

The chemistry of compounds of the type $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ (X = Cl, Br or I)

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Abstract

The title compounds react with unidentate ligands, L, containing either phosphorus or arsenic donor atoms to yield the corresponding compounds of the type $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{LX}$; with didentate phosphorus donor ligands the major species formed is the bridged complex $\{\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{X}\}_2\{\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2\}$ $n = 1$, X = Br; $n = 2$, X = Cl). In contrast, unidentate ligands containing nitrogen donor atoms such as pyridine did not react with $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ although reaction with 1,10-phenanthroline or diethylenetriamine yielded the ionic products $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{L}]^+\text{Cl}^-$ (L = phen or $(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NH}$). Reaction of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ with AgOAc yielded the corresponding acetato complex $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{OAc}$. $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ reacts with AgY (Y = BF_4 or PF_6) in either acetone or dichloromethane to give the useful solvent intermediates $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{solvent})]^+\text{Y}^-$, which readily react with ligands L to yield ionic derivatives of the type $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{L}]^+\text{Y}^-$ (where L = CO, NCMe, py, C_2H_4 or $\text{MeO}_2\text{CCCCO}_2\text{Me}$).

Keywords: Carbonyl; Ruthenium; Ethyltetramethylcyclopentadienyl; Phosphines; Synthesis

1. Introduction

Peralkylcyclopentadienyl ligands have proved to be extremely valuable ligands in organometallic chemistry because of their general robustness and their influence upon the chemistry at the metal centre [1]. In the case of ruthenium, pentamethylcyclopentadienyl has been the principal peralkylcyclopentadienyl ligand used and much of this chemistry has been derived from $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]_4$ [2], $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2$ [3] or $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)_2\text{Cl}$ [4]. It has also been reported that $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\text{Cl}]_4$ shows better crystallinity than the C_5Me_5 analogue and therefore this compound has also been used as a general entry into ethyltetramethylcyclopentadienylruthenium chemistry [5]. Several years ago, however, we reported the syntheses of ethyltetramethylcyclopentadienylruthenium complexes of the type $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ (X = Cl, Br or I) [6] and a kinetic study of their carbonyl substitution reactions [7]. We report herein the detailed chemistry of the title compounds and, where appropriate, contrast this with

the reactions of the corresponding C_5H_5 and C_5Me_5 analogues. The reactions studied are summarised in Scheme 1.

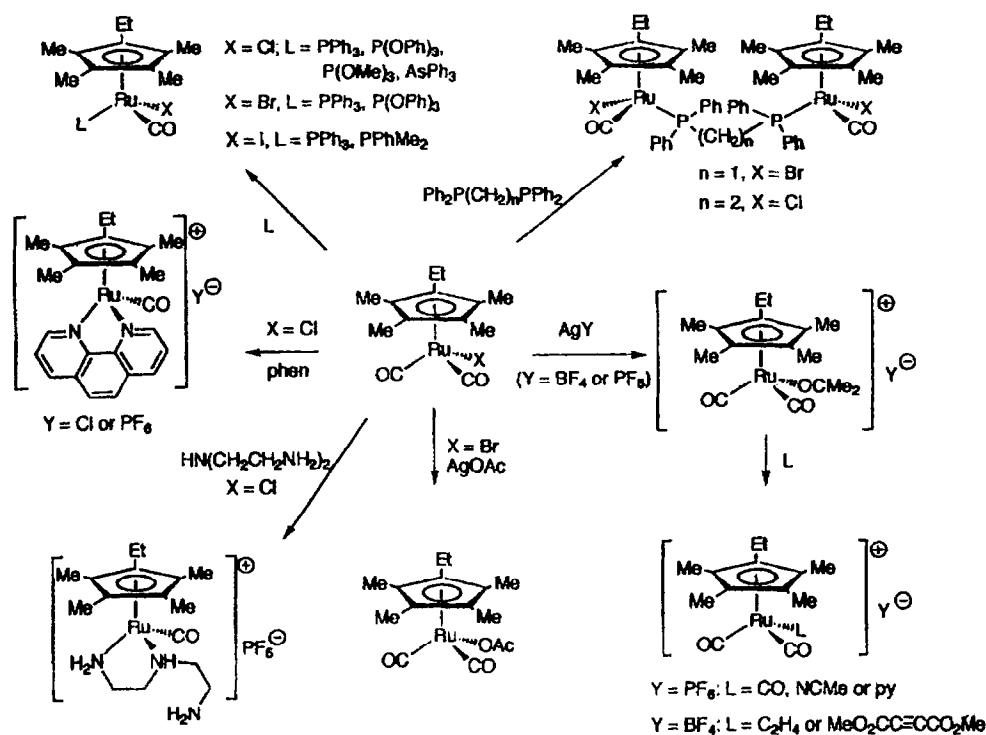
2. Results and discussion

Reactions of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ (X = Cl, Br or I) with unidentate phosphorus and arsenic donor ligands: Complexes of the type $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{LX}$ (Table 1) were prepared by heating under reflux $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ and a slight excess of the appropriate phosphine, arsine or phosphite ligand in either benzene or toluene under nitrogen. The time for the reaction to go to completion depended upon the halide used, increasing along the series $\text{Cl} < \text{Br} < \text{I}$, in keeping with the anticipated Ru–CO bond strength.

No reaction occurred when tri-*o*-tolylphosphine and $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ were heated together in benzene under reflux for 24 h; even after heating for an additional 20 h in toluene only the starting complex $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ was recovered. Tri-*o*-tolylphosphine is a very bulky ligand (cone angle 194°) [8] and presumably steric hindrance with the bulky ethyltetramethylcyclopentadienyl ligand inhibits the formation of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{P}(\text{o-C}_6\text{H}_4\text{Me})_3\}\text{Cl}$, al-

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Scheme 1.

though we do note that $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}\text{Cl}$ has been prepared by carbonylation of coordinatively unsaturated $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\{\text{P}(\text{C}_6\text{H}_{11})_3\}\text{Cl}$ [9]. Attempts to prepare bis-substituted compounds also failed; even with small ligands such as $\text{P}(\text{OMe})_3$ no further reaction occurred when the complex $\text{Ru}(\eta^5\text{-}$

$\text{C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Cl}$ was heated under reflux in benzene with another equivalent of $\text{P}(\text{OMe})_3$ for 24 h. In this respect it should be noted that although compounds of the type $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)\text{L}_2\text{X}$ are well known they are not prepared from $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{X}$ [10,11].

Table 1
Conditions used to synthesise compounds of the type $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{LX}$

Compound	Reflux time (h)	Solvent	Yield (%)	Recrystallised from	Microanalysis (%) ^a		
					C	H	Other
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{PPh}_3\}\text{Br}$	6	toluene	89	$\text{CH}_2\text{Cl}_2/\text{hexane}$	57.8 (58.0)	5.1 (5.2)	
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{PPh}_3\}\text{I}$	24	toluene	52	$\text{CH}_2\text{Cl}_2/\text{pentane}$	54.2 (54.0)	4.8 (4.8)	I, 18.9 (19.0)
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{P}(\text{OMe})_3\}\text{Cl}$	30	benzene	66	hexane at -70°C	40.9 (41.1)	5.9 (6.0)	Cl, 7.9 (8.1)
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Cl}$	24	benzene	63	$\text{CH}_2\text{Cl}_2/\text{hexane}$	57.6 (57.7)	5.2 (5.2)	Cl, 6.1 (5.7)
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{P}(\text{OPh})_3\}\text{Br}$	10	toluene	94	$\text{CH}_2\text{Cl}_2/\text{hexane}$	54.5 (53.9)	4.9 (4.8)	Br, 13.7 (12.0)
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{PPhMe}_2\}\text{I}$	48	benzene	58	hexane	44.1 (44.2)	5.1 (5.2)	I, 23.0 (23.3)
$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{AsPh}_3\}\text{Cl}$	16	toluene	59	$\text{CH}_2\text{Cl}_2/\text{hexane}$	58.3 (58.1)	5.1 (5.2)	
$\{\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{Cl}\}_2\{\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2\}$	24	benzene	69	$\text{CH}_2\text{Cl}_2/\text{hexane}$	58.3 (58.5)	6.0 (5.7)	Cl, 6.9 (6.9)
$\{\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{Br}\}_2\{\text{Ph}_2\text{PCH}_2\text{PPh}_2\}\text{CH}_2\text{Cl}_2$	16	toluene	81	$\text{CH}_2\text{Cl}_2/\text{hexane}$	50.6 (50.6)	5.1 (4.9)	Cl, 5.8, Br, 13.1 (6.0), (13.5)

^a Calculated values in parentheses.

Table 2

IR (recorded in CH₂Cl₂) and ¹H NMR (recorded in CDCl₃) data for compounds of the type Ru(η⁵-C₅Me₄Et)(CO)LX

Compound	ν_{CO} (cm ⁻¹)	C ₅ Me ₄ Et	C ₅ Me ₄ Et	Other
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(PPh ₃)Br	1970	1.48 (d, 3H), 1.53 (d, 3H) 1.63 (dd, 6H), $J_{\text{P-H}} 2$	1.91 (m, 2H) 0.93 (t, 3H) $J_{\text{H-H}} 7.5$	Ph: 7.45 (m, 15H)
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(PPh ₃)I	1940	1.59 (d, 3H), 1.60 (d, 3H) 1.69 (d, 3H), 1.74 (d, 3H) $J_{\text{P-H}} 2$	2.0 (m, 2H) 0.92 (t, 3H) $J_{\text{H-H}} 8$	Ph: 7.45 (m, 15H)
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(P(OMe) ₃)Cl	1955 ^a	1.78 (m, 12H)	2.21 (q, 2H) 1.03 (t, 3H) $J_{\text{H-H}} 7$	P(OMe) ₃ : 3.67 (d, 9H) $J_{\text{P-H}} 13$
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(P(OPh) ₃)Cl	1968	1.58 (d, 9H), 1.62 (d, 3H) $J_{\text{P-H}} 3$	2.02 (q, 2H) 0.88 (t, 3H) $J_{\text{H-H}} 8$	Ph: 7.15 (m, 15H)
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(P(OPh) ₃)Br	1970	1.70 (d, 6H), 1.71 (d, 3H) 1.74 (d, 3H) $J_{\text{P-H}} 3$	2.12 (m, 2H) 0.94 (t, 3H) $J_{\text{H-H}} 8$	Ph: 7.18 (m, 15H)
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(PPhMe ₂)I	1933	1.65 (d, 3H), 1.68 (d, 3H) 1.73 (d, 3H), 1.74 (d, 3H) $J_{\text{P-H}} 3$	1.92 (m, 2H) 0.93 (t, 3H) $J_{\text{H-H}} 7$	Ph: 7.55 (m, 5H)
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(AsPh ₃)Cl	1935	1.49 (s, 3H), 1.53 (s, 3H) 1.62 (s, 3H), 1.64 (s, 3H) $J_{\text{P-H}} 3$	1.95 (m, 2H) 0.93 (t, 3H) $J_{\text{H-H}} 8$	Ph: 7.35 (m, 15H)
{Ru(η ⁵ -C ₅ Me ₄ Et)(CO)Cl} ₂ - {Ph ₂ PCH ₂ CH ₂ PPh ₂ }	1930	1.31 (d, 12H), 1.47 (d, 12H) $J_{\text{P-H}} 3$	1.75 (m, 4H) 0.84 (m, 6H)	Ph: 7.35 (m, 20H) PCH ₂ : 2.45 (m, 4H)
{Ru(η ⁵ -C ₅ Me ₄ Et)(CO)Br} ₂ - {Ph ₂ PCH ₂ PPh ₂ }CH ₂ Cl ₂	1945	1.42 (d, 12H), 1.54 (d, 12H) $J_{\text{P-H}} 2$	1.80 (m, 4H) 0.87 (t, 6H) $J_{\text{H-H}} 8$	Ph: 7.64 (m, 4H), 7.15 (m, 16H) PCH ₂ : 4.50 (m, 2H) CH ₂ Cl ₂ : 5.30 (s, 2H)

^a Recorded in CHCl₃.

Table 3

¹³C NMR (recorded in CDCl₃) data for compounds of the type Ru(η⁵-C₅Me₄Et)(CO)LX

Compound	CEt	C ₄ Me ₄	C ₅ Me ₄ Et	CH ₂ Me	CH ₂ Me	CO	Other
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(PPh ₃)Br	100.0 (d) $J_{\text{P-C}} 3$	94.8 (d), 95.2 (d), 97.3 (d, 2C), $J_{\text{P-C}} 3$	9.3, 9.5	18.1	13.9	206.1(d), $J_{\text{P-C}} 21.4$	Ph: 127.8, 134.1, 129.8, 135.5 (d) $J_{\text{P-C}} 10.7$
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(PPh ₃)I	100.4 (d) $J_{\text{P-C}} 3.1$	95.0 (d), 95.5 (d), 96.9 (d, 2C), $J_{\text{P-C}} 3.1$	9.9, 10.3	18.7	14.3	206.1 (d), $J_{\text{P-C}} 21.4$	Ph: 127.8, 134.3, 129.7, 136.1 (d) $J_{\text{P-C}} 10.7$
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(P(OMe) ₃)Cl	100.9 (d) $J_{\text{P-C}} 3$	96.6 (d), 96.8 (d), 98.5 (d, 2C)	9.5	18.2	14.3	204.8 (d), $J_{\text{P-C}} 30.5$	P(OMe) ₃ : 52.5 (d) $J_{\text{P-C}} 3.1$
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(P(OPh) ₃)Cl	101.5 (d) $J_{\text{P-C}} 3$	96.9 (d), 97.3 (d), 99.0 (d, 2C) $J_{\text{P-C}} 3$	9.3	18.0	14.1	203.5 (d), $J_{\text{P-C}} 30.5$	Ph: 151.5 (d, $J_{\text{P-C}} 9.2$), 121.3 (d, $J_{\text{P-C}} 4.6$), 129.4, 124.5
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(P(OPh) ₃)Br	101.6 (d) $J_{\text{P-C}} 4.6$	96.8(d), 97.3 (d), 98.7 (d, 2C) $J_{\text{P-C}} 4.6$	9.6	18.2	14.1	203.3 (d), $J_{\text{P-C}} 29.0$	Ph: 151.5 (d, $J_{\text{P-C}} 9.2$), 121.4 (d, $J_{\text{P-C}} 4.6$), 129.4, 124.5
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(PPhMe ₂)I	99.8	94.6, 96.0	9.9, 10.1	18.7	14.6	205.4 (d), $J_{\text{P-C}} 19.9$	Ph: 128.3 (d, $J_{\text{P-C}} 9.1$), 129.5 (s) 130.3 (d, $J_{\text{P-C}} 9.1$), 137.3 (d, $J_{\text{P-C}} 42.7$) Me ₂ : 17.8 (d, $J_{\text{P-C}} 30.6$), 21.4 (d, $J_{\text{P-C}} 36.6$)
Ru(η ⁵ -C ₅ Me ₄ Et)(CO)(AsPh ₃)Cl	98.3	93.4 (2C), 95.7, 96.0,	9.4, 9.5	18.2	14.0	205.6	Ph: 128.4, 133.5, 129.7, 135.1
{Ru(η ⁵ -C ₅ Me ₄ Et)(CO)Cl} ₂ - {Ph ₂ PCH ₂ CH ₂ PPh ₂ }	99.6	94.9, 95.6, 97.1, 97.4	9.1	17.7	13.9	206.8 (m)	Ph: 129.0, 129.8, 133.5 (m)

The reactions of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}$, Br or I) with phosphorus donor atoms are analogous to those of the corresponding cyclopentadienyl complexes [12], although, as we have previously reported, substitution occurs more rapidly in the ethyltetramethylcyclopentadienyl complex [7]. In contrast to the corresponding iron complexes $\text{Fe}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}$, Br or I) [13], no ionic products were formed in the reactions of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ with phosphorus ligands. This is interesting in that it might have been expected that the electron-donating properties of the ethyltetramethylcyclopentadienyl ligand would favour the formation of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{L}]\text{X}$ or $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{L}_2]\text{X}$ in the same way that the electron-donating properties of triphenylphosphine leads to facile displacement of chloride ligand from $\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{PPh}_3)_2\text{Cl}$ [11].

Apart from $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})\{\text{P}(\text{C}_6\text{H}_{11})_3\}\text{Cl}$ discussed previously, the only reported pentamethylcyclopentadienyl analogue of the above class of compounds is $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})(\text{PPh}_3)\text{Cl}$, prepared by carbonylation of the corresponding bis(triphenylphosphine) derivative [4]. In general the spectroscopic properties reported for this compound are similar to those of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{PPh}_3)\text{Cl}$; in particular, the electron donating abilities of the two peralkylated cyclopentadienyl ligands should be comparable and this is reflected in the carbonyl stretching frequencies, e.g. $\text{RuCp}'(\text{CO})(\text{PPh}_3)_2\text{Cl}$ $\nu_{\text{max}} \text{CO}$ (nujol) $\text{Cp}' = \text{C}_5\text{H}_5$ 1958 cm^{-1} [14], $\text{Cp}' = \text{C}_5\text{Me}_5$ 1918 cm^{-1} [4], $\text{Cp}' = \text{C}_5\text{Me}_4\text{Et}$ 1915 cm^{-1} . One important difference is that, unlike the C_5Me_5 ligand, the ethyltetramethylcyclopentadienyl reflects the presence of the chiral ruthenium centre. Thus, the ^1H NMR spectrum of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{PPh}_3)\text{Cl}$ shows four nonequivalent methyl ring-substituents although the ring-carbon signals in the ^{13}C NMR spectrum shows a 1:1:1:2 pattern rather than five separate resonances. Inspection of Tables 2 and 3 reveals a general rule of thumb that for complexes of the type $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{LX}$ the chemical shift difference observed for enantiotopic ^1H and ^{13}C atoms in the NMR spectra increases with steric crowding around the ruthenium centre.

2.1. Reaction of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ with didentate phosphorus ligands

Heating the complex $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ under reflux with half a molar equivalent of dppe in benzene for 24 h gave the bridged product $(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\{\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{Cl}\}_2$. A similar reaction between $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ and dpmm gave the corresponding $(\mu\text{-Ph}_2\text{PCH}_2\text{PPh}_2)\{\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{Br}\}_2$. These formulations are supported by elemental analyses and spectroscopic data. An interesting feature of these compounds is that each

ruthenium centre is chiral but attempts to detect diastereoisomers by IR spectroscopy failed in that even in non-polar solvents only one carbonyl band was detected (e.g. for the dppe complex ν_{CO} (CCl_4) 1940 cm^{-1}), although it was noted that this band was rather broad. Both the ^1H and ^{13}C NMR spectra indicated that an asymmetric ruthenium centre was present but the clearest evidence for the presence of diastereoisomers comes from the ^{31}P NMR spectra recorded in CDCl_3 , which contain two signals for each complex (i.e. dppe complex δ 42.4, 42.8; dpmm complex δ 42.6, 43.8). Although no attempt was made to separate the diastereoisomers it is apparent that some separation occurred during recrystallisation since the two ^{31}P NMR signals differed in intensity.

Reaction of the complex $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ with an equimolar amount of dppe was more complex. The product obtained exhibited only one ν_{CO} in the IR spectrum (1940 cm^{-1} in heptane); however, the ^1H , ^{13}C and ^{31}P NMR spectra all showed that more than one compound was present. Further, from the NMR spectra it was evident that the bridged species described above was the major component in the reaction mixture. Attempts to separate the products by chromatography or recrystallisation failed; this, together with the fact that all the product mixture was soluble in benzene and other non-polar solvents would appear to exclude the formation of the ionic compound $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)]^+\text{Cl}^-$. In view of the previously discussed difficulty of replacing both carbonyl ligands, the formation of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}]$ also appears unlikely and we therefore conclude that the reaction mixture contains the compound $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\text{Cl}]$ having unidentate dppe together with the previously characterised bridged compound $(\mu\text{-Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2)\{\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{Cl}\}_2$.

2.2. Reaction of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ with nitrogen donor ligands

An attempt to prepare the complex $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{NC}_5\text{H}_5)\text{Cl}$ by reacting $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ with an excess of pyridine failed; no reaction occurred after heating the mixture under reflux in benzene for 15 h. However, when the chloro complex was heated under reflux in acetonitrile in the presence of ammonium hexafluorophosphate, a slow reaction occurred to give $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{NCMe})]^+\text{PF}_6^-$. The reaction required about a week to go to completion and it is therefore more convenient to prepare this product from $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{OCMe}_2)]^+\text{PF}_6^-$ as described below.

A more rapid reaction occurred between $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ and an equimolar quantity of 1,10-phenanthroline. After heating the mixture under reflux

in benzene for 24 h the ionic product $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{phen})]^+\text{Cl}^-$ was isolated; treatment with NH_4PF_6 gave the corresponding hexafluorophosphate derivative $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{phen})]^+\text{PF}_6^-$. Heating $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ with an excess of diethylenetriamine yielded the cation $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{\text{HN}(\text{CH}_2\text{CH}_2\text{NH}_2)_2\}]^+$ which again was isolated as the hexafluorophosphate derivative. Consistent with this formulation, the IR spectrum of this compound contained one $\nu_{(\text{CO})}$ at 1938 cm^{-1} . It is significant that only one carbonyl group of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ is displaced by this potentially terdentate ligand. Evidence for the bidentate bonding of the diethylenetriamine ligand comes from the asymmetry of the ^{13}C NMR spectrum which contains four methylene signals for this ligand. The ^{13}C NMR spectrum was invariant up to 110°C , suggesting that exchange between the coordinated and uncoordinated nitrogen donor atoms is slow on the NMR time scale.

An attempt to synthesise the tris-pyrazoylborate complex $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})\{(\text{N}_2\text{C}_3\text{H}_3)_3\text{BH}\}$ by heating $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ and $\text{K}\{(\text{N}_2\text{C}_3\text{H}_3)_3\text{BH}\}$ together in dimethylformamide under reflux for 24 h yielded only starting material. The steric hindrance in the anticipated product would be considerable and this is clearly a factor in the failure of this reaction.

2.3. Reactions involving substitution of the halide

Silver acetate reacted readily at room temperature with $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ to give the corresponding acetate complex $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{OAc})$. An attempt to convert this to the corresponding trifluoroacetate complex by heating in trifluoroacetic acid yielded unreacted starting material.

As indicated earlier, ionic derivatives of the type $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{L}]\text{X}$ are not formed when $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ reacts with monodentate donor ligands L. Such ionic compounds can, however, be prepared via the corresponding acetone complex $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{OCMe}_2)]\text{Y}$ ($\text{Y} = \text{BF}_4$ or PF_6), which is generated by treatment of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ with AgY in acetone. For example, although pyridine does not react with $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ under reflux in benzene, the ionic derivative $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{NC}_5\text{H}_5)]\text{PF}_6$ is immediately formed when $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{OCMe}_2)]\text{PF}_6$ is treated with pyridine. Similarly, the corresponding compounds $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{NCMe})]\text{PF}_6$ and $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_3]\text{PF}_6$ are formed upon treating the acetone solvent complex $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{OCMe}_2)]\text{PF}_6$ with acetonitrile and carbon monoxide respectively. The analogous $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_3]\text{BF}_4$ has been prepared by a similar procedure [15].

The alkene and alkyne complexes $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})-$

$(\text{CO})_2(\text{h}^2\text{-C}_2\text{H}_4)]\text{BF}_4$ and $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{h}^2\text{-MeO}_2\text{CCCCO}_2\text{Me})]\text{BF}_4$ were synthesised by a related method involving reaction of ethene and dimethyl acetylenedicarboxylate respectively with $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{CH}_2\text{Cl}_2)]\text{BF}_4$, generated from $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ and AgBF_4 in dichloromethane. The ^1H spectrum of the ethene complex $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]\text{BF}_4$ contains only one signal for the coordinated unsaturated ligand, even at -80°C , implying that rotation about the ruthenium–ethene bond is a facile process. A similar observation has been made for the analogous $[\text{Ru}(\eta^5\text{-C}_5\text{H}_5)(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]\text{BF}_4$ [16].

Ethene complexed to a positively charged metal centre is known to be susceptible to nucleophilic attack [17]. To test that this was also true for the ethene complex $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]\text{BF}_4$ it was reacted with triphenylphosphine and the corresponding phosphonium salt $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{CH}_2\text{CH}_2\text{-PPh}_3^+\text{BF}_4^-)]$ was isolated in good yield.

In summary, the chemistry of the compounds $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ or I) is essentially little different from that of the analogous cyclopentadienyl analogues. Although substitution of one carbonyl ligand is relatively facile, the displacement of a second carbonyl ligand is not observed. This, together with the fact that the halide ligand is not particularly labile, limits the range of derivatives that can be prepared compared to related compounds such as $\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)(\text{PPh}_3)_2\text{Cl}$, $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}]_4$ or $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$ which have two or three relatively labile sites.

3. Experimental

Microanalytical data were obtained by the University of Sheffield Microanalytical service. All reactions were carried out under an atmosphere of nitrogen although all the products were subsequently found to be stable to air in the solid state.

1-Ethyl-2,3,4,5-tetramethylcyclopentadiene was prepared by the method of Feitler and Whitesides [18] and the starting complexes $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$ or I) were prepared as described previously [6,7]. Dichloromethane was dried by distillation from calcium hydride; acetone was dried over calcium sulphate and distilled before use; all other solvents were used as received.

Compounds of the type $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\text{LX}$ ($\text{L} = \text{phosphorus}$ or arsenic donor ligand, $\text{X} = \text{Cl}, \text{Br}$ or I) were prepared by the same general procedure. This is described in detail below for the preparation of one such compound, $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{PPh}_3)\text{Cl}$, and modifications to this procedure for the other complexes of this type are given in Table 1; the IR spectra and ^1H NMR spectra of these compounds are tabulated in Table

2 and the corresponding ^{13}C NMR data are collected in Table 3.

3.1. Carbonylchloro(η^5 -ethyltetramethylcyclopentadienyl)(triphenylphosphine)ruthenium

A mixture of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ (0.250 g, 0.73 mmol) and triphenylphosphine (0.210 g, 0.8 mmol) in benzene (150 cm^3) was heated under reflux for 20 h. After cooling, the benzene was removed on the rotary evaporator and the residue recrystallised from dichloromethane–petroleum ether (40–60 $^\circ\text{C}$) to give the product as orange crystals (0.350 g, 83%). (Found: C, 62.1; H, 5.6; Cl, 6.4%. $\text{C}_{30}\text{H}_{32}\text{ClOPRu}$ requires C, 62.5; H, 5.6; Cl, 6.2%.) ν_{max} cm^{-1} (CO) 1943 (CHCl_3); δ_{H} (220 MHz, CDCl_3): 7.5 (5H, m, ArH), 1.88 (2H, m, CH_2), 0.93 (3H, t, J 8 Hz, CH_2Me), 1.43 (d), 1.49 (d), 1.59 (d), 1.60 (d), 12 H, $J_{\text{H-P}}$ 2 Hz, Me_4 . δ_{C} (25.15 MHz, CDCl_3): 206.3 (d, $J_{\text{C-P}}$ 21.4 Hz, CO), 135.5, 134.0, 129.8, 127.9 (d, $J_{\text{C-P}}$ 10.6 Hz, ArC), 100.1 (d, $J_{\text{C-P}}$ 3.1 Hz, CEt), 97.7 (d), 95.5 (d), 94.9 (2C, d, $J_{\text{C-P}}$ 3.1 Hz, C_4Me_4), 17.9 (s, CH_2Me), 13.9 (s, CH_2Me), 9.2 (s, Me_4).

3.2. Carbonyl(η^5 -ethyltetramethylcyclopentadienyl)(1,10-phenanthroline)ruthenium hexafluorophosphate

1,10-Phenanthroline (0.350 g, 1.94 mmol) was added to a solution of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ (0.500 g, 1.46 mmol) in benzene (50 cm^3) and the mixture was heated under reflux overnight. The following day the solution was allowed to cool and the precipitate was filtered off and washed with benzene (2×10 cm^3) to give the product $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{phen})]^+\text{Cl}^-$ (0.320 g, 45%). Removal of the solvent from the filtrate in vacuo gave unreacted starting material $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ (0.100 g). The product was dissolved in acetone (15 cm^3) and saturated aqueous NH_4PF_6 was added dropwise to give a yellow precipitate of the hexafluorophosphate derivative $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})(\text{N}_2\text{C}_{12}\text{H}_8)]\text{PF}_6$ (Found: C, 47.6; H, 4.2; N, 4.7%. $\text{C}_{24}\text{H}_{25}\text{F}_6\text{N}_2\text{OPRu}$ requires C, 47.8; H, 4.2; N, 4.6%.) ν_{max} cm^{-1} (CO) 1970 (CH_2Cl_2); δ_{H} (220 MHz, CDCl_3): 9.39 (2H, dd, $J_{\text{H}_2\text{-H}_3}$ 5.0 Hz, $J_{\text{H}_2\text{-H}_4}$ 1.0 Hz, $\text{H}_{2,9}$), 8.93 (2H, dd, $J_{\text{H}_4\text{-H}_3}$ 8.0 Hz, $\text{H}_{4,7}$), 8.33 (2H, s, $\text{H}_{5,6}$), 8.20 (2H, dd, $\text{H}_{3,8}$), 2.32 (2H, q, J 8 Hz, CH_2), 1.12 (3H, t, CH_2Me), 1.87 (6H, s), 1.82 (6H, s), Me_4 . δ_{C} (25.15 MHz, CDCl_3): 199.4 (s, CO), 154.5, 146.7, 138.3, 130.7, 128.0, 126.6 (s, phen), 97.1 (CEt), 94.4, 93.7 (s, C_4Me_4), 18.1 (s, CH_2Me), 13.9 (s, CH_2Me), 9.5 (s, Me_4).

3.3. Carbonyl(η^5 -ethyltetramethylcyclopentadienyl)(diethylenetriamine)ruthenium hexafluorophosphate

$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ (1.0 g, 2.92 mmol) was dissolved in benzene (100 cm^3), diethylenetriamine (2

cm^3) was added and the mixture heated under reflux for 20 h. The solution was allowed to cool, the precipitate filtered off and washed with benzene (2×10 cm^3) and petroleum ether (40–60 $^\circ\text{C}$) 2×5 cm^3) to remove unreacted starting material. Recrystallisation from dichloromethane/petroleum ether (40–60 $^\circ\text{C}$) gave yellow crystals of the product $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NH}\}]^+\text{Cl}^-$ (0.680 g, 56%). Benzene was removed from the filtrate of the original reaction mixture and unreacted starting material $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ (80 mg) was recovered. The ionic product was stirred with excess NH_4PF_6 in dichloromethane overnight, then the mixture was filtered to remove unreacted NH_4PF_6 and the filtrate was taken to dryness to give the hexafluorophosphate derivative $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})\{(\text{NH}_2\text{CH}_2\text{CH}_2)_2\text{NH}\}]\text{PF}_6$. (Found: C, 36.7; H, 6.1; N, 7.9%. $\text{C}_{16}\text{H}_{30}\text{F}_6\text{N}_3\text{OPRu}$ requires C, 36.5; H, 5.7; N, 8.0%.) ν_{max} cm^{-1} (CO) 1938 (CH_2Cl_2); δ_{H} (220 MHz, CD_2Cl_2): 4.59 (1H, s, br, NH), 3.89 (1H, s, br, NH), 2.80 (10H, m, NH_2 and $\{\text{CH}_2\text{CH}_2\}_2$), 2.17 (3H, m, NH and CH_2), 1.06 (3H, t, J 8 Hz, CH_2Me), 1.79 (12H, s, Me_4). δ_{C} (25.15 MHz, CDCl_3): 204.2 (s, CO), 95.0, (CEt), 92.5, 92.2, 91.8, 91.6 (s, C_4Me_4), 63.9 (s), 53.6 (s), 45.9 (s), 39.0 (s, $\{\text{CH}_2\text{CH}_2\}_2$), 18.2 (s, CH_2Me), 14.4 (s, CH_2Me), 9.8 (s, Me_4).

3.4. Acetato dicarbonyl(η^5 -ethyltetramethylcyclopentadienyl)ruthenium

Silver acetate (0.650 g, 3.9 mmol) was added to $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ (1.0 g, 2.6 mmol) in benzene (70 cm^3) and the mixture stirred overnight in the dark under nitrogen. The following day the solution was filtered through a cellulose column (1×3 cm^3), the benzene removed in vacuo and the residue recrystallised from light petroleum ether to give the product $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{O}_2\text{CCH}_3)$ as a yellow–green solid (0.650 g, 68.5%). (Found: C, 48.9; H, 5.8%. $\text{C}_{15}\text{H}_{20}\text{O}_4\text{Ru}$ requires C, 49.3; H, 5.5%.) ν_{max} cm^{-1} 2038, 1988, 1966(sh) (CO), 1635 (CO_2) (hexane); δ_{H} (220 MHz, CD_2Cl_2): 2.02 (3H, s, Ac), 2.29 (2H, q, J 8 Hz, CH_2Me), 1.07 (3H, t, CH_2Me), 1.87 (12H, s, Me_4). δ_{C} (25.15 MHz, CDCl_3): 199.8 (s, CO), 177.0 (Ac), 101.9 (CEt), 99.9, 99.6, (s, C_4Me_4), 23.2 (s, Ac), 18.2 (s, CH_2Me), 14.7 (s, CH_2Me), 9.9, 9.6 (s, Me_4).

3.5. Acetonedicarbonyl(η^5 -ethyltetramethylcyclopentadienyl)ruthenium hexafluorophosphate

$\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Cl}$ (0.350 g, 1.0 mmol) was dissolved in distilled acetone (60 cm^3), AgPF_6 (0.258 g, 1.0 mmol) was then added and the mixture stirred in the dark for 1 h. The precipitate of AgCl was then filtered off through a cellulose column (1×3 cm^3) and the

filtrate divided in two and used for the following two preparations.

3.6. Tricarbonyl(η^5 -ethyltetramethylcyclopentadienyl)-ruthenium hexafluorophosphate

Carbon monoxide was bubbled for 1.5 h through a solution of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{OCMe}_2)]\text{PF}_6$ prepared as described above. The solution was left stirring under a carbon monoxide atmosphere overnight and the following day the solvent was removed in vacuo. Recrystallisation of the residue from dichloromethane/petroleum ether (40–60 °C) gave white crystals of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_3]\text{PF}_6$ (0.070 g, 28.5%). (Found: C, 34.9; H, 3.4%. $\text{C}_{14}\text{H}_{17}\text{F}_6\text{O}_3\text{PRu}$ requires C, 35.1; H, 3.6%.) $\nu_{\text{max}} \text{ cm}^{-1}$ (CO) 2120, 2062 (CH_2Cl_2); δ_{H} (220 MHz, CDCl_3): 2.21 (6H, s), 2.20 (6H, s, Me_4), 2.25 (2H, q, J 8 Hz, CH_2Me), 1.06 (3H, t, CH_2Me); δ_{C} (25.15 MHz, CDCl_3): 190.4 (s, CO), 109.3 (CEt), 106.5, 106.3. (s, C_4Me_4), 18.3 (s, CH_2Me), 14.7 (s, CH_2Me), 10.1, 9.9 (s, Me_4).

3.7. Dicarboxyl(η^5 -ethyltetramethylcyclopentadienyl)-pyridineruthenium hexafluorophosphate

Pyridine (0.045 g, 0.57 mmol) was added to the other portion of the $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{OCMe}_2)]\text{PF}_6$ prepared as described above and mixture was stirred for 3 h. The solvent was then removed and the residue crystallised from dichloromethane/ether to give $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{NC}_5\text{H}_5)]\text{PF}_6$ as a yellow solid (0.14 g, 52%). (Found: C, 40.7; H, 3.9; N, 2.5%. $\text{C}_{18}\text{H}_{22}\text{F}_6\text{NO}_2\text{PRu}$ requires C, 40.8; H, 4.2; N, 2.6%.) $\nu_{\text{max}} \text{ cm}^{-1}$ (CO) 2048, 2002 (CH_2Cl_2); δ_{H} (220 MHz, CD_2Cl_2): 8.49 (2H, d, J 3 Hz, *py*), 7.95 (1H, br, *py*), 7.57 (2H, m, *py*), 2.26 (2H, q, J 9 Hz, CH_2Me), 1.10 (3H, t, CH_2Me), 1.87 (12H, s, Me_4). δ_{C} (25.15 MHz, CDCl_3): 196.7 (s, CO), 157.2, 139.7, 127.9 (*py*), 104.7 (CEt), 102.2, 101.6. (s, C_4Me_4), 18.0 (s, CH_2Me), 14.2 (s, CH_2Me), 9.3 (s, Me_4).

3.8. Acetonitriledicarbonyl(η^5 -ethyltetramethylcyclopentadienyl)ruthenium hexafluorophosphate

Acetonitrile (5 cm^3) was added to $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\text{OCMe}_2)]\text{PF}_6$ prepared by the method described above using $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ (0.400 g, 1.04 mmol) and AgPF_6 (0.270 g, 1.04 mmol) in acetone (50 cm^3). After 30 min the solvent was removed in vacuo to leave a yellow oil which was crystallised from dichloromethane/ether to yield the product as pale yellow crystals (0.370 g, 72%). (Found: C, 37.1; H, 4.1; N, 3.0%. $\text{C}_{15}\text{H}_{20}\text{F}_6\text{NO}_2\text{PRu}$ requires C, 36.6; H, 4.1; N, 2.9%.) $\nu_{\text{max}} \text{ cm}^{-1}$ 2300w (CN), 2060s, 2010s (CO) (CH_2Cl_2); δ_{H} (220 MHz, CD_2Cl_2): 2.47 (3H, s, *MeCN*), 2.35 (2H, q, J 8 Hz, CH_2Me),

1.11 (3H, t, CH_2Me), 2.00, 1.98 (12H, s, Me_4). δ_{C} (25.15 MHz, CDCl_3): 195.4 (s, CO), 129.0 (*MeCN*) 104.6 (CEt), 102.1, 101.9. (s, C_4Me_4), 18.0 (s, CH_2Me), 14.4 (s, CH_2Me), 9.36, 9.5 (s, Me_4), 3.8 (*MeCN*).

3.9. Dicarboxyl(η^2 -ethene)(η^5 -ethyltetramethylcyclopentadienyl)ruthenium tetrafluoroborate

A mixture of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ (1.000 g, 2.56 mmol) and AgBF_4 (0.500 g, 1.13 mmol) in dried dichloromethane (20 cm^3) was stirred in the dark for 1 h before bubbling ethene through the solution overnight. The solution was then filtered through a cellulose column (1 \times 3 cm^3) to remove silver salts and the filtrate taken to dryness in vacuo to leave a yellow oil. Crystallisation from dichloromethane/ether gave the desired product as white crystals (0.950 g, 87%). (Found: C, 42.5; H, 5.0%. $\text{C}_{15}\text{H}_{21}\text{BF}_4\text{O}_2\text{Ru}$ requires C, 42.8; H, 5.0%.) $\nu_{\text{max}} \text{ cm}^{-1}$ (CO) 2070, 2030 (CHCl_3); δ_{H} (220 MHz, CD_2Cl_2): 3.36 (4H, br, C_2H_4), 2.42 (2H, q, J 8 Hz, CH_2Me), 1.14 (3H, t, CH_2Me), 2.00, 2.03 (12H, s, Me_4). δ_{C} (25.15 MHz, CDCl_3): 196.9 (s, CO), 107.5 (CEt), 104.9, 104.2 (s, C_4Me_4), 57.8 (C_2H_4), 18.1 (s, CH_2Me), 14.1 (s, CH_2Me), 9.5 (s, Me_4).

3.10. Dicarboxyl(η^2 -dimethyl-2-butynedioate)(η^5 -ethyltetramethylcyclopentadienyl)ruthenium tetrafluoroborate

A mixture of $\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2\text{Br}$ (0.300 g, 0.78 mmol) and AgBF_4 (0.152 g, 0.78 mmol) in dried dichloromethane (20 cm^3) was stirred in the dark for 1 h; dimethyl acetylenedicarboxylate (0.600g, 4.22 mmol) was added and the mixture stirred for an additional 48 h. The solvent was then removed in vacuo and the residual oil was washed with ether (3 \times 5 cm^3) then dissolved in chloroform and filtered through a cellulose column (1 \times 3 cm^3). Addition of ether to the filtrate precipitated the product as pale green crystals (0.125 g, 30%). (Found: C, 42.5; H, 4.5%. $\text{C}_{19}\text{H}_{23}\text{BF}_4\text{O}_6\text{Ru}$ requires C, 42.6; H, 4.3%.) $\nu_{\text{max}} \text{ cm}^{-1}$ 2040, 1992 (CO), 1740, (CO₂) (CHCl_3); δ_{H} (220 MHz, CDCl_3): 3.85 (6H, br, CO_2Me), 2.50 (2H, q, J 8 Hz, CH_2Me), 1.18 (3H, t, CH_2Me), 2.18 (12H, s, Me_4).

3.11. Dicarboxyl(η^5 -ethyltetramethylcyclopentadienyl)-{(triphenylphosphonium)ethyl}ruthenium tetrafluoroborate

Triphenylphosphine (0.140 g, 0.53 mmol) was added in portions to a solution of $[\text{Ru}(\eta^5\text{-C}_5\text{Me}_4\text{Et})(\text{CO})_2(\eta^2\text{-C}_2\text{H}_4)]\text{BF}_4$ (0.210 g, 0.50 mmol) in nitromethane (10 cm^3) over a period of 15 min and the mixture stirred for an additional 30 min. The solution was cooled to 0 °C and diethyl ether was added to precipitate the product which was recrystallised from dichloromethane/ether

(0.282 g, 83%). Found: C, 57.3; H, 5.2%. $C_{33}H_{36}BF_4O_2PRu$ requires C, 58.0; H, 5.3%.) ν_{max} cm^{-1} (CO) 2000, 1940 (CH_2Cl_2); δ_H (220 MHz, CD_2Cl_2): 7.70 (15H, m PPh_3), 3.35 (4H, br, C_2H_4), 2.20 (2H, q, J 8 Hz, CH_2Me), 1.00 (3H, t, CH_2Me), 1.81, 1.79 (12H, s, Me_4). δ_C (25.15 MHz, $CDCl_3$): 203.3 (s, CO), 135.1–116.6 (PPh_3), 104.5 (s, CEt), 100.0, 99.1 (s, C_4Me_4), 31.2 (d, J_{C-P} 31.8, PCH_2), 18.1 (s, CH_2Me), 15.4 (s, CH_2Me), 9.5 (s, Me_4), –8.7 (d, J_{C-P} 13.6, $RuCH_2$); δ_P (40.48 MHz, $CDCl_3$): δ 19.8.

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