Allylic Alkylation of Complexed Cyclo-octatetraene (cot) *via* the Reaction of $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$ with $[M(CO)_3(\eta^4\text{-cot})]$ (M = Fe or Ru) Derivatives; *X*-Ray Structure of $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_8R)][PF_6]\cdot0.5CH_2Cl_2$ $[R = CH_2C(Me)=CH_2]$*

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The reaction of $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ [**1**; allyl = CH_2CHCH_2 or $CH_2C(Me)CH_2$] with $[Ru(CO)_2L(\eta^4\text{-cot})]$ (L = CO or PPh_3, cot = cyclo-octatetraene) gives $[Ru(CO)_2L(\eta^2,\eta^3\text{-}C_8H_8R)][PF_6]$ [**2**; R = $CH_2CH=CH_2$ or $CH_2C(Me)=CH_2$] whereas that of (**1**; allyl = $CH_2CHCHMe$) yields [**2**; R = $CH(Me)CH=CH_2$], as a mixture of two diastereomers, and (**2**; R = $CH_2CH=CHMe$). The *X*-ray structure of [**2**; R = $CH_2C(Me)=CH_2$] shows that the addition of the 2-methylallyl group to the C_8 ring yields the *exo* isomer, and confirms that the resulting cyclo-octatrienyl ligand is η^2,η^3-co-ordinated to ruthenium. The η^2-alkene unit is *trans* to the PPh_3 ligand, and the η^3-allyl moiety is transoid to the two carbonyl ligands. Complex (**1**) and $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$ give $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_8R)][PF_6]$ as a mixture of cyclo-octatrienyl (**3**) and bicyclo[5.1.0]octadienyl (**4**) isomers, the former showing rotamerism of the $Fe(CO)_2(CNBu^t)$ group with respect to the η^5-bound hydrocarbon; diastereomerism is observed for [**3**; R = $CH(Me)CH=CH_2$]. The cationic iron and ruthenium complexes (**2**)—(**4**) are deprotonated by NEt_3 in CH_2Cl_2 to give the allyl-substituted cot complexes $[M(CO)_2L(\eta^4\text{-}C_8H_7R)]$ [**5**; M = Fe, L = $CNBu^t$, R = $CH_2CH=CH_2$, $CH_2C(Me)=CH_2$, $CH(Me)CH=CH_2$, or $CH_2CH=CHMe$; M = Ru, L = PPh_3, R = $CH_2C(Me)=CH_2$] which undergo two dynamic processes in solution, namely rotamerism (M = Fe) and oscillation of the $M(CO)_2L$ unit with respect to the η^4-bound hydrocarbon. The compounds $[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_7R)]$ [R = $CH_2CH=CH_2$ or $CH_2C(Me)=CH_2$] react sequentially with [**1**; R = CH_2CHCH_2 or $CH_2C(Me)CH_2$] and NEt_3 to give the difunctionalised cyclo-octatetraene derivatives $[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_6R_2)]$ [**6**; R = $CH_2CH=CH_2$ or $CH_2C(Me)=CH_2$]. The substituted cyclo-octatetraenes $C_8H_7[CH_2C(Me)=CH_2]$ and $C_8H_6[CH_2C(Me)=CH_2]_2$ are detached from the appropriate iron complexes, (**5**) or (**6**), on reaction with $ONMe_3\cdot2H_2O$.

Transition-metal allyl complexes, particularly of palladium,[1] have been widely used in the allylic functionalisation of organic substrates. The extent to which C–C bond formation is stereo- and/or regio-specific depends on various factors including the nature of the metal and its ancillary ligands and the nucleophilicity of the substrate. With palladium, nucleophilic addition usually occurs at the less substituted end of the allyl group, and similar regiochemistry is observed in the reactions of $[Fe(CO)_4(\eta^3\text{-}CH_2CHCHMe)]^+$ [2] and $[Fe(CO)_2(NO)(\eta^3\text{-}CH_2CHCHMe)]$.[3] Here we give details[4] of the allylation of iron- and ruthenium-bound cyclo-octatetraene (cot) by $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$ where the addition of the 1-methylallyl group occurs predominantly *via* the more substituted end of the C_3 chain. We also describe the *X*-ray structure of the adduct $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_8R)]^+$ [R = $CH_2C(Me)=CH_2$], and the synthesis of mono- and di-substituted cyclo-octatetraenes *via* sequential allylic alkylation, deprotonation, and ring detachment from the metal centre.

Results and Discussion

The addition of $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ [**1**; allyl = CH_2CHCH_2, $CH_2CHCHMe$, or $CH_2C(Me)CH_2$] to $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$ (prepared by a modification of the published procedure[5]) or $[Ru(CO)_2L(\eta^4\text{-cot})]$ (L = CO or PPh_3) in CH_2Cl_2 gives red-brown solutions from which yellow (M = Fe) or white (M = Ru) salts $[M(CO)_2L(C_8H_8R)][PF_6]$ (R = allyl) are isolable. As might be expected, the susceptibility of the cot ring towards electrophilic attack is enhanced by carbonyl replacement at the metal centre; the room-temperature allylation of $[Ru(CO)_2L(\eta^4\text{-cot})]$ requires 90 min when L is CO but only 30 min when L is PPh_3.

The cationic allylation products were characterised by elemental analysis and by i.r. (Table 1) and n.m.r.† spectroscopy (Table 2), the last revealing major differences between the iron and ruthenium complexes.

The ^1H and ^{13}C n.m.r. spectra of $[Ru(CO)_2L(\eta^2,\eta^3\text{-}C_8H_8R)]^+$ [**2**; L = CO, R = $CH_2CH=CH_2$; L = PPh_3, R = $CH_2CH=CH_2$ or $CH_2C(Me)=CH_2$] are relatively simple and indicate the presence of an η^2,η^3-bound cyclo-octatrienyl ring (Scheme 1); the major difference between the ^1H n.m.r. spectra of the tricarbonyl and dicarbonylphosphine analogues is an upfield shift of the resonances due to H(1), H(2), and H(3) of the latter.

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* Dicarbonyl[1—3-η, 6—7-η-8-(2′-methylallyl)cyclo-octa-2,4,6-trien-1-yl](triphenylphosphine)ruthenium hexafluorophosphate–dichloromethane (1/1).

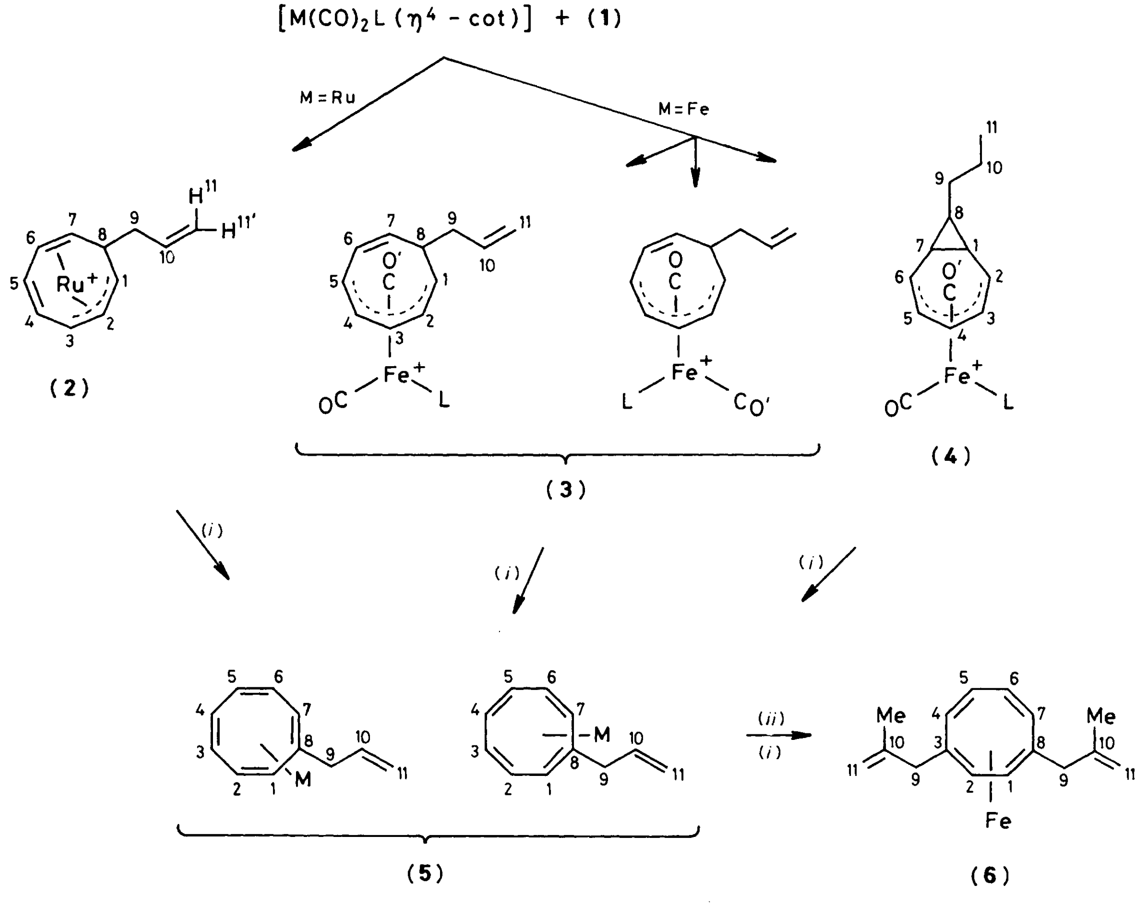
Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

† The complex n.m.r. spectra reported have been assigned as fully as possible with the aid of $^1H\text{-}\{^1H\}$ decoupling experiments. In some cases, parts of the spectrum of a minor component of an isomeric mixture are obscured by the spectrum of the major isomer. In all cases, the spectral data reported for an individual isomer have been taken from the spectrum of the inseparable isomeric mixture. It should also be noted that isomer ratios were estimated from the ^1H n.m.r. spectra of mixtures isolated after purification.

Table 1. Analytical and i.r. spectroscopic data for complexes (**2**)—(**6**)

						Analysis[a]/%			I.r.[b]/cm^{-1}	
Complex	M	L	R	Yield/%	Colour	C	H	N	$\tilde{\nu}$(CO)	$\tilde{\nu}$(CN)
(**2**)	Ru	CO	C_3H_5	58	White	35.4(35.4)	2.5(2.7)	—	2 130, 2 081, 2 071	—
		PPh_3	C_3H_5	64	White	52.3(52.5)	3.9(4.0)	—	2 063, 2 018	—
		PPh_3	1-MeC_3H_4	36	White	53.2(53.1)	4.3(4.2)	—	2 063, 2 018	—
		PPh_3	2-MeC_3H_4	58	White	56.0(51.0)[c]	4.2(4.1)	—	2 064, 2 018	—
(**3**)/(**4**)[d]	Fe	$CNBu^t$	C_3H_5	78	Yellow	44.7(44.6)	4.6(4.6)	3.0(2.9)	2 074, 2 037	2 199
		$CNBu^t$	1-MeC_3H_4	67	Yellow	45.4(45.7)	4.8(4.9)	3.0(2.8)	2 072, 2 037	2 197
		$CNBu^t$	2-MeC_3H_4	74	Yellow	45.4(45.7)	4.9(4.9)	2.7(2.8)	2 072, 2 035	2 197
(**5**)	Fe	$CNBu^t$	C_3H_5	89	Orange-red	63.9(63.7)	6.5(6.3)	4.2(4.1)	1 994, 1 945[e]	2 146
									2 002, 1 956[f]	2 126
		$CNBu^t$	1-MeC_3H_4	68	Orange-red	64.4(64.6)	6.5(6.6)	4.2(4.0)	1 993, 1 944[e]	2 146
									2 001, 1 955[f]	2 122
		$CNBu^t$	2-MeC_3H_4	89	Orange-red	64.4(64.6)	6.6(6.6)	3.8(4.0)	1 993, 1 945[e]	2 146
									2 002, 1 956[f]	2 124
	Ru	PPh_3	2-MeC_3H_4	28	Orange	66.2(66.6)	5.1(5.0)	—	2 002, 1 946[e]	—
(**6**)	Fe	$CNBu^t$	2-MeC_3H_4	29	Red-purple	68.3(67.8)	7.4(7.2)	3.5(3.4)	1 993, 1 944[e]	2 144
									1 999, 1 954[f]	2 125

[a] *Calculated values in* parentheses. [b] In CH_2Cl_2 unless stated otherwise. [c] Analysed as a 0.5CH_2Cl_2 solvate. [d] The data are for the mixture of isomers (see text). [e] In n-hexane. [f] Minor rotamer.



Scheme 1. (*i*) NEt_3; (*ii*) $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$

The ^1H n.m.r. spectrum of the product of the reaction between compound (**1**; allyl = $CH_2CHCHMe$) and $[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$ is more complex, showing the presence of three inseparable isomers. The two major components (total *ca.* 85%) comprise a diastereomeric pair (1 : 1 ratio), the linking of the C_8 ring to the CHMe terminus of the 1-methylallyl group [to form bond C(8)–C(9) (Scheme 1)] introducing the second chiral centre, at C(9) [in addition to that at C(8)]. The third isomer in the mixture has not been fully characterised, much of its ^1H n.m.r. spectrum being obscured by that of the diastereomeric pair. Nevertheless, a methyl resonance at δ 1.61 coupled (*J* 6 Hz) to a proton in the olefinic region (*ca.* δ 5.5) of the spectrum indicates an adduct in which C(8) is linked to the CH_2 end of the 1-methylallyl substituent.

Table 2. N.m.r. spectroscopic data[a] for complexes (**2**)—(**6**)

Complex	L	R	^{1}H(δ)[b]	^{13}C(p.p.m.)[c]
(**2**)	CO	$CH_2CH{=}CH_2$	2.40 [1 H, m, *J*(H^{9}H$^{9'}$) 15, *J*(H^{9}H^8) 9, H^9], 2.51 [1 H, m, *J*($^{9'}$H^9) 15, *J*(H$^{9'}$H^8) 8, H$^{9'}$], 4.12 (1 H, m, H^8), 4.29 [1 H, dd, *J*(H^{7}H^8) 9, *J*(H^{7}H^6) 9, H^7], 4.89 [1 H, dd, *J*(H^{3}H^2), 10, *J*(H^{3}H^4), 4, H^3], 4.98 [1 H, d, *J*(H$^{11'}$H^{10}) 8, H$^{11'}$], 5.1 (3 H, m, H^1, H^2, H^{11}], 5.58 [1 H, dd, *J*(H^{5}H^4) 8, *J*(H^{5}H^6) 2, H^5], 5.66 [2 H, m, H^4, H^{10}], 6.21 [1 H, dd, *J*(H^{6}H^7) 9, *J*(H^{6}H^5) 2, H^6][d,e]	35.8 (C^9), 40.6 (C^8), 56.4(C^7), 72.2 (C^1), 80.9 (C^3), 101.4 (C^2), 115.4 (C^6), 118.7 (C^{11}), 127.5 (C^{10}), 132.2, 133.0 (C^4, C^5), 184.0, 185.1, 190.5 (CO)[e,f]
	PPh_3	$CH_2CH{=}CH_2$	2.36 [2 H, m, *J*(H^{9}H$^{9'}$) 13.9, *J*(H^{9}H^{10}) 5.9, *J*(H^{9}H^8) 7.6, *J*(H$^{9'}$H^{10}) 6.6, *J*(H$^{9'}$H^8) 7.9, H^9, H$^{9'}$], 3.72 [2 H, ddd, *J*(H^{3}H^2) 11.7, *J*(H^{3}H^4) 3.9, *J*(^{31}PH^3) 2.4, H^3], 4.14 (3 H, m, H^2, H^7, H^8), 4.70 [1 H, dd, *J*(H^{1}H^8) 8.3, *J*(H^{1}H^2) 8.3, H^1], 5.02 [1 H, dd, *J*(H^{11}H^{10}) 17.0, *J*(H^{11}H$^{11'}$) 1.7, H^{11}], 5.09 [1 H, dd, *J*(H$^{11'}$H^{10}) 10.0, *J*($^{11'}$H^{11}) 2.0, H$^{11'}$], 5.51 (2 H, m, H^4, H^5), 5.71 [1 H, dddd, *J*(H^{10}H^{11}) 17.1, *J*(H^{10}H$^{11'}$) 10.0, *J*(H^{10}H^9) = *J*(H^{10}H$^{9'}$) 6.8, H^{10}], 5.99 [1 H, br d, *J*(H^{6}H^7) 8.5, H^6], 7.50 (15 H, m, PPh$_3$)[d,e]	36.6 (C^9), 41.2 (C^8), 57.5 (C^7), 74.5 [d, *J*(CP) 2.1, C^1], 78.3 [d, *J*(CP) 4.3, C^3], 104.4 (C^2), 112.9 [d, *J*(CP) 8.6, C^6], 118.2 (C^{11}), 127.0, 128.3 (C^4, C^5), 129.1 (C^{10}), 130.1 [d, *J*(CP) 10.7, PPh$_3$], 132.9 (PPh$_3$), 133.3 [d, *J*(CP) 10.8, PPh$_3$], 193.5 [d, *J*(CP) 14.0, CO], 198.8 [d, *J*(CP) 11.9, CO][e]
	PPh_3	$CH_2C(Me){=}CH_2$	1.76 (3 H, s, Me), 2.33 [2 H, m, *J*(H^{9}H$^{9'}$) 15, H^9, H$^{9'}$], 3.72 [1 H, m, *J*(H^{3}H^2) 9, H^3], 4.06 [1 H, ddd, *J*(H^{2}H^3) 9, *J*(H^{2}H^1) 8, *J*(H^{2}H^8) 4.5, H^2], 4.28 (2 H, m, H^7, H^8), 4.62 (1 H, s, H^{11}), 4.69 [1 H, dd, *J*(H^{1}H^2) 8, *J*(H^{1}H^8) 8, H^1], 4.82 (1 H, s, H$^{11'}$), 5.51 (2 H, m, H^4, H^5), 5.97 (1 H, m, br, H^6), 7.5 (15 H, m, PPh$_3$)[d,e]	21.3 (Me), 34.3 (C^9), 44.0 (C^8), 56.5 (C^7), 73.3 (C^1), 77.6 [d, *J*(CP) 4, C^3], 103.3 (C^2), 111.4 [d, *J*(CP) 8, C^6], 112.3 (C^{11}), 125.9, 132.5 (C^4, C^5), 127.4 [d, *J*(C^{α}P) 47, C^α(PPh$_3$)], 128.8 [d, *J*(CP) 11, PPh$_3$], 131.7 [d, *J*(CP) 3, PPh$_3$], 132.2 [d, *J*(CP) 11, PPh$_3$], 139.9 (C^{10}), 192.3 [d, *J*(CP) 12, CO], 197.6 [d, *J*(CP) 14, CO][e,f]
	PPh_3	$CH(Me)CH{=}CH_2$[g]	0.81 [3 H, d, *J*(MeH^9) 7, Me], 2.40 (1 H, m, H^9), 3.70 (2 H, m, H^2, H^8), 4.20 (2 H, m, H^3, H^7), 4.58 [1 H, dd, *J*(H^{1}H^2) 9, *J*(H^{1}H^8) 8, H^1], 5.02 (1 H, m, H^{11}), 5.14 [1 H, dd, *J*(H$^{11'}$H^{10}) 10, *J*(H$^{11'}$H^{11}) 1, H$^{11'}$], 5.47 (2 H, m, H^4, H^5), 5.75 (1 H, m, H^{10}), 5.93 [1 H, d, br, *J*(H^{6}H^7) 8, H^6], 7.6—7.8 (15 H, m, PPh$_3$)[d,e,h]	14.7 (Me), 37.2 (C^9), 42.9 (C^8), 57.1 (C^7), 74.3 (C^1), 78.6 [d, *J*(CP) 4, C^3], 104.0 (C^2), 111.7 [d, *J*(CP) 9, C^6], 116.3 (C^{11}), 126.6, 128.2 (C^4, C^5), 130.0 [d, *J*(CP) 11, PPh$_3$], 132.9 (PPh$_3$), 133.2 [d, *J*(CP) 11, PPh$_3$], 138.4 (C^{10}), 193.4 [d, *J*(CP) 12, CO], 198.8 [d, *J*(CP) 14, CO][e,h,i]
			1.11 [3 H, d, *J*(MeH^9) 7], 2.40 (1 H, m, H^9), 3.70 (2 H, m, H^2, H^8), 4.20 (2 H, m, H^3, H^7), 4.69 [1 H, dd, *J*(H^{1}H^2) 9, *J*(H^{1}H^8) 8, H^1], 4.89 [1 H, m, *J*(H^{11}H^{10}) 13, H^{11}], 5.02 (1 H, m, H$^{11'}$), 5.47 (2 H, m, H^4, H^5), 5.75 (1 H, m, H^{10}), 6.03 [1 H, d, br, *J*(H^{6}H^7) 8, H^6], 7.6—7.8 (15 H, m, PPh$_3$)[d,e,j]	17.5 (Me), 40.1 (C^9), 44.2 (C^8), 57.8 (C^7), 74.7 (C^1), 78.8 [d, *J*(CP) 4, C^3], 104.4 (C^2), 111.8 [d, *J*(CP) 9, C^6], 117.0 (C^{11}), 127.1, 129.3 (C^4, C^5), 130.0 [d, *J*(CP) 11, PPh$_3$], 132.9 (PPh$_3$), 133.2 [d, *J*(CP) 11, PPh$_3$], 140.1 (C^{10}), 193.4 [d, *J*(CP) 12, CO], 198.8 [d, *J*(CP) 14, CO][d,e,f]
(**3**)	CNBu^t	$CH_2CH{=}CH_2$[g]	1.52 (9 H, s, CNBu^t), 2.30 (1 H, m, H^9), 2.60 (1 H, m, H$^{9'}$), 3.35 (1 H, m, br, H^8), 4.25 [1 H, dd, *J*(H^{1}H^2) 11.0, *J*(H^{1}H^8) 5.9, H^1], 4.31 (1 H, m, H^5), 5.11 (2 H, m, H^{11}, H$^{11'}$), 5.43 (1 H, m, H^{10}), 5.73 [1 H, dd, *J*(H^{7}H^6) 11.2, *J*(H^{7}H^8) 8.3, H^7], 5.87 [1 H, dd, *J*(H^{6}H^7) 11.3, *J*(H^{6}H^5) 6.9, H^6], 6.05 (2 H, m, H^2, H^4), 7.21 [1 H, t, *J*(H^{3}H^2) = *J*(H^{3}H^4) 7.2, H^3][k,l,m]	29.5 (CNC*Me*$_3$), 39.1 (C^9), 41.7 (C^8), 60.9 (CN*C*Me$_3$), 66.1 (C^5), 73.4 (C^1), 92.8 (C^4), 99.8 (C^2), 106.4 (C^3), 119.5 (C^{11}), 121.7 (C^7), 132.7 (C^6), 135.7 (C^{10}), 139.1 [t, *J*(^{13}C^{14}N) 20.5, *C*NCMe$_3$], 203.8 (CO), 212.4 (CO′)[l,m,n]
			1.56 (9 H, s, CNBu^t), 2.30 (1 H, m, H^9), 2.60 (1 H, m, H$^{9'}$), 3.35 (1 H, m, br, H^8), 4.31 (2 H, m, H^1, H^5), 5.11 (2 H, m, H^{11}, H$^{11'}$), 5.43 (1 H, m, H^{10}), 5.72 [1 H, dd, *J*(H^{7}H^6) 11.2, *J*(H^{7}H^8) 8.3, H^7], 5.86 [1 H, dd, *J*(H^{6}H^7) 11.1, *J*(H^{6}H^5) 7.1, H^6], 6.05 (2 H, m, H^2, H^4), 7.23 [1 H, t, *J*(H^{3}H^2) = *J*(H^{3}H^4) 7.1, H^3][k,l,o]	29.5 (CNC*Me*$_3$), 38.8 (C^9), 42.0 (C^8), 60.9 (CN*C*Me$_3$), 66.8 (C^5), 72.1 (C^1), 95.8 (C^4), 103.1 (C^2), 106.6 (C^3), 119.6 (C^{11}), 122.3 (C^7), 132.1 (C^6), 135.6 (C^{10}), 139.3 [t, *J*(^{13}C^{14}N) 20.5, *C*NCMe$_3$], 203.2 (CO), 212.3 (CO′)[k,n,o]
(**4**)	CNBu^t	$CH_2CH{=}CH_2$[g]	1.44 (9 H, s, CNBu^t), 2.78 (1 H, m, H^1 or H^7), 2.90 (1 H, m, H^1 or H^7), 5.00 (2 H, m, H^{11}, H$^{11'}$), 5.43 (1 H, m, H^{10}), 5.64 (2 H, m, H^3, H^5), 8.10 [1 H, t, *J*(H^{4}H^3) = *J*(H^{4}H^5) 6.1, H^4][k,l]	27.5 (C^9), 29.5 (CNC*Me*$_3$), 38.1, 39.8 (C^1, C^7), 60.8 (C^8), 95.9, 97.7, 98.2, 98.7, 104.7 (C^2, C^3, C^4, C^5, C^6), 116.2 (C^{11}), 136.9 (C^{10}), 202.5 (CO), 216.6 (CO′)[k,n]
(**3**)	CNBu^t	$CH_2C(Me){=}CH_2$[g]	1.52 (9 H, s, CNBu^t), 1.69 (3 H, s, br, Me), 2.22 (2 H, m, H^9, H$^{9'}$), 3.33 (1 H, m, br, H^8), 4.29 [1 H, dd, *J*(H^{1}H^2), 10.8, *J*(H^{1}H^8) 6.2, H^1], 4.38 (1 H, m, H^5), 4.77 (1 H, s, H^{11}), 4.90 (1 H, s, br, H$^{11'}$), 5.75 (1 H, m, H^7), 5.86 [1 H, m, *J*(H^{6}H^7) 11.3, *J*(H^{6}H^5) 7.1, H^6], 6.09 [2 H, m, *J*(H^{2}H^1) = *J*(H^{4}H^5) 10.1, H^2, H^4], 7.24 [1 H, t, *J*(H^{3}H^2) = *J*(H^{3}H^4) 7.1, H^3][k,l,m]	21.9 (Me), 29.5 (CNC*Me*$_3$), 37.3 (C^9), 47.7 (C^8), 61.0 (CN*C*Me$_3$), 66.7 (C^5), 74.7 (C^1), 93.2 (C^4), 102.2 (C^2), 106.8 (C^3), 115.4 (C^{11}), 120.7 (C^7), 133.2 (C^6), 143.5 (C^{10}), 203.6 (CO)[k,l,p]

Table 2 (*continued*)

Complex	L	R	^{1}H(δ)[b]	^{13}C(p.p.m.)[c]
			1.56 (9 H, s, CNBu^t), 1.69 (3 H, s, br, Me), 2.22 (2 H, m, H^9, H$^{9'}$), 3.33 (1 H, m, br, H^8), 4.38 (2 H, m, H^1, H^5), 4.80 (1 H, s, H^{11}), 4.90 (1 H, s, br, H$^{11'}$), 5.75 (1 H, m, H^7), 5.86 (1 H, m, H^6), 6.09 (2 H, m, H^2, H^4), 7.25 [1 H, t, *J*(H^{3}H^2) = *J*(H^{3}H^4) 7.1, H^3][k,l,o]	22.8 (Me), 29.5 (CNC*Me*$_3$), 37.1 (C^9), 47.8 (C^8), 61.0 (CN*C*Me$_3$), 67.4 (C^5), 73.3 (C^1), 94.8 (C^4), 100.2 (C^2), 106.9 (C^3), 115.5 (C^{11}), 120.9 (C^7), 132.9 (C^6), 143.3 (C^{10}), 203.2 (CO)[k,l,o,p]
(4)	CNBu^t	CH$_2$C(Me)=CH$_2$[g]	1.45 (9 H, s, CNBu^t), 2.46 (2 H, m, H^9, H$^{9'}$), 2.81 (1 H, m, H^1 or H^7), 2.93 (1 H, m, H^1 or H^7), 4.65 (1 H, s, H^{11}), 4.72 (1 H, s, H$^{11'}$), 5.09 (2 H, m, H^2, H^6), 5.64 (2 H, m, H^3, H^5), 8.10 [1 H, t, *J*(H^{4}H^3) = *J*(H^{4}H^5) 6.1, H^4][k,l]	22.9 (Me), 29.5 (CNC*Me*$_3$), 38.2, 40.1 (C^1, C^7), 60.7 (C^8), 95.8, 97.6, 98.3, 98.9, 104.8 (C^2, C^3, C^4, C^5, C^6), 111.5 (C^{11}), 144.6 (C^{10}), 216.6 (CO′)[k,l,p]
(3)	CNBu^t	CH(Me)CH=CH$_2$[d,g]	0.95 [d, *J*(MeH^9) 6.6, Me],[h] 0.99 [d, *J*(MeH^9) 6.2, Me],[j] 1.51 (9 H, s, br, CNBu^t), 2.71 (1 H, br, H^9), 3.24 (1 H, m, br, H^8), 4.15 (2 H, br, H^1, H^5), 5.08 (2 H, m, H^{11}, H$^{11'}$), 5.55 (1 H, m, H^{10}), 5.78 (4 H, m, H^2, H^4, H^6, H^7), 7.03 (1 H, m, br, H^3)[q]	*r*
	CNBu^t	CH$_2$CH=CHMe[d,g]	1.65 [3 H, d, *J*(MeH^{11}) 6.2, Me], 2.22 (1 H, m, H^9), 2.44 (1 H, m, br, H$^{9'}$), 5.55 (2 H, m, H^{10}, H^{11})[q]	
(5) M = Ru	PPh$_3$	CH$_2$C(Me)=CH$_2$	1.57 (3 H, s, Me), 2.67 [2 H, s, br, H^9, H$^{9'}$], 4.52 [2 H, d, *J*(H^{1}H^2), *J*(H^{7}H^6) 10, H^1, H^7], 4.71 (2 H, s, br, H^{11}, H$^{11'}$), 5.00 [2 H, dt, *J*(H^{2}H^1), *J*(H^{2}H^3), *J*(H^{6}H^7), *J*(H^{6}H^5) 10, *J*(H^{2}P), *J*(H^{6}P) 2, H^2, H^6], 5.30 [1 H, dd, *J*(H^{4}H^3), *J*(H^{4}H^5) 10, H^4], 5.58 [2 H, dd, *J*(H^{3}H^4), *J*(H^{3}H^2), *J*(H^{5}H^4), *J*(H^{5}H^6) 10, H^3, H^5], 6.96 (9 H, m, PPh$_3$), 7.53 (6 H, m, PPh$_3$)[d,s]	22.2 (Me), 51.7 (C^9), 82.0 (C^1, C^7), 91.6 (C^2, C^6), 106.8 (C^8), 111.9 (C^{11}), 114.2 (C^3, C^5), 114.7 (C^4), 127.6 (PPh$_3$), 129.9 (PPh$_3$), 133.6 [d, *J*(CP) 11, PPh$_3$], 136.1 [d, *J*(C$^\alpha$P) 43, C$^\alpha$(PPh$_3$)], 145.9 (C^{10}), 205.0 [d, *J*(CP) 11, CO][i,s]
(5) M = Fe	CNBu^t	CH$_2$CH=CH$_2$	0.80 (9 H, s, CNBu^t), 2.57 [2 H, dt, *J*(H^{9}H^{10}) = *J*(H$^{9'}$H^{10}) 6.6, H^9, H$^{9'}$], 4.36 [2 H, d, *J*(H^{1}H^2) = *J*(H^{7}H^6) 9.9, H^1, H^7], 4.93 [1 H, ddt, *J*(H$^{11'}$H^{10}) 10.3, *J*(H$^{11'}$H^{11}) 2.0, *J*(H$^{11'}$H^9) = *J*(H$^{11'}$H$^{9'}$) 1.3, H$^{11'}$], 4.95 [1 H, ddt, *J*(H^{11}H^{10}) 17.0, *J*(H^{11}H$^{11'}$) 1.8, *J*(H^{11}H^9) = *J*(H^{11}H$^{9'}$) 1.7, H^{11}], 5.12 [2 H, t, *J*(H^{2}H^1) = *J*(H^{2}H^3) = *J*(H^{6}H^5) = *J*(H^{6}H^7) 10.4, H^2, H^6], 5.52 [1 H, t, *J*(H^{4}H^3) = *J*(H^{4}H^5) 10.0, H^4], 5.72 [1 H, ddt, *J*(H^{10}H^{11}) 17.0, *J*(H^{10}H$^{11'}$) 10.2, *J*(H^{10}H^9) = *J*(H^{10}H$^{9'}$) 6.7, H^{10}], 5.78 [2 H, t, *J*(H^{3}H^2) = *J*(H^{3}H^4) = *J*(H^{5}H^4) = *J*(H^{5}H^6) 10.3, H^3, H^5][s]	30.4 (CNC*Me*$_3$), 46.2 (C^9), 55.6 (CN*C*Me$_3$), 81.2 (C^1, C^7), 94.9 (C^2, C^6), 109.2 (C^4), 112.0 (C^8), 116.5 (C^{11}), 117.4 (C^3, C^5), 137.0 (C^{10}), 161.3 (*C*NCMe$_3$), 217.6 (CO)[s]
	CNBu^t	CH$_2$C(Me)=CH$_2$	0.81 (9 H, s, CNBu^t), 1.60 (3 H, s, Me), 2.53 (2 H, s, H^9, H$^{9'}$), 4.41 [2 H, d, *J*(H^{1}H^2) = *J*(H^{7}H^6) 10.0, H^1, H^7], 4.75 (2 H, s, br, H^{11}, H$^{11'}$), 5.12 [2 H, t, *J*(H^{2}H^1) = *J*(H^{2}H^3) = *J*(H^{6}H^5) = *J*(H^{6}H^7) 10.4, H^2, H^6], 5.49 [1 H, t, *J*(H^{4}H^3) = *J*(H^{4}H^5) 9.9, H^4], 5.77 [2 H, t, *J*(H^{3}H^2) = *J*(H^{3}H^4) = *J*(H^{5}H^4) = *J*(H^{5}H^6) 10.0, H^3, H^5][d,s]	22.3 (Me), 30.4 (CN*Me*$_3$), 51.6 (C^9), 82.2 (C^1, C^7), 94.9 (C^2, C^6), 108.6 (C^4, C^8), 112.1 (C^{11}), 116.9 (C^3, C^5), 145.5 (C^{10}), 217.5 (CO)[f,s]
	CNBu^t	CH(Me)CH=CH$_2$[g]	0.82 (9 H, s, CNBu^t), 1.06 [3 H, d, *J*(MeH^9) 7.0, Me], 2.56 (1 H, m, H^9), 4.24 [1 H, d, *J*(H^{1}H^2) or *J*(H^{7}H^6), 9.2, H^1 or H^7], 4.27 [1 H, d, *J*(H^{1}H^2) or *J*(H^{7}H^6) 9.5, H^1 or H^7], 4.95 [1 H, dt, *J*(H^{11}H^{10}) 10.5, *J*(H$^{11'}$H^{11}) = *J*(H$^{11'}$H^9) 1.6, H$^{11'}$], 4.97 [1 H, t, *J*(H^{2}H^1) = *J*(H^{2}H^3) or *J*(H^{6}H^5) = *J*(H^{6}H^7) 10.7, H^2 or H^6], 4.99 [1 H, dt, *J*(H^{11}H^{10}) 17.2, *J*(H^{11}H$^{11'}$) = *J*(H^{11}H^9) 1.7, H^{11}], 5.33 [1 H, t, *J*(H^{2}H^1) = *J*(H^{2}H^3) or *J*(H^{6}H^5) = *J*(H^{6}H^7) 10.6, H^2 or H^6], 5.62 [1 H, t, *J*(H^{4}H^3) = *J*(H^{4}H^5) 10.3, H^4], 5.77 [1 H, ddd, *J*(H^{10}H^{11}) 17.4, *J*(H^{10}H$^{11'}$) 10.4, *J*(H^{10}H^9) 6.1, H^{10}], 5.86 [1 H, t, *J*(H^{3}H^2) = *J*(H^{3}H^4) or *J*(H^{5}H^4) = *J*(H^{5}H^6) 10.4, H^3 or H^5], 5.89 [1 H, t, *J*(H^{3}H^2) = *J*(H^{3}H^4) or *J*(H^{5}H^4) = *J*(H^{5}H^6) 10.5, H^3 or H^5]	19.9 (Me), 30.9 (CNC*Me*$_3$), 47.8 (C^9), 55.0 (CN*C*Me$_3$), 79.3, 80.2 (C^1, C^7), 95.0, 98.3 (C^2, C^6), 112.5 (C^4), 114.6 (C^{11}), 116.6 (C^8), 119.0, 119.7 (C^3, C^5), 142.6 (C^{10}), 217.7 (CO)[k]
	CNBu^t	CH$_2$CH=CHMe[g]	0.82 (9 H, s, br, CNBu^t), 1.50 [3 H, d, *J*(MeH^{11}) 4.8, Me], 2.56 (2 H, m, H^9, H$^{9'}$), 4.37 [2 H, d,	18.1 (Me), 30.6 (CNC*Me*$_3$), 45.4 (C^9), 55.0 (CN*C*Me$_3$), 76.3 (C^1, C^7), 91.8 (C^2, C^6), 111.1

Table 2 (*continued*)

Complex	L	R	$^1H(\delta)^b$	^{13}C(p.p.m.)^c
			$J(H^1H^2) = J(H^7H^6)$ 9.9, H^1, H^7], 5.14 [2 H, t, $J(H^2H^1) = J(H^2H^3) = J(H^6H^5) = J(H^6H^7)$ 10.3, H^2, H^6], 5.36 (2 H, m, H^{10}, H^{11}), 5.58 [1 H, t, $J(H^4H^3) = J(H^4H^5)$ 10.1, H^4], 5.83 [2 H, t, $J(H^3H^2) = J(H^3H^4) = J(H^5H^4) = J(H^5H^6)$ 10.3, H^3, H^5]	(C^4), 112.7 (C^8), 120.6 (C^3, C^5), 127.5 (C^{11}), 130.5 (C^{10}), 217.9 (CO)$^{g\,k}$
(6)	$CNBu^t$	$CH_2C(Me){=}CH_2{}^t$	0.92 (9 H, s, $CNBu^t$), 1.68 (6 H, s, Me), 2.77 (4 H, s, H^9, $H^{9\prime}$), 4.65 (2 H, s, H^1, H^2), 4.81 (2 H, s, br, H^{11} or $H^{11\prime}$), 4.84 (2 H, s, br, H^{11} or $H^{11\prime}$), 4.93 [2 H, m, $J(H^6H^7) = J(H^4H^5)$ 11.3, $J(H^4H^6) = J(H^5H^7)$ −1.2, $J(H^4H^7)$ 0, H^4, H^7], 5.46 [2 H, m, $J(H^5H^6)$ 8.0, $J(H^6H^7) = J(H^4H^5)$ 11.3, $J(H^4H^6) = J(H^5H^7)$ −1.2, H^5, H^6]^{s,u}	22.1 (Me), 30.80 ($CNCMe_3$), 52.3 (C^9), 56.7 ($CNCMe_3$), 86.1 (C^1, C^2), 95.8 (C^4, C^7), 108.0 (C^5C^6), 112.0 (C^{11}), 117.6 (C^3, C^8), 145.6 (C^{10}), 162.4 ($CNCMe_3$), 216.7 (CO)^v
	$C_8H_6[CH_2C(Me){=}CH_2]_2$		1.65 (2.4 H, s, Me), 1.70 (3.6 H, s, Me), 2.66 (4 H, s, br, CH_2), 4.83 (4 H, s, br, $=CH_2$), 5.5—5.8 (6 H, m, CH)^s	22.33, 22.37 (Me) 47.39, 47.44, 47.50 (CH_2), 112.58, 112.61, 112.93 ($=CH_2$), 129.45, 129.93, 130.16, 132.68, 132.77, 132.85, 134.41, 134.78, 135.47, 142.61, 143.31, 143.46 (C_8H_6), 145.22, 145.69 (CMe)^w

[a] At room temperature unless stated otherwise. The atom numbering is as shown in Scheme 1. *J* values are in Hz. [b] 270-MHz Spectra unless stated otherwise. [c] 67.9-MHz Spectra unless stated otherwise. [d] 200-MHz Spectrum. [e] In CD_2Cl_2. [f] 22.5-MHz Spectrum. [g] The spectrum of each isomer has been taken from that of the mixture of isomers. [h] First diastereomer. [i] 50-MHz Spectrum. [j] Second diastereomer. [k] In $[^2H_6]$acetone. [l] At −35 °C. [m] First rotational isomer. [n] At −50 °C. [o] Second rotational isomer. [p] Other ^{13}CO signal obscured by solvent. [q] In CD_3NO_2. [r] Not measured. [s] In C_6D_6. [t] Data for the 1,4 isomer. [u] At 70 °C. [v] In $[^2H_8]$toluene, at 90 °C. [w] 100.5-MHz Spectrum in CD_3NO_2.

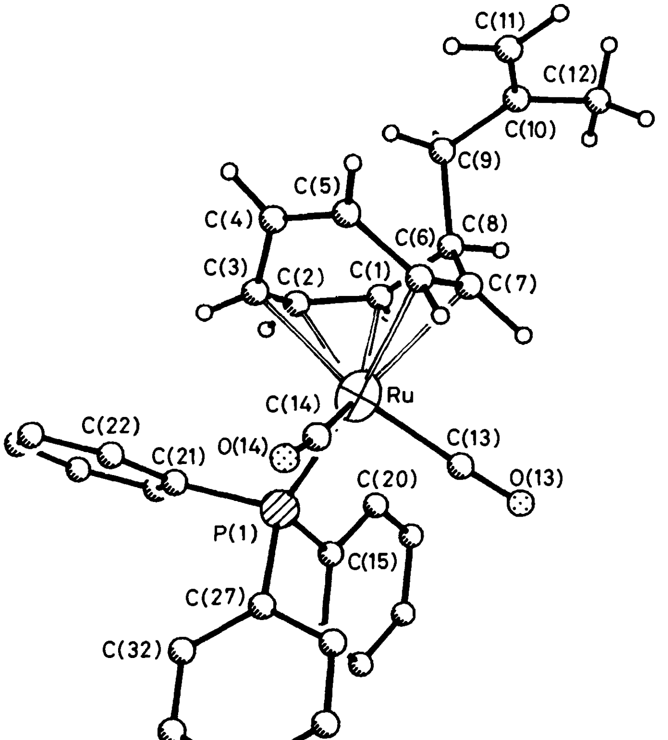


Figure 1. The molecular structure of the cation of [2; L = PPh_3, R = $CH_2C(Me){=}CH_2$] showing the atom labelling scheme. The ruthenium atom is represented as an ellipsoid enclosing 50% probability density; other atoms are represented as spheres of arbitrary radius

The ^{13}C n.m.r. spectrum is also consistent with the presence of three isomers. The diastereomerism noted above leads to the doubling of all the signals associated with the CHMe linked complex; the signals of the chiral carbon atoms, C(8) and C(9), show the greatest shift differences between the diastereomers [*i.e.* C(9), 37.2 and 40.1 p.p.m.; C(8), 42.9 and 44.2 p.p.m.; *cf.* C(2), 104.0 and 104.4 p.p.m.].

Although the η^2,η^3 bonding of the cyclo-octatrienyl ligand to the metal is apparent from the n.m.r. spectra, the stereochemistry of allyl addition (*i.e. exo* or *endo*) to C(8) could not be determined. An *X*-ray structural analysis of [2; L = PPh_3, R = $CH_2C(Me){=}CH_2$] was therefore carried out.

The geometry of the cation $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_8R)]^+$ [R = $CH_2C(Me){=}CH_2$] is shown in Figure 1 and derived bond lengths and selected bond angles for the unconstrained atoms of the cation are listed in Table 3. The *exo* site of addition of the 2-methylallyl substituent on the C_8 ring [at C(8)] is apparent from Figure 1. The η^2,η^3 co-ordination of the cyclo-octatrienyl ligand is likewise clear. The co-ordination sphere at ruthenium is completed by a PPh_3 ligand *trans* to the η^2-alkene of the C_8 ring, and two carbonyl ligands which lie transoid to the η^3-allyl function of the cyclo-octatrienyl.

Examples of η^2,η^3-co-ordinated cyclo-octatrienyl ligands are known (see, for example, ref. 6). As in other cases, the η^3-allyl function binds to ruthenium in an asymmetric manner in [2; L = PPh_3, R = $CH_2C(Me){=}CH_2$] with Ru–C(1) longer [2.336(6) Å] than Ru–C(2) and Ru–C(3) [2.210(6) and 2.232(6) Å respectively]. The source of this asymmetry may be traced to the conformation of the C_8 ring in these species, which is derived from the tub conformation preferred by η^2,η^2-co-ordinated cyclo-octatetraene by contraction of the Ru–C(1) distance to bonding dimensions.

The ^1H and ^{13}C n.m.r. spectra of the cationic products formed from compound (1) and $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$ again show the formation of mixtures, but this time of isomers with the formula $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_8R)]^+$ and containing cyclo-octatrienyl (3) or bicyclo[5.1.0]octadienyl (4) rings (in *ca.* 5:1 to 10:1 ratios) (Scheme 1).

The room-temperature ^1H n.m.r. spectrum of $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_8R)]^+$ (R = $CH_2CH{=}CH_2$) shows broad unresolved peaks for the ring protons but sharp signals for the protons of the allyl substituent. A fluxional process of the type observed for $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_7H_9)]^+$ [7] and $[Fe(CO)_2L(\eta^5\text{-dienyl})]^+$ (L = 4-ethyl-1-phospha-2,6,7-trioxabicyclo[2.2.2]octane; dienyl = cyclohexadienyl or cycloheptadienyl),[8]

Table 3. Bond lengths (Å) and angles (°) for compound [**2**; L = PPh_3, R = $CH_2C(Me){=}CH_2$]$\cdot0.5CH_2Cl_2$

Ru–C(1)	2.336(6)	Ru–C(2)	2.210(6)	C(10)–C(12)	1.501(16)	C(13)–O(13)	1.117(7)
Ru–C(3)	2.232(6)	Ru–C(6)	2.420(7)	C(14)–O(14)	1.130(9)	P(1)–C(15)	1.838(5)
Ru–C(7)	2.393(7)	Ru–C(13)	1.941(5)	P(1)–C(21)	1.811(6)	P(1)–C(27)	1.833(6)
Ru–C(14)	1.912(7)	Ru–P(1)	2.363(2)	C(15)–C(16)	1.387(8)	C(15)–C(20)	1.382(9)
C(1)–C(2)	1.367(9)	C(1)–C(8)	1.499(10)	C(16)–C(17)	1.370(9)	C(17)–C(18)	1.371(11)
C(1)–H(1)	0.876(43)	C(2)–C(3)	1.413(9)	C(18)–C(19)	1.376(10)	C(19)–C(20)	1.391(9)
C(2)–H(2)	0.886(37)	C(3)–C(4)	1.463(10)	C(21)–C(22)	1.394(9)	C(21)–C(26)	1.379(9)
C(3)–H(3)	0.840(61)	C(4)–C(5)	1.306(11)	C(22)–C(23)	1.374(9)	C(23)–C(24)	1.383(14)
C(5)–C(6)	1.448(10)	C(6)–C(7)	1.356(9)	C(24)–C(25)	1.369(14)	C(25)–C(26)	1.403(10)
C(6)–H(6)	0.968(55)	C(7)–C(8)	1.501(9)	C(27)–C(28)	1.380(9)	C(27)–C(32)	1.394(9)
C(7)–H(7)	1.118(54)	C(8)–C(9)	1.508(10)	C(28)–C(29)	1.368(10)	C(29)–C(30)	1.384(12)
C(9)–C(10)	1.494(12)	C(10)–C(11)	1.283(14)	C(30)–C(31)	1.364(11)	C(31)–C(32)	1.383(10)

C(1)–Ru–C(2)	34.9(2)	C(1)–Ru–C(3)	66.3(2)	C(1)–C(2)–H(2)	115.4(25)	C(3)–C(2)–H(2)	114.8(26)
C(2)–Ru–C(3)	37.1(2)	C(1)–Ru–C(6)	82.9(2)	Ru–C(3)–C(2)	70.6(3)	Ru–C(3)–C(4)	110.6(4)
C(2)–Ru–C(6)	92.5(2)	C(3)–Ru–C(6)	76.3(2)	C(2)–C(3)–C(4)	125.9(6)	Ru–C(3)–H(3)	112.1(39)
C(1)–Ru–C(7)	60.6(2)	C(2)–Ru–C(7)	85.4(2)	C(2)–C(3)–H(3)	112.6(41)	C(4)–C(3)–H(3)	115.6(41)
C(3)–Ru–C(7)	89.5(2)	C(6)–Ru–C(7)	32.7(2)	C(3)–C(4)–C(5)	124.0(7)	C(4)–C(5)–C(6)	121.3(7)
C(1)–Ru–C(13)	98.2(2)	C(2)–Ru–C(13)	129.1(2)	Ru–C(6)–C(5)	106.1(5)	Ru–C(6)–C(7)	72.6(4)
C(3)–Ru–C(13)	164.3(2)	C(6)–Ru–C(13)	100.7(2)	C(5)–C(6)–C(7)	124.9(6)	Ru–C(6)–H(6)	97.0(32)
C(7)–Ru–C(13)	80.6(2)	C(1)–Ru–C(14)	154.3(3)	C(5)–C(6)–H(6)	119.5(33)	C(7)–C(6)–H(6)	115.2(33)
C(2)–Ru–C(14)	127.9(2)	C(3)–Ru–C(14)	91.7(3)	Ru–C(7)–C(6)	74.7(4)	Ru–C(7)–C(8)	95.8(4)
C(6)–Ru–C(14)	79.1(3)	C(7)–Ru–C(14)	108.6(3)	C(6)–C(7)–C(8)	127.8(6)	Ru–C(7)–H(7)	92.7(33)
C(13)–Ru–C(14)	102.9(3)	C(1)–Ru–P(1)	107.7(2)	C(6)–C(7)–H(7)	110.6(33)	C(8)–C(7)–H(7)	121.1(33)
C(2)–Ru–P(1)	91.6(2)	C(3)–Ru–P(1)	99.5(2)	C(1)–C(8)–C(7)	105.4(6)	C(1)–C(8)–C(9)	116.4(6)
C(6)–Ru–P(1)	166.3(2)	C(7)–Ru–P(1)	160.9(2)	C(7)–C(8)–C(9)	118.4(6)	C(8)–C(9)–C(10)	114.9(6)
C(13)–Ru–P(1)	86.8(2)	C(14)–Ru–P(1)	88.1(2)	C(9)–C(10)–C(11)	120.3(10)	C(9)–C(10)–C(12)	117.6(8)
Ru–C(1)–C(2)	67.5(4)	Ru–C(1)–C(8)	98.2(4)	C(11)–C(10)–C(12)	122.1(11)	Ru–C(13)–O(13)	176.6(5)
C(2)–C(1)–C(8)	130.2(6)	Ru–C(1)–H(1)	120.5(28)	Ru–C(14)–O(14)	174.6(6)	Ru–P(1)–C(15)	115.2(2)
C(2)–C(1)–H(1)	111.7(29)	C(8)–C(1)–H(1)	116.1(30)	Ru–P(1)–C(21)	115.9(2)	C(15)–P(1)–C(21)	105.1(3)
Ru–C(2)–C(1)	77.6(4)	Ru–C(2)–C(3)	72.3(3)	Ru–P(1)–C(27)	113.3(2)	C(15)–P(1)–C(27)	101.7(3)
C(1)–C(2)–C(3)	128.0(6)	Ru–C(2)–H(2)	111.2(24)	C(21)–P(1)–C(27)	104.1(3)		

namely rotation of the $Fe(CO)_2(CNBu^t)$ group relative to the η^5-hydrocarbon ligand, is implied.

When the sample was cooled to −35 °C the rotational process was slowed sufficiently so that the n.m.r. spectra of the individual isomers (rotational and structural) became apparent. The major structural isomer (**3**; R = $CH_2CH{=}CH_2$), *i.e.* that containing the η^5-cyclo-octatrienyl ring, exists as an approximate 1:1 mixture of the two rotamers shown in Scheme 1; the ring structure was determined with the aid of homonuclear decoupling experiments and the chemical shifts and coupling constants given in Table 2 are in close agreement with those for the η^5-cyclo-octatrienyl complexes $[Fe(CO)_3(\eta^5\text{-}C_8H_8R)]^+$ (R = H[9] or CPh_3[10]). Most of the ^1H n.m.r. spectrum of (**4**; R = $CH_2CH{=}CH_2$) is obscured by that of the cyclo-octatrienyl isomer but a low-field triplet resonance, at δ 8.10, may be assigned to the central dienyl proton (H^4) of a bicyclo-[5.1.0]octadienyl ligand {*cf.* δ 7.82 for $[Fe(CO)_3(\eta^5\text{-}C_8H_9)]^+$[9] and δ 7.68 for $[Fe_2(CO)_6(\eta^5{:}\eta^{5\prime}\text{-}C_{16}H_{16})]^{2+}$}.[11]

The structures of compounds (**3**) and (**4**) were confirmed by the ^{13}C n.m.r. spectrum of the mixture at −50 °C. The signals due to the hydrocarbon framework of (**3**) are again doubled up due to the presence of two rotamers, and the chemical shifts are again in close agreement with those of $[Fe(CO)_3(\eta^5\text{-}C_8H_8CPh_3)]^+$.[10] In addition, two apical* (*i.e.* CO′ in Scheme 1; 212.3 and 212.4 p.p.m.) and two 'basal' (*i.e.* CO in Scheme 1; 203.2 and 203.8 p.p.m.) carbonyl resonances are observed at low field, one each for the two rotamers (R = $CH_2CH{=}CH_2$), together with two *C*NBu^t signals each split into a triplet (*J* = 20.5 Hz) by coupling to the isocyanide nitrogen atom. These carbonyl and isocyanide carbon shifts are closely similar to those of $[Fe(CO)_2(CNMe)(\eta^5\text{-}C_7H_9)]^+$[7] which, at −52 °C, adopts a configuration in which the isocyanide is 'basal'.

The ^{13}C n.m.r. spectrum of compound (**4**; R = $CH_2CH{=}CH_2$) was fully assigned by comparison with that of $[Fe(CO)_2(CNMe)(\eta^5\text{-}C_8H_9)]^+$[7] which also contains the bicyclo[5.1.0]octadienyl framework. Complex (**4**; R = $CH_2CH{=}CH_2$) exhibits one 'apical' and one 'basal' carbonyl signal at low temperature due to the enantiomeric pair of preferred rotamers shown in Scheme 1.

The reaction between $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$ and [**1**; R = $CH_2C(Me)CH_2$] gives a similar mixture of monocyclic [**3**; R = $CH_2C(Me){=}CH_2$] and bicyclic [**4**; R = $CH_2C(Me){=}CH_2$] isomers; the various spectroscopic data are given in Table 2. With (**1**; R = $CH_2CHCHMe$), however, the reaction is more complex in that, as in the case of ruthenium described above, the allyl substituent may bind *via* either the CHMe (giving diastereomers) or CH_2 terminus. The ^1H n.m.r. spectrum shows the presence of the cyclo-octatrienyl and bicyclo[5.1.0]-octadienyl isomers in an approximate 7:1 ratio with the ratio of CHMe to CH_2 bonded isomers *ca.* 2:1. The low-temperature spectra were impossible to assign (due to the complexities noted above, compounded by rotamerism). At room temperature, however, the three η^5-cyclo-octatrienyl isomers were distinguishable, most readily by the methyl(allyl) resonances at δ 0.95 and 0.99 [coupled to H(9) by 6.6 and 6.2 Hz respectively] for the CHMe bonded diastereomers (**3**; R = $CHMeCH{=}CH_2$), and at δ 1.65 [coupled to H(11) by 6.2 Hz] for the CH_2 bonded isomers (**3**; R = $CH_2CH{=}CHMe$).

The initial steps in the formation of complexes (**2**)—(**4**) are no doubt similar to those discussed for the reactions between (**1**) and $[Co(\eta^4\text{-cot})(\eta\text{-}C_5R_5)]$ (R = H or Me).[13] The ensuing C_8-ring transformations largely follow established patterns de-

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* Following the notation used in ref. 12, the complexes may be regarded as having square pyramidal structures with one carbonyl ligand in the apical site, and the dienyl (occupying two positions), second carbonyl, and isocyanide ligands in the four basal sites.

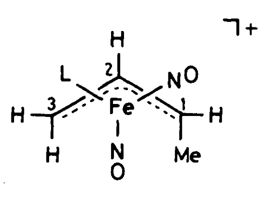

Figure 2. L = $P(OMe)_3$

duced for reactions of iron- and ruthenium-co-ordinated cot with other electrophiles. Thus, for example, the protonation of $[Ru(CO)_2(PPh_3)(\eta^4\text{-cot})]$ gives $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_9)]^+$ [14] whereas the same reaction with $[Fe(CO)_3(\eta^4\text{-}C_8H_7R)]$ (R = H or Me) yields the η^5-bicyclo[5.1.0]octadienyl cation $[Fe(CO)_3(\eta^5\text{-}C_8H_8R)]^+$ *via* the η^5-cyclo-octatrienyl isomer.[9] These observed preferences, of iron and ruthenium for the various C_8H_9 isomers, have been rationalised by molecular orbital (m.o.) studies,[15] and ascribed to the affinity of iron for conjugated dienyls and the ability of 4*d* and 5*d* metals to form more stable η^2,σ-alkyls.

The reactions between compound (**1**) and $[M(CO)_2L(\eta^4\text{-cot})]$, described above in terms of electrophilic attack at the co-ordinated cot, may also be visualised as involving nucleophilic attack of the cot ligand on the allyl group of (**1**). In all cases, the reactions occur exclusively at a terminal carbon atom of the C_3 fragment, as observed for the majority of nucleophilic additions to π-allyl ligands.[16]

As described above, nucleophilic addition to (**1**; allyl = $CH_2CHCHMe$) by both the iron and ruthenium cot complexes $[M(CO)_2L(\eta^4\text{-cot})]$ occurs preferentially to give CHMe bonded products with regiospecificity, over the CH_2 bonded isomers, of the order of 5:1 to 10:1. This preference, for attack at the substituted carbon atom of the allyl group, contrasts with the regiochemistry generally observed for palladium,[1] and also for $[Fe(CO)_4(\eta^3\text{-}CH_2CHCHMe)]^+$ [2] and $[Fe(CO)_2(NO)(\eta^3\text{-}CH_2CHCHMe)]$,[3] but is similar to that observed for the tungsten-catalysed addition of carbanions to allylic substrates.[17] In this last case, regiospecificity was thought to result from the steric demands of the allyltungsten intermediate, and similar arguments may be applied to the reaction described herein. For compound (**1**; allyl = $CH_2CHCHMe$), which has the *anti* configuration shown in Figure 2 at −40 °C (with only slow allyl rotation at room temperature),[18] attack *trans* to the phosphite ligand, *i.e.* at C(1) rather than C(3), would result in a less crowded $[Fe\{P(OMe)_3\}(NO)_2(\eta^2\text{-alkene})]$ intermediate since a terminal rather than internal olefin would result. Thus, attack at the CHMe terminus may be favoured because of the steric demands of the ancillary ligands of (**1**).

Despite the differences in the hydrocarbon ring structures of (**2**)—(**4**), all of these cationic complexes are deprotonated by NEt_3 in CH_2Cl_2 to give allyl-substituted η^4-cyclo-octatetraene derivatives $[M(CO)_2L(\eta^4\text{-}C_8H_7R)]$ [**5**; M = Fe, L = $CNBu^t$, R = $CH_2CH{=}CH_2$, $CH_2C(Me){=}CH_2$, $CH(Me)CH{=}CH_2$, or $CH_2CH{=}CHMe$; M = Ru, L = PPh_3, R = $CH_2C(Me){=}CH_2$] as orange to red liquids or low-melting solids. Each has been characterised by elemental analysis, i.r. (Table 1) and n.m.r. spectroscopy (Table 2), and by its mass spectrum which shows a parent ion (P^+) or $[P - CO]^+$.

The i.r. spectra of the iron complexes reveal the presence of rotamers, each mixture showing four $\tilde{\nu}(CO)$ and two $\tilde{\nu}(CN)$ absorptions. The rotation of the $Fe(CO)_2(CNBu^t)$ group is too rapid for its effects to be detected by n.m.r. spectroscopy, but the ^1H and ^{13}C n.m.r spectra of both the iron and ruthenium complexes (**5**) do reveal a second room-temperature fluxional process by which pairs of ring atoms [*e.g.* H(1) and H(7), C(2) and C(6), *etc.*, Scheme 1] are rendered equivalent.

Apart from signals due to the allyl substituent, R, and the ligand, L, the ^1H n.m.r. spectra of compounds (**5**) are very similar to those of $[Fe(CO)_3(\eta^4\text{-}C_8H_7R)]$ where R is an electron-releasing group such as Me[19] or $SiMe_3$.[20] The observed shifts of the ring protons indicate[19] that the metal remains co-ordinated to a diene group with the substituent on an internal carbon atom (Scheme 1); oscillation between the two possibilities accounts for the equivalence of proton pairs H(1), H(7); H(2), H(6); and H(3), H(5). The ^{13}C n.m.r. spectra are also affected by the fluxional process in that the ring carbons give rise to only five signals; single resonances are observed for the carbonyl (and isocyanide) ligands. No attempt was made to quantify the fluxional process; $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$ requires[5] cooling to −142 °C before the ^{13}C n.m.r. spectrum corresponds to that expected for the static structure.

The n.m.r. spectra obtained when the mixture of compounds (**3**) and (**4**) (R = $CHMeCH{=}CH_2$ or $CH_2CH{=}CHMe$) is deprotonated are more complex than those of [**5**; M = Fe, R = $CH_2CH{=}CH_2$ or $CH_2C(Me){=}CH_2$] in that the product is a mixture of (**5**; M = Fe, R = $CH_2CH{=}CHMe$) and (**5**; M = Fe, R = $CHMeCH{=}CH_2$). However, the fluxional process noted above again leads to the simplification of the spectra so that a complete assignment of the signals of the two structural isomers was possible (Table 2). Unlike the cation (**3**; R = $CHMeCH{=}CH_2$), complex (**5**; M = Fe, R = $CHMeCH{=}CH_2$) cannot exhibit diastereoisomerism; loss of H(8) by deprotonation removes the chirality at C(8). However, the remaining chiral centre at C(9) does render the carbon pairs C(1), C(7); C(2), C(6); and C(3), C(5) inequivalent despite the fluxional motion of the $Fe(CO)_2(CNBu^t)$ group. Hence, eight ring carbon and seven ring proton signals are observed in the ^{13}C and ^1H n.m.r. spectrum of (**5**; M = Fe, R = $CHMeCH{=}CH_2$). By contrast, compound (**5**; M = Fe, R = $CH_2CH{=}CHMe$), with no chirality at C(9), exhibits five ring carbon and four ring proton signals as observed for [**5**; M = Fe, R = $CH_2CH{=}CH_2$ or $CH_2C(Me){=}CH_2$].

Relatively low yields of (**5**; M = Ru, L = PPh_3) result from the deprotonation of (**2**). However, the iron analogues (**5**; M = Fe, L = $CNBu^t$) are readily available in more significant quantities and have therefore been subjected to further reaction with (**1**) to give difunctionalised cot derivatives.

The reaction of compound [**5**; M = Fe, L = $CNBu^t$, R = $CH_2C(Me){=}CH_2$] with [**1**; R = $CH_2C(Me)CH_2$] gave, after purification from CH_2Cl_2–diethyl ether, a moderate yield (*ca.* 40%) of a yellow solid whose i.r. spectrum [$\tilde{\nu}(CN)(CH_2Cl_2)$ = 2 185, $\tilde{\nu}(CO)$ = 2 070 and 2 035 cm^{-1}] was indicative of $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_7R_2)][PF_6]$. Similarly, (**5**; M = Fe, L = $CNBu^t$, R = $CH_2CH{=}CH_2$) and the corresponding allyldinitrosyl cation gave a yellow oil [$\tilde{\nu}(CN)(CH_2Cl_2)$ = 2 194, $\tilde{\nu}(CO)$ = 2 070 and 2 036 cm^{-1}]. The ^1H n.m.r. spectra of these products were complex and ill defined and further characterisation was not possible. However, the complexes are readily deprotonated by NEt_3 in CH_2Cl_2 to give $[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_6R_2)]$ [**6**; R = $CH_2CH{=}CH_2$ or $CH_2C(Me){=}CH_2$]. Complex (**6**; R = $CH_2CH{=}CH_2$) was shown by ^1H and ^{13}C n.m.r. spectroscopy to be a mixture of at least three isomers and was characterised only by its mass spectrum (M^+ = 379). However, the red-purple solid [**6**; R = $CH_2C(Me){=}CH_2$] was isolated as a mixture of only two isomers (*ca.* 3:1 ratio) characterised by mass spectrometry, elemental analysis, i.r. (Table 1) and n.m.r. spectroscopy (Table 2).

The room-temperature ^1H n.m.r. spectrum of compound [**6**; R = $CH_2C(Me){=}CH_2$] shows broad signals for the ring protons indicating that the fluxional process observed for (**5**) was slower in the disubstituted-cot derivative. At 70 °C the signals are sharpened (and simplified) to give a well resolved spectrum revealing the structures of the two isomers. The major component contains a 1,4-disubstituted cot ring identified by a second-order $[AX]_2$ pattern, with two multiplets centred at δ

Scheme 2. R = $CH_2C(Me)$=CH_2

4.93 and 5.46, typical of a butadiene moiety. An analysis of this pattern gives $J(H^4H^5) = J(H^6H^7) = 11.3$, $J(H^5H^6) = 8.0$, $J(H^4H^6) = J(H^5H^7) = -1.2$, and $J(H^4H^7) = 0$ Hz, consistent with the structure shown (Scheme 1). Protons H(1) and H(2) appear as a singlet at δ 4.65. The low-field shift of H(5) and H(6) indicates that the probable mechanism of the fluxional process involves oscillation of the metal atom between diene fragments C(5)–C(4)–C(3)–C(2), C(4)–C(3)–C(2)–C(1), C(3)–C(2)–C(1)–C(8), C(2)–C(1)–C(8)–C(7), and C(1)–C(8)–C(7)–C(6). This fluxionality is rapid on the n.m.r. time-scale at 70 °C and the high-temperature limiting ^1H n.m.r. spectrum is observed, though a temperature of 90 °C was required to give a sharp ^{13}C n.m.r. spectrum. Since the energy barrier to oscillation appears to be higher than in the monosubstituted cot complexes, an attempt was made to measure the low-temperature limiting ^1H n.m.r. spectrum. Although the spectrum sharpened below −40 °C, the apparent coalescence temperature, it was still very broad at −70 °C.

Apart from resonances due to the allyl substituents, the second isomer of [**6**; R = $CH_2C(Me)$=CH_2] displayed only one ring signal, a narrow multiplet integrating for six protons at δ 5.07. This is reminiscent of the ^1H n.m.r. spectrum of $[Fe(CO)_3(\eta^4\text{-}C_8H_7Ph)]$ in which complete fluxionality of the metal group around the ring renders the shifts of the ring protons nearly equivalent.[21] A 1,5-disubstituted structure is therefore likely, since oscillation of the metal between preferred co-ordination sites would result in complete fluxionality around the ring; 1,2 and 1,3 isomers are less likely, as a large spread of ring proton chemical shifts would be expected.

Assuming a mixture of 1,4- and 1,5-disubstituted isomers is produced from the reaction of compound [**1**; allyl = $CH_2C(Me)CH_2$] with $[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_7R)]$ [R = $CH_2C(Me)$=CH_2], the regiochemistry of electrophilic attack is similar to that observed in the protonation[9] and formylation[21] of $[Fe(CO)_3(\eta^4\text{-}C_8H_7Me)]$, when a 2:1 ratio of 1,4 and 1,5 products is obtained. This implies attack of the electrophile at the inner carbons of the unco-ordinated diene moiety of the cot ring. Substantial electronic coupling of the co-ordinated and unco-ordinated parts of the ring has been proposed[9] since free dienes protonate at the terminal carbons.

The substituted cot ligands of compounds (**5**) and (**6**) may be detached from the metal by refluxing the iron complexes with $ONMe_3 \cdot 2H_2O$ in benzene. For example, small scale reactions with (**5**; M = Fe, L = $CNBu^t$, R = CH_2CH=CH_2) and with the mixture (see above) of (**5**; M = Fe, L = $CNBu^t$, R = $CHMeCH$=CH_2) and (**5**; M = Fe, L = $CNBu^t$, R = CH_2CH=CHMe) gave moderate (*ca.* 40%) yields of yellow oils after chromatography on alumina. The ^1H n.m.r. spectra of the oils verified the formation of intact cyclo-octatetraenes, with that of $C_8H_7CH_2CH$=CH_2 consistent with the spectrum previously reported,[22] and that from the methylallyl derivatives showing a 2:1 mixture of C_8H_7R (R = $CHMeCH$=CH_2 and CH_2CH=CHMe).

Similar treatment of compound (**6**) gave *ca.* 60% of the free ligand $C_8H_6[CH_2C(Me)$=$CH_2]_2$ after filtration of the reaction mixture and solvent removal. The product showed a parent ion ($M^+ = 212$) in the mass spectrum and two methyl singlets (ratio *ca.* 2:1) in the ^1H n.m.r. spectrum indicating the same substitution pattern as observed for [**6**; R = $CH_2C(Me)$=CH_2]. The ^{13}C n.m.r. spectrum has allowed the structures of the two isomers of $C_8H_6[CH_2C(Me)$=$CH_2]_2$ to be determined.

Cyclo-octatetraene and its substituted analogues exist in the tub conformation[23] and undergo bond-shift and ring-inversion processes, with the former generally having a higher energy barrier.[24] With disubstituted cyclo-octatetraenes, structural and optical isomers are possible and these are interconverted by the fluxional processes. 1,4-Disubstituted cyclo-octatetraenes exist as a mixture of two interconverting structural isomers (Scheme 2), each of which is symmetrical. Thus the room-temperature ^{13}C n.m.r. spectrum of $1,4\text{-}C_8H_6(CO_2Me)_2$[25] shows eight ring signals and a doubling up of each substituent signal since the exchange process is slow on the n.m.r. time-scale. 1,2-Disubstituted cyclo-octatetraenes also exist as a mixture of two symmetrical isomers.[26] For 1,3-disubstituted isomers, the fluxional processes merely interconvert two enantiomers, However, the structures are unsymmetrical (C_1 point group) and therefore eight ring carbon signals and inequivalent substituents are observed in the ^{13}C n.m.r. spectrum of $1,3\text{-}C_8H_6Bu^t{}_2$.[27] Finally, 1,3-disubstituted isomers exist as a pair of enantiomers,[23] but each is symmetrical so that only four ring signals and equivalent substituents would be expected in the ^{13}C n.m.r. spectrum. Since the 100.5-MHz ^{13}C n.m.r. spectrum of the $C_8H_6[CH_2C(Me)$=$CH_2]_2$ sample obtained from compound [**6**; R = $CH_2C(Me)$=CH_2] displays twelve ring carbon singlets and the allyl signals are present as either two or three singlets (Table 2), a mixture of 1,4- and 1,5-disubstituted isomers, as found for the co-ordinated ligands, is most likely.

The preparation of allylcyclo-octatetraene from $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$ in an unoptimised yield of *ca.* 30%, and therefore from cot in an approximate yield of 23%, is comparable to the previously published method[22] whereby allylcyclo-octatetraene was obtained from C_8H_7Br *via* a Grignard intermediate in 44% yield (*ca.* 37% from cot). Isolation of $C_8H_6[CH_2C(Me)$=$CH_2]_2$ *via* the double allylation of $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$, though in lower overall yield, suggests metal-mediated electrophilic addition as an alternative to the known methods[23] of preparing polysubstituted cyclo-octatetraenes. In particular it may provide a means by which different allyl substituents may be incorporated into cyclo-octatetraene.

Conclusion

The cation $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})]^+$ is a convenient and easily handled reagent which can be used to introduce the allyl substituent onto the η^4-cot ligand. The regiospecificity of the addition of the 1-methylallyl group, *i.e.* preferential C–C coupling at the CHMe terminus of the C_3 chain, is opposite to that observed using complexes such as $[Fe(CO)_4(\eta^3\text{-}CH_2CHCHMe)]^+$ with nucleophiles such as $CH(CO_2Me)_2{}^-$. The rate of allylation of co-ordinated cot is enhanced using easily prepared, electron-rich derivatives such as $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$.

Deprotonation of the cationic allylation products gives substituted cyclo-octatetraene complexes from which the pure hydrocarbon ligand can be detached by reaction with $ONMe_3 \cdot 2H_2O$. The multiple application of the allylation–deprotonation sequence followed by decomplexation has been used to prepare difunctionalised cot compounds and may provide a route by which two or more, not necessarily identical, allyl substituents can be added to the ring.

Experimental

The preparation, purification, and reactions of the complexes described were carried out under an atmosphere of dry nitrogen. Unless otherwise stated, products were purified by dissolution in CH_2Cl_2, filtration, and addition of diethyl ether to induce precipitation. Unless otherwise stated, the complexes are air-stable, dissolving in polar solvents such as acetone and CH_2Cl_2 to give solutions which slowly decompose in air. The complexes $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-allyl})][PF_6]$ [allyl = CH_2CHCH_2, $CH_2C(Me)CH_2$, or $CH_2CHCHMe$][18] and $[Ru(CO)_2L(\eta^4\text{-cot})]$[14] (L = CO or PPh_3) were prepared by published methods.

Infrared spectra were recorded on a Nicolet MX-1 FT instrument, proton and ^{13}C n.m.r. spectra on JEOL FX90Q, FX200, GX270, or GX400 spectrometers and calibrated against $SiMe_4$ as an internal reference, and mass spectra on an AEI MS902 spectrometer. Microanalyses were by the staff of the Microanalytical Service of the School of Chemistry, University of Bristol.

Dicarbonyl(η^4-cyclo-octatetraene)(t-butyl isocyanide)iron, $[Fe(CO)_2(CNBu^t)(\eta^4\text{-cot})]$.—A mixture of $[Fe(CO)_3(\eta^4\text{-cot})]$ (4.10 g, 16.8 mmol), $CNBu^t$ (2.20 g, 26.5 mmol), and $ONMe_3{\cdot}2H_2O$ (2.76 g, 24.8 mmol) in acetonitrile (185 cm^3) was stirred for 18 h. The solvent was then removed *in vacuo* and the residue extracted with n-hexane (3 × 100 cm^3). The extract was evaporated to minimum volume and chromatographed on an n-hexane–alumina column (15 × 5 cm). Elution of the orange band with n-hexane, evaporation to low volume, and cooling to −10 °C gave the product as maroon crystals, yield 4.32 g (86%).

$[Ru(CO)_3(\eta^2,\eta^3\text{-}C_8H_8R)][PF_6]$ ($R = CH_2CH{=}CH_2$).—To a stirred solution of $[Ru(CO)_3(\eta^4\text{-cot})]$ (0.30 g, 1.0 mmol) in CH_2Cl_2 (30 cm^3) was added $[Fe\{P(OMe)_3\}(NO)_2(\eta^3\text{-}CH_2CHCH_2)][PF_6]$ (0.45 g, 1.0 mmol). After 90 min the orange-brown solution was filtered, and addition of diethyl ether precipitated a cream solid. Purification from CH_2Cl_2–diethyl ether gave the product as a white solid, yield 0.28 g (58%).

The complexes $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_8R)][PF_6]$ and $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_8R)][PF_6]$ [$R = CH_2CH{=}CH_2$, $CH_2C(Me){=}CH_2$, $CH(Me)CH{=}CH_2$, or $CH_2CH{=}CHMe$], the last two as an isomeric mixture (see text), were prepared similarly; stirring of the reaction mixtures required only 30 min. All of the complexes are air-stable in the solid state, and dissolve in polar solvents such as CH_2Cl_2 or acetone to give colourless (M = Ru) or yellow (M = Fe) solutions which slowly decompose in air.

$[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_7R)]$ ($R = CH_2CH{=}CH_2$).—A solution of $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_8R)][PF_6]$ ($R = CH_2CH{=}CH_2$) (0.25 g, 0.52 mmol) and NEt_3 (1.4 mmol) was stirred in CH_2Cl_2 (25 cm^3) for 3 h. The solvent was then removed *in vacuo*, the residue was extracted with toluene (2 cm^3), and the extract was chromatographed on an n-hexane–alumina column (5 × 2 cm). Elution with diethyl ether–n-hexane (1:4) gave an orange solution from which the product was isolated as an orange-red liquid on removal of the solvent *in vacuo*, yield 0.16 g (89%).

The complexes $[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_7R)]$ [$R = CH(Me)CH{=}CH_2$, $CH_2CH{=}CHMe$, or $CH_2C(Me){=}CH_2$] and $[Ru(CO)_2(PPh_3)(\eta^4\text{-}C_8H_7R)]$ [$R = CH_2C(Me){=}CH_2$] were prepared similarly, the first pair as a mixture of isomers (see text) and the second pair as crystalline solids from cold (−20 °C) n-hexane. All dissolve in common organic solvents to give solutions which decompose only slowly in air.

$[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_7R_2][PF_6]$ [$R = CH_2C(Me){=}CH_2$].—A mixture of $[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_7R)]$ [$R = CH_2C(Me){=}CH_2$] (0.33 g, 0.93 mmol) and $[Fe\{P(OMe)_3\}(NO)_2\{\eta^3\text{-}CH_2C(Me)CH_2\}][PF_6]$ (0.37 g, 0.87 mmol) in CH_2Cl_2 (30 cm^3) was stirred for 25 min. After filtration and evaporation of the filtrate to low volume, addition of diethyl ether gave a brown precipitate. Purification gave a yellow solid, yield 0.20 g (42%) [i.r. (CH_2Cl_2) $\tilde{\nu}$(CN) 2 195, $\tilde{\nu}$(CO) 2 070 and 2 035 cm^{-1}].

$[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_6R_2)]$ [$R = CH_2C(Me){=}CH_2$].—A solution of $[Fe(CO)_2(CNBu^t)(\eta^5\text{-}C_8H_7R_2)][PF_6]$ [$R = CH_2C(Me){=}CH_2$] (0.09 g, 0.17 mmol) and NEt_3 (0.7 mmol) was stirred in CH_2Cl_2 (25 cm^3) for 5 h. After removing the solvent *in vacuo*, the residue was extracted with toluene (2 cm^3) and the extract chromatographed on an n-hexane–alumina column (5 × 2 cm). Elution with n-hexane–diethyl ether (2:1) gave an orange solution from which the product was isolated as an orange-red liquid upon removal of the solvent, yield 0.02 g (29%). The product dissolves in non-polar solvents such as n-hexane to give solutions which slowly decompose in air.

$C_8H_6[CH_2C(Me){=}CH_2]_2$.—A mixture of $[Fe(CO)_2(CNBu^t)(\eta^4\text{-}C_8H_6R_2)]$ [$R = CH_2C(Me){=}CH_2$] (0.03 g, 0.08 mmol) and $ONMe_3{\cdot}2H_2O$ (0.30 g, 2.70 mmol) was refluxed in benzene for 4 h. The solution was then filtered and the solvent removed *in vacuo* to give the product as a yellow oil, yield 0.01 g (62%). Mass spectrum, M^+ 212.

Crystal Structure Analysis of $[Ru(CO)_2(PPh_3)(\eta^2,\eta^3\text{-}C_8H_8R)][PF_6]{\cdot}0.5CH_2Cl_2$ [$R = CH_2C(Me){=}CH_2$].—*Crystal data.* [**2**; $L = PPh_3$, $R = CH_2C(Me){=}CH_2$]$\cdot 0.5CH_2Cl_2$, $C_{32.5}H_{31}ClF_6P_2Ru$, $M_r = 765.5$, monoclinic, space group $P2_1/n$ (no. 14), $a = 12.984(8)$, $b = 11.602(2)$, $c = 21.991(10)$ Å, $\beta = 96.57(5)°$, $U = 3\,291(3)$ Å^3, $Z = 4$, $D_c = 1.55$ g cm^{-3}, $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-K_α) = 7.05 cm^{-1}, $F(000) = 1\,548$, $T = 295$ K. Crystal faces [distance from origin in mm]: (101)[0.05], $(\bar{1}0\bar{1})$[0.05], $(\bar{1}01)$[0.17], $(10\bar{1})$[0.17], (012)[0.22], $(0\bar{1}2)$[0.23], and $(01\bar{2})$[0.23].

A single crystal of compound [**2**; $L = PPh_3$, $R = CH_2C(Me){=}CH_2$] (dimensions *ca.* 0.1 × 0.5 × 0.7 mm) grown from CH_2Cl_2–n-hexane was mounted in a thin-walled glass capillary under N_2. All diffraction measurements were made on a Nicolet P3m diffractometer at room temperature, using graphite-monochromated Mo-K_α *X*-radiation. Unit-cell dimensions were determined from 15 centred reflections in the range $27.0 < 2\theta < 31.0°$. A total of 6 235 diffracted intensities, including check reflections, was measured in a unique quadrant of reciprocal space for $4.0 < 2\theta < 55.0°$ by ω—2θ scans: for $2\theta > 40°$ only those reflections with count rates > 10 counts s^{-1} were recorded. Two check reflections remeasured after every 100 ordinary data showed a variation of ±2% over the period of data collection. An appropriate correction was therefore applied. Of the intensity data collected, 5 172 unique observations remained after averaging of duplicate and equivalent measurements and deletion of systematic absences. Of these, 3 686 with $I > 2\sigma(I)$ were retained for use in structure solution and refinement. An absorption correction was applied on the basis of the indexed crystal faces; maximum and minimum transmission coefficients were 0.93 and 0.78 respectively. Lorentz and polarisation corrections were applied.

The structure was solved by conventional heavy-atom (Patterson and Fourier) methods. All non-hydrogen atoms were assigned anisotropic displacement parameters and all hydrogen atoms fixed isotropic displacement parameters. All non-hydrogen atoms (other than the atoms of the $[PF_6]^-$ anion) and the hydrogen atoms H(1), H(2), H(3), H(6), and H(7) were refined without positional constraints. All other hydrogen atoms were constrained to idealised geometries (C–H 0.96 Å). The $[PF_6]^-$ anion was subject to a disorder in which two orientations of the octahedral species were observed, related by rotation about the F(1)–P(2)–F(2) axis. The two $[PF_6]^-$ anion geometries which resulted were each constrained to be near octahedral symmetry and their occupancies refined [F(3)—F(6) 0.497(9), F(7)—F(10) 0.503(9)]. The dichloro-

Table 4. Atomic co-ordinates (× 10^4) for compound [**2**; L = PPh_3, R = $CH_2C(Me)=CH_2$]·$0.5CH_2Cl_2$

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ru	2 800(1)	1 164(1)	1 083(1)	C(22)	3 472(5)	2 107(7)	−564(3)
C(1)	1 040(5)	1 620(5)	1 029(3)	C(23)	3 232(6)	2 255(8)	−1 184(3)
C(2)	1 364(5)	1 479(5)	464(3)	C(24)	2 821(7)	3 296(10)	−1 400(4)
C(3)	1 863(5)	513(5)	239(3)	C(25)	2 639(7)	4 164(8)	−1 004(4)
C(4)	1 576(6)	−693(7)	314(4)	C(26)	2 881(5)	4 008(6)	−371(3)
C(5)	1 766(6)	−1 266(6)	825(3)	C(27)	5 061(4)	2 569(5)	738(3)
C(6)	2 204(5)	−706(5)	1 384(3)	C(28)	5 590(5)	2 234(7)	1 290(3)
C(7)	1 713(5)	101(5)	1 691(3)	C(29)	6 649(5)	2 188(8)	1 378(3)
C(8)	735(5)	741(6)	1 476(3)	C(30)	7 211(6)	2 483(7)	903(4)
C(9)	−231(6)	54(7)	1 278(4)	C(31)	6 701(6)	2 802(7)	352(4)
C(10)	−517(7)	−803(8)	1 737(4)	C(32)	5 631(5)	2 853(6)	259(3)
C(11)	−427(7)	−1 886(8)	1 640(7)	P(2)	9 779(1)	4 019(2)	2 296(1)
C(12)	−962(11)	−349(11)	2 291(5)	F(1)	10 888(4)	3 526(6)	2 219(3)
C(13)	3 243(4)	1 837(5)	1 878(2)	F(2)	8 697(5)	4 395(7)	2 343(4)
O(13)	3 449(4)	2 240(4)	2 337(2)	F(3)[a]	9 897(9)	3 355(10)	2 900(5)
C(14)	3 952(5)	216(6)	939(3)	F(4)[a]	10 393(11)	4 989(9)	2 631(5)
O(14)	4 591(4)	−365(5)	810(3)	F(5)[a]	9 291(12)	2 987(15)	1 939(10)
P(1)	3 647(1)	2 722(1)	660(1)	F(6)[a]	9 758(13)	4 757(15)	1 717(6)
C(15)	3 493(4)	4 125(4)	1 027(2)	F(7)[b]	10 115(14)	5 225(8)	2 179(8)
C(16)	4 289(5)	4 928(5)	1 089(3)	F(8)[b]	9 640(13)	3 757(15)	1 618(4)
C(17)	4 164(6)	5 962(5)	1 372(3)	F(9)[b]	9 466(13)	2 765(10)	2 442(7)
C(18)	3 248(6)	6 208(5)	1 598(3)	F(10)[a]	9 955(14)	4 216(16)	2 979(5)
C(19)	2 434(6)	5 441(5)	1 537(3)	Cl	9 510(2)	3 900(2)	15(2)
C(20)	2 570(5)	4 390(5)	1 252(3)	C(33)[c]	9 894(13)	5 124(18)	393(7)
C(21)	3 298(4)	2 976(5)	−150(2)				

[a] Site occupancy 0.497(9). [b] Site occupancy 0.503(9). [c] Site occupancy 0.5.

methane solvate is disordered around a centre of inversion. Full-matrix least-squares refinement of this model (464 parameters) converted to final residual indices $R = 0.052$, $R' = 0.061$, and $S = 1.28$.* Weights, w, were set equal to $[\sigma_c^2(F_o) + gF_o^2]^{-1}$, where $\sigma_c^2(F_o)$ is the variance in F_o due to counting statistics and $g = 0.0010$ was chosen to minimise the variation in S as a function of $|F_o|$. Final difference electron-density maps showed no features outside the range +0.67 to −0.58 e Å^{-3}, the largest of these being close to the ruthenium atom. Table 4 lists the final atomic positional parameters for the non-hydrogen atoms. All calculations were carried out on a Nicolet P3m/E structure determination system using programs of the SHELXTL package.[28] Complex neutral-atom scattering factors were taken from ref. 29.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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* $R = \Sigma|\Delta|/\Sigma|F_o|$, $R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$, and $S = [\Sigma w\Delta^2/(N_o - N_v)]^{\frac{1}{2}}$, where $\Delta = F_o - F_c$, N_o = number of observations, and N_v = number of variables.