate table. Complexes **2a**, **2b**, **3a**, **3c**, **4a** and **4b** have been synthesised previously [4,5,7,8] but, where pertinent, ^{13}C NMR data obtained in this work are included in Table 3.

Inspection of Table 1 reveals ν(C≡C) dependent upon all four variables M, L, R and R' in [M(C≡CR)L_2(η-$C_5R'_5$)] with the general trend, within any series (commencing with the highest wavenumber) $Bu^n > Bu^t >$ Ph; Ru > Fe; Cp > C_5Me_5, although, in these complexes, the limit of variation in ν(C≡C) does not exceed 60 cm^{-1}. The ^{13}C NMR data exhibit some chemical shift dependence of C_α and C_β upon both the metal and alkynyl substituent R and, although we have not attempted to distinguish signals arising from C_α and C_β, in those complexes for which phosphorus coupling $J(C_\alpha$–P) is resolved (R = Bu^n or Bu^t only) C_α is to high field of C_β. These results may be compared with the alkynyl carbon chemical shift assignments reported for [Ru(C≡$CCH_2CH_2C_2H$)$(PPh_3)_2$(η-Cp)] (95.3, triplet $J(C_\alpha$–P) 25 Hz, C_α; 109.1 C_β [9]) and [Fe(C≡CMe)(dppe)(η-Cp)] (112.6 C_α; 97.5 C_β [10]). Finally, the identity of **5** as a phenylvinylidene complex is confirmed by the low field resonance of the C_α vinylidene carbon in the ^{13}C NMR and the observation of the vinylidene hydrogen in the ^1H NMR spectrum.

The results of cyclic voltammetric studies on the twelve alkynyl complexes investigated are summarised in Table 4; potentials $(E_{p,c} + E_{p,a})/2$, which are taken as a good estimate of the formal reduction potential $E^\ominus$, are quoted vs. a saturated

Table 1

Infrared and analytical data

Complex	Yield (%)	ν(C≡C) [a] (cm^{-1})	Analysis (Found (calc) (%)) C	H	*M* [b]
[Fe(C≡CPh)(dppe)(η-C_5Me_5)] [c] (**1a**)	47	2054	72.6 (72.9)	6.3 (6.2)	690
[Ru(C≡CPh)(dppe)(η-C_5Me_5)] (**1b**)	40	2071	71.3 (71.8)	6.0 (6.0)	
[Ru(C≡CBu^t)(dppe)(η-C_5Me_5)] (**1c**)	64	2086	70.3 (70.5)	6.8 (6.8)	
[Fe(C≡CBu^t)(dppe)(η-Cp)] (**2c**)	23	2071	74.0 (74.0)	6.5 (6.4)	600
[Ru(C≡CBu^n)(PPh_3)$_2$(η-Cp)] (**3b**)	62	2094	73.4 (73.1)	5.8 (5.7)	510 [d]
[Fe(C≡CBu^t)(CO)(PPh_3)(η-Cp)] (**4c**)	27	2094 [e]	73.2 (73.2)	5.8 (5.9)	492
[Fe(C=CHPh)(dppe)(η-C_5Me_5)][PF_6] (**5**)	55		62.4 (63.2)	5.9 (5.4)	

[a] In CH_2Cl_2, ν(C≡C) data for other complexes (cm^{-1}): **2a**, 2061; **2b**, 2077; **3a**, 2074; **3c**, 2089; **4a**, 2089; **4b**, 2105. [b] By electron impact mass spectroscopy. [c] Analytical data consistent with $\frac{1}{2}CH_2Cl_2$ solvent of crystallisation, Cl Found 5.1%, calcd. 4.8%. [d] $M^+ - PPh_3$. [e] ν(CO) 1941 cm^{-1}.

calomel electrode and standardised with respect to the couple $[Fe(\eta\text{-}Cp)_2]^+ - [Fe(\eta\text{-}Cp)_2]$ ($E^{\ominus}$ +0.56 V) or $[Fe(\eta\text{-}C_5Me_5)_2]^+ - [Fe(\eta\text{-}C_5Me_5)_2]$ ($E^{\ominus}$ +0.02 V) as internal calibrant. At a glassy carbon electrode in dichloromethane, each of com-

Table 2

^{1}H NMR data [a]

[Fe(C≡CPh)(dppe)(η-C_5Me_5)] [b] (**1a**)	8.12, 7.26 [m, 25H, Ph], 2.71 [br, 2H, CH_2], 1.88 [br, 2H, CH_2], 1.57 [s,15H, C_5Me_5]
[Ru(C≡CPh)(dppe)(η-C_5Me_5)] (**1b**)	7.98, 7.22 [m, 25H, Ph], 2.70 [br, 2H, CH_2], 1.92 [br, 2H, CH_2], 1.69 [s, 15H, C_5Me_5]
[Ru(C≡CBu^t)(dppe)(η-C_5Me_5)] (**1c**)	8.01, 7.39, 7.12 [m, 20H, Ph], 2.81 [br, 2H, CH_2] 2.03 [br, 2H, CH_2], 1.69 [s, 15H, C_5Me_5], 1.24 [s, 9H, Bu^t]
[Fe(C≡CBu^t)(dppe)(η-Cp)] (**2c**)	8.16, 7.34, 7.26, 7.06 [m, 20H, Ph], 4.28 [t, 5H, Cp, *J*(P–H) 1], 2.69 [br, 2H, CH_2], 2.14 [br, 2H, CH_2], 1.03 [s, 9H, Bu^t]
[Ru(C≡CBu^n)(PPh_3)$_2$(η-Cp)] (**3b**)	7.78, 7.02 [m, 30H, Ph], 4.46 [s, 5H, Cp], 2.86 [m, 2H, Bu^n], 1.72 [m, 2H, Bu^n], 1.60 [m, 2H, Bu^n], 1.00 [t, 3H, Bu^n, *J*(H–H) 7]
[Fe(C≡CBu^t)(CO)(PPh_3)(η-Cp)] (**4c**)	7.90, 7.10 [m, 15H, Ph], 4.25 [s, 5H, Cp], 1.29 [s, 9H, Bu^t]
[Fe(C=CHPh)(dppe)(η-C_5Me_5)][PF_6] [b] (**5**)	7.70–7.30, 7.20, 7.02, 6.38 [m, 25H, Ph], 5.11 [t, 1H, C=CHPh, *J*(P–H) 5], 3.08 [br, 2H, CH_2], 2.50 [br, 2H, CH_2] 1.59 [s, 15H, C_5Me_5]

[a] In C_6D_6 unless stated otherwise, 300 MHz spectra, chemical shifts (δ) downfield from $SiMe_4$, *J* values in Hz. [b] In $CDCl_3$.

Table 3

^{13}C NMR data [a]

Complex	Phenyl carbons	C_α and C_β	$C_5R'_5$	CH_2 [b] (dppe)	$\mathrm{Bu^t}$ or $\mathrm{Bu^n}$ carbons
1a	140.6–127.4	121.4, 123.9	88.5, 11.3	31.7	
1b	140.2–127.2	111.2, 123.6	93.2, 10.9	30.3	
1c	141.2–126.9	102.2 [c], 116.4	92.7, 11.1	30.4	33.9 C*Me*$_3$
2a [d]	142.5–127.3	120.5, 122.8	79.2	28.4	
2c	144.8–127.9	95.1 [e]	80.0	29.7	33.6 C*Me*$_3$ 31.0 *C*Me$_3$
3b	140.3–126.9	89.4 [c], 111.3	85.4		34.2, 23.7, 22.9, 14.6
3c	140.6–127.6	87.8 [c], 120.9	85.9		34.0 C*Me*$_3$ 31.1 *C*Me$_3$
5 [d]	135.7–119.8	359.8 [f]	100.3, 10.5	29.4	

[a] In C_6D_6 unless stated otherwise, 75 MHz spectra, chemical shifts in ppm downfield from $SiMe_4$. [b] AA′X triplet pattern. [c] Triplet, $J(C_\alpha\text{–}P)$ 25 Hz. [d] In $CDCl_3$. [e] Triplet, $J(C_\alpha\text{–}P)$ 44 Hz, C_β not distinguished from phenyl carbons. [f] Triplet $J(C_\alpha\text{–}P)$ 33 Hz, C_β not distinguished from phenyl carbons.

plexes **1**, **2**, **3** and **4c** undergo a diffusion controlled one-electron oxidation with the separation between anodic and cathodic peak potentials in good agreement with that measured for ferrocene or $[Fe(\eta\text{-}C_5Me_5)_2]$ under identical conditions. However, **4a** and **4b** exhibit a highly irreversible anodic oxidation wave for which only peak potentials $E_{p,a}$ have been determined. Five of the complexes investigated **1a**, **1b**, **1c**, **2a** and **2c** exhibit chemical reversibility on the electrochemical timescale with the ratio of cathodic to anodic peak currents unity over the scan range 50 to 500 mV s^{-1} for switching potentials E_λ not more than 300 mV to positive potential of $E^{\ominus}$. The remainder, **2b** and all of the complexes **3** and **4**, display chemical irreversibility over the scan range investigated with a reduction peak current $i_{p,c}$ either depressed in magnitude or, in the case of **4a** and **4b**, completely undetectable.

Table 4

Electrochemical data for $[M(C{\equiv}CR)L_2(\eta\text{-}C_5R'_5)]$

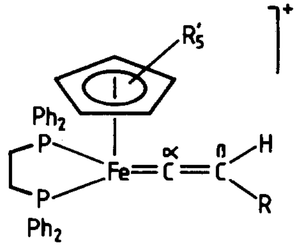
Complex	$E^{\ominus}$ (V) [a]	$i_{p,c}/i_{p,a}$ [b]
$[Fe(C{\equiv}CPh)(dppe)(\eta\text{-}C_5Me_5)]$ (**1a**)	−0.04	1.0
$[Ru(C{\equiv}CPh)(dppe)(\eta\text{-}C_5Me_5)]$ (**1b**)	0.35	1.0
$[Ru(C{\equiv}C\mathrm{Bu^t})(dppe)(\eta\text{-}C_5Me_5)]$ (**1c**)	0.22	1.0
$[Fe(C{\equiv}CPh)(dppe)(\eta\text{-}Cp)]$ (**2a**)	0.17	1.0
$[Ru(C{\equiv}CPh)(dppe)(\eta\text{-}Cp)]$ (**2b**)	0.50	0.5 [c]
$[Fe(C{\equiv}C\mathrm{Bu^t})(dppe)(\eta\text{-}Cp)]$ (**2c**)	0.03	1.0
$[Ru(C{\equiv}CPh)(PPh_3)_2(\eta\text{-}Cp)]$ (**3a**)	0.56	0.5 [c]
$[Ru(C{\equiv}C\mathrm{Bu^n})(PPh_3)_2(\eta\text{-}Cp)]$ (**3b**)	0.50	0.7 [d]
$[Ru(C{\equiv}C\mathrm{Bu^t})(PPh_3)_2(\eta\text{-}Cp)]$ (**3c**)	0.49	0.9 [d]
$[Fe(C{\equiv}CPh)(CO)(PPh_3)(\eta\text{-}Cp)]$ (**4a**)	0.76 [e]	
$[Fe(C{\equiv}C\mathrm{Bu^n})(CO)(PPh_3)(\eta\text{-}Cp)]$ (**4b**)	0.70 [e]	
$[Fe(C{\equiv}C\mathrm{Bu^t})(CO)(PPh_3)(\eta\text{-}Cp)]$ (**4c**)	0.67	0.9 [f]

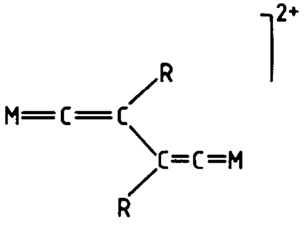
[a] vs. SCE at a carbon electrode in CH_2Cl_2. [b] At scan rate of 100 mVs^{-1}, $i_{p,c}/i_{p,a}$ ratios calculated as detailed in ref. 11. [c] Switching potential E_λ +0.80 V. [d] E_λ +0.75 V. [e] Completely irreversible wave, value for $E_{p,a}$ at 100 mV s^{-1}. [f] E_λ +0.95 V.

By comparison with [Mo(C≡CR)(dppe)(η-C_7H_7)], the alkynyl compounds [M(C≡CR)L_2(η-$C_5R'_5$)] in this study are especially informative for cyclic voltammetric investigations since the effect of altering the metal, phosphorus-donor ligand, and alkynyl or ring substituent may all be examined; indeed all four variables influence the magnitude of $E^{\ominus}$ and the chemical reversibility of the system. As noted in previous electrochemical studies on analogous cyclopentadienyl complexes of iron and ruthenium [3] the ruthenium derivatives are more difficult to oxidise; in this work $E^{\ominus}$ values were approximately 0.35 V more positive for Ru derivatives **1b** and **2b** than for the corresponding Fe systems **1a** and **2a**. Moreover, comparison of data for **2a** and **2b** reveals that the identity of the metal may also determine the chemical reversibility of the couple. Permethylation of the cyclopentadienyl ring depresses $E^{\ominus}$ values by approximately 0.15 V as demonstrated by consideration of the data for the pairs of complexes **1a**, **2a** and **1b**, **2b**. The nature of the alkynyl substituent, Ph, Bu^n or Bu^t, has a minimal effect on $E^{\ominus}$ values; typically in the pairs **3a**, **3c** and **4a**, **4c**, the phenylalkynyl derivative has $E^{\ominus}$ (or $E_{p,a}$) only 0.1 V more positive than the t-butylalkynyl analogue. However, the Bu^t substituent has a pronounced effect upon the chemical reversibility of the system and in fact, at scan rates of 200 mV s^{-1} or greater, the t-butylalkynyl complexes **3c** and **4c** give $i_{p,c}/i_{p,a}$ ratios of unity. This effect may be steric in origin; we note the stability of the related t-butylvinylidene complex [Ru(C=CHBu^t)$(PPh_3)_2$(η-Cp)]$^+$ towards addition of methanol across the vinylidene carbons [8]. As expected, $E^{\ominus}$ values are strongly dependent upon the degree of phosphine substitution although comparison of data for ruthenium complexes **2b** and **3a** suggests little effect on exchanging dppe for two PPh_3 ligands.

It is notable that, despite the extensive variations possible for the complexes [M(C≡CR)L_2(η-$C_5R'_5$)], the $E^{\ominus}$ values observed were in all cases to positive potential of those exhibited by the cycloheptatrienylmolybdenum species [Mo(C≡CR)(dppe)(η-C_7H_7)] (R = Ph, $E^{\ominus}$ −0.15 V, R = Bu^t, $E^{\ominus}$ −0.28 V [1], measured under identical conditions to the work described in this paper).

Our success in isolation of the radical cations [Mo(C≡CR)(dppe)(η-C_7H_7)][BF_4] (R = Ph, Bu^t) [1] together with the magnitudes of $E^{\ominus}$ and reversibility of the one-electron oxidations of the iron complexes **1a**, **2a** and **2c** suggested that chemical oxidation to the corresponding radicals [Fe(C≡CR)(dppe)(η-$C_5R'_5$)]$^+$ (R = Ph, R′ = H or Me; R = Bu^t, R = H) might be achieved by one-electron oxidants such as the ferrocenium ion. Treatment of **2a** or **2c** with [Fe(η-Cp)$_2$][BF_4] in CH_2Cl_2 gives, respectively, emerald-green and deep purple solutions which, however, in contrast to cycloheptatrienylmolybdenum analogues, afford unstable products rendering characterisation attempts inconclusive. During the course of this work a report appeared on the oxidative carbon–carbon coupling of vinylidenes **6a** and **6b** to give binuclear diiron divinylidene complexes **7a** and **7b** [12]. A suggested mechanism involves one-electron oxidation of **6** coupled with proton extrusion to afford the alkynyl radicals [Fe(C≡CR)(dppe)(η-Cp)]$^+$ (R = Me or Ph). Subsequent alkynyl ligand centred radical–radical coupling is proposed to give **7**. This may explain our failure to isolate the alkynyl radical cations [Fe(C≡CR)(dppe)(η-Cp)]$^+$ (R = Ph, Bu^t), although we are unable to confirm the formation of complexes of type **7** by direct one-electron oxidation of neutral alkynyls **2a** and **2c**. It is clear however that the radicals derived from one-electron oxidation of the complexes in this work, [M(C≡CR)L_2(η-$C_5R'_5$)], are much more reactive than the cycloheptatrienylmo-





	R′	R
(5)	Me	Ph
(6a)	H	Ph
(6b)	H	Me

M=Fe(dppe)(η-Cp)

(7a) R=Ph

(7b) R=Me

lybdenum analogues $[Mo(C{\equiv}CR)(dppe)(\eta\text{-}C_7H_7)]^+$. In addition to differences in $E^{\ominus}$ values, this contrasting reactivity may arise from the extent of localisation of the HOMO on the alkynyl ligand [13] and the large steric requirements of the cycloheptatrienyl ring [14]. Synthetic studies now in progress are directed towards the isolation of a stable alkynyl radical cation derived from a pentamethylcyclopentadienyliron complex and characterisation of the secondary redox products resulting from the chemically irreversible oxidations of **3** and **4**.

Experimental

The preparation, purification and reactions of the complexes described were carried out under dry nitrogen. All solvents were dried by standard methods, and distilled and deoxygenated before use. The complexes $[Fe(NCMe)(dppe)(\eta\text{-}C_5Me_5)]^+$ [6], $[RuCl(dppe)(\eta\text{-}C_5Me_5)]$ [15], $[FeCl(dppe)(\eta\text{-}Cp)]$ [16], and $[Fe(\eta\text{-}C_5Me_5)_2]$ [17] were prepared by published procedures. Alkynes $HC{\equiv}CPh$, $HC{\equiv}CBu^n$ and $HC{\equiv}CBu^t$ were supplied by Aldrich Chemical Co., Fluka A.G. or Lancaster Synthesis and Alumina (Brockmann activity II) for column chromatography was purchased from B.D.H. Chemicals Ltd.

Infrared spectra were recorded on a Perkin–Elmer FT 1710 instrument and electron impact mass spectra were obtained using an AEI MS 30 spectrometer. Hydrogen-1 NMR spectra were recorded on a Varian Associates SC 300 spectrometer and ^{13}C NMR spectra at 75 MHz on a Varian Associates XL 300 instrument. Microanalyses were by the staff of the Microanalytical Service of the Department of Chemistry, University of Manchester.

Cyclic voltammetric studies were made using a Princeton Applied Research Model 173 Potentiostat in conjunction with a Model 175 Signal Waveform Generator and a three electrode cell. The working electrode was glassy carbon and a platinum wire served as the auxiliary; the reference electrode was an aqueous saturated calomel electrode (SCE) which was separated from the test solution by a bridge tube fitted with a porous glass membrane. Test solutions were made up under a purge of dry nitrogen using solvents containing 1×10^{-3} mol dm^{-3} of complex and 0.2 mol dm^{-3} $[NBu_4{}^n][BF_4]$ as supporting electrolyte. All potentials are standardised and quoted vs. the SCE; under these conditions $E^{\ominus}$ for the couple $[Fe(\eta\text{-}Cp)_2]^+ - [Fe(\eta\text{-}Cp)_2]$ is 0.56 V.

Preparation of $[Fe(C{=}CHPh)(dppe)(\eta\text{-}C_5Me_5)][PF_6]$ (5)

A mixture of $[Fe(NCMe)(dppe)(\eta\text{-}C_5Me_5)][PF_6]$ (0.76 g, 0.98 mmol) and HC≡CPh (0.40 g, 3.9 mmol) was refluxed in 1,2-dichloroethane for 3 h to afford a brown solution. Evaporation to dryness and repeated recrystallisation of the residue from CH_2Cl_2/diethyl ether gave the product **5** as a brown solid, yield 0.46 g (55%). An identical procedure was employed to prepare the tetrafluoroborate salt of **5** starting from $[Fe(NCMe)(dppe)(\eta\text{-}C_5Me_5)][BF_4]$.

Preparation of $[Fe(C{\equiv}CPh)(dppe)(\eta\text{-}C_5Me_5)] \cdot \frac{1}{2}CH_2Cl_2$ (1a)

A red-brown solution of $[Fe(C{=}CHPh)(dppe)(\eta\text{-}C_5Me_5)][BF_4]$ (0.70 g, 0.90 mmol) in acetone (70 cm^3) was treated, with 1,8-bis(dimethylamino)naphthalene (proton sponge) (0.23 g, 1.1 mmol) and the mixture stirred for 2 h. The resulting dark brown solution was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (5 cm^3) and the solution transferred to an alumina/n-hexane chromatography column. Elution with n-hexane/acetone (10/1) gave an orange-red band which was collected, reduced in volume and the product crystallised out at −20 °C. Further crystallisation from CH_2Cl_2/n-hexane at −20 °C afforded deep red crystals of **1a**, yield 0.31 g (47%).

Preparation of $[Ru(C{\equiv}CPh)(dppe)(\eta\text{-}C_5Me_5)]$ (1b)

A solution of $[RuCl(dppe)(\eta\text{-}C_5Me_5)]$ (0.42 g, 0.62 mmol) and HC≡CPh (0.19 g, 1.86 mmol) in methanol (80 cm^3) was refluxed with stirring for 1 h. The resulting orange-brown solution was allowed to cool, then sodium methoxide solution (formed from sodium (0.06 g, 3.0 mmol) in methanol (10 cm^3)) was added dropwise and stirring continued for 20 min. Reduction in volume afforded a yellow precipitate which was separated from the mother liquors, washed with methanol (20 cm^3) and finally recrystallised from n-hexane (−20 °C) to give the product as yellow crystals, yield 0.18 g (40%).

An identical procedure, starting from $[RuCl(dppe)(\eta\text{-}C_5Me_5)]$ (1.00 g, 1.49 mmol) and $HC{\equiv}CBu^t$ (0.37 g, 4.50 mmol) gave yellow crystals of $[Ru(C{\equiv}CBu^t)(dppe)(\eta\text{-}C_5Me_5)]$ (**1c**), yield 0.68 g (64%). Yellow $[Ru(C{\equiv}CBu^n)(PPh_3)_2(\eta\text{-}Cp)]$ was similarly prepared in 62% yield from $[RuCl(PPh_3)_2(\eta\text{-}Cp)]$ (0.74 g, 1.02 mmol) and $HC{\equiv}CBu^n$ (0.17 g, 2.2 mmol).

Preparation of $[Fe(C{\equiv}CBu^t)(dppe)(\eta\text{-}Cp)]$ (2a)

A solution of $[FeCl(dppe)(\eta\text{-}Cp)]$ (0.85 g, 1.53 mmol) and $HC{\equiv}CBu^t$ (0.38 g, 4.63 mmol) in methanol (100 cm^3) was refluxed with stirring for 1 h. The resulting red-brown solution was allowed to cool then sodium methoxide solution (formed from Na (0.18 g) in methanol (10 cm^3)) was added dropwise and stirring continued for 1 h. Removal of solvent afforded an orange-red oil, which was dissolved in CH_2Cl_2 (5 cm^3) and the solution transferred to an alumina/n-hexane column. Elution with n-hexane/acetone (2/1) gave an orange band which was collected, evaporated to dryness and the residue recrystallised from CH_2Cl_2/n-hexane (1/5, in a total volume of 12 cm^3) at −20 °C to give red crystals of **2c**, yield 0.21 g (23%).

Preparation of [Fe(C≡CBu^t)(CO)(PPh$_3$)(η-Cp)] (4c)

[FeI(CO)(PPh$_3$)(η-Cp)] was prepared in 88% yield in a one-step synthesis from [FeI(CO)$_2$(η-Cp)] via reaction with PPh$_3$ in refluxing toluene. A mixture of Ag[BF$_4$] (0.35 g, 1.78 mmol) and [FeI(CO)(PPh$_3$)(η-Cp)] (0.96 g, 1.78 mmol), cooled in an ice bath, was treated with a solution of HC≡CBu^t (0.29 g, 1.78 mmol) in CH$_2$Cl$_2$ (40 cm^3). After stirring for 1 h the solution was filtered through an alumina plug (20 × 30 mm) from which the product was eluted as an orange band with CH$_2$Cl$_2$. The filtrate was reduced in volume to 5 cm^3 then rechromatographed on alumina using n-hexane/acetone (2/1) as eluent. The resulting orange band was collected, solvent removed and the residue recrystallised from n-hexane (−20 °C) to afford orange crystals of **4c**, yield 0.24 g (27%).

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