Syntheses, Structures and Fluxional Behaviour of η^4-1,4-Di-*tert*-butylbuta-1,3-diene Complexes of Iron and Ruthenium†

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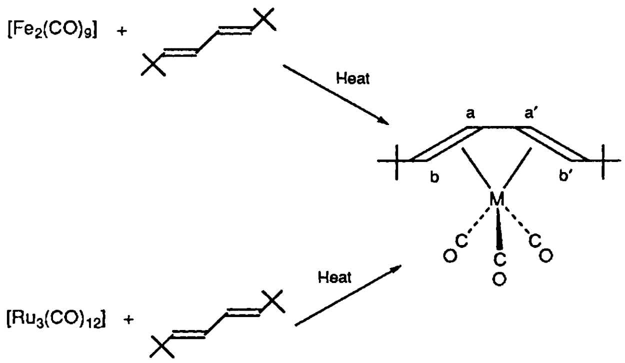
The complexes [M(CO)$_3$(η^4-diene)] (M = Fe or Ru; diene = 1,4-di-*tert*-butylbuta-1,3-diene) have been synthesised and their crystal structures and solution fluxional behaviour determined. While they adopt square-pyramidal geometries in the solid state, the carbonyl ligands show fluxional behaviour in solution (E_a = 44.6, $\Delta H^‡$ = 42.2 kJ mol^{-1}, $\Delta S^‡$ = −29.8 J K^{-1} mol^{-1} where M = Fe; 52.6, 50.0 kJ mol^{-1} and −30.5 J K^{-1} mol^{-1} where M = Ru). These activation parameters are the largest reported for simple [M(CO)$_3$(diene)] complexes. An inverse correlation between E_a and the diene 'bite' angle θ_1 for a range of [M(CO)$_3$(diene)] complexes is described and used to account for variations in activation barriers.

The dynamic carbonyl-scrambling process in five-co-ordinate [M(CO)$_3$(diene)] complexes of the Group 8 metals has become of renewed interest recently.[1,2] The observation of a temperature dependence of the IR spectrum of [Fe(CO)$_3$(η^4-nbd)] (nbd = bicyclo[2.2.1]hepta-2,5-diene) and certain related complexes has been interpreted in terms of a very fast ($k > 10^{12}$ s^{-1}) carbonyl-exchange phenomenon.[3] Studies of the ruthenium complexes [Ru(CO)$_3$(diene)] are considerably rarer than those of their iron analogues, often because they show more limited thermal stability; decomposition to free diene and [Ru$_3$(CO)$_{12}$] is common.[4]

We have recently described the use of the bulky diene 1,4-di-*tert*-butylbuta-1,3-diene for the synthesis of novel first-row transition-metal complexes.[5,6] The steric bulk imparts kinetic stability to co-ordinatively and electronically unsaturated complexes. We therefore decided to carry out the synthesis of new butadiene derivatives of iron and ruthenium, and investigate their structures and solution dynamic behaviour.

Results and Discussion

Reaction of [Fe$_2$(CO)$_9$] with 1,4-di-*tert*-butylbuta-1,3-diene at 40–60 °C yields yellow crystals of [Fe(CO)$_3$(η^4-C$_4$H$_4$Bu$^t_2$)] **1**, Scheme 1. Similarly, [Ru(CO)$_3$(η^4-C$_4$H$_4$Bu$^t_2$)] **2** may be prepared by the thermal reaction of [Ru$_3$(CO)$_{12}$] and 1,4-di-*tert*-butylbuta-1,3-diene at 140 °C as colourless crystals. Complexes **1** and **2** are thermally robust, mildly air-sensitive materials. Their analytical and spectroscopic data are given in Table 1. The low-temperature (*ca.* 230 K) crystal structures of the compounds have been determined, and show **1** and **2** to be ismorphous, crystallising in the triclinic space group $P\bar{1}$. The fractional atomic coordinates are given in Table 2 and selected bond lengths and angles in Table 3. Views of the molecular structures are shown in Fig. 1. Complex **1** has a square-pyramidal geometry broadly similar to that of the unsubstituted analogue [Fe(CO)$_3$(C$_4$H$_6$)], with the diene ligand occupying two of the basal positions and two carbonyl ligands at the other basal positions. The third apical carbonyl and the iron atom lie directly above the basal plane. The molecule possesses a mirror plane passing through the apical CO group and the iron atom, bisecting the central C–C bond of the diene. The Fe–CO bond lengths lie in the region 1.79–1.80 Å and fall within the range of those previously reported for other [Fe(CO)$_3$(diene)] complexes.[8] The basal carbonyl ligands subtend an angle of 87.8° at the iron, which is a significant compression in comparison to related complexes where 92–93° is typical. This effect presumably arises as a result of steric strain between the Bu^t substituents and the carbonyl ligands. Similar effects can be seen in the molecular structure of **2**, which is the first crystallographically characterised mononuclear Ru(CO)$_3$ complex containing a co-ordinated η^4-butadiene analogue. The related compounds [Ru(CO)$_3$(diene)] (diene = tetraphenylcyclopentadienone,[9] 1,1-dimethyl-2,5-diphenyl-1-silacyclopentadiene,[10] cyclooctatetraene[11h] or a tricyclohexadeca-4,6,11,13,15-pentaene[12]) which represent the other structurally characterised complexes contain cyclic or polyfunctionalised dienes.



Scheme 1 Synthesis of complexes **1** and **2**

The mode of bonding of the butadiene moiety to transition metals can be described as an σ^2,π-metallacyclopentene structure **A** or as an π^2-diene structure **B**.[11c,13] It is well documented that the bonding of butadienes to early transition metals leads to structures resembling type **A**, whereas complexes of the middle and late transition metals are more often formulated as type **B**. The difference in M–C bond lengths, Δ [= average(M–C$_{\text{int}}$) − average(M–C$_{\text{ter}}$)] has been used as a parameter for distinguishing the bonding modes; Δ is large and positive for complexes of type **A**, and small and often negative for those of type **B**. Some representative data are summarised in Table 4. Clearly, reaction of early transition metals (often bearing good σ-donor ligands) leads to 'metallacyclopentene'

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Non-SI unit employed: mmHg ≈ 133 Pa.

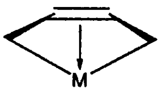
Table 1 Analytical and spectroscopic data for complexes **1** and **2**

		1	**2**
Analysis[a] (%)	C	58.75 (58.85)	51.35 (51.30)
	H	7.30 (7.25)	6.65 (6.25)
IR data[b] (cm^{-1})		2039s, 1974vs, 1959s	2054s, 1992vs, 1975s
^1H NMR data[c]		4.67 [1 H, m, $J(H_aH_b)$ = 10.05, $J(H_aH_{a'})$ = 5.26, H_a]	4.81 [1 H, m, $J(H_aH_b)$ = 10.15, $J(H_aH_{a'})$ = 6.34, H_a]
		0.93 (9 H, s, Bu^t)	1.14 [1 H, m, $J(H_bH_{b'})$ = 0.94, $J(H_bH_{a'})$ = −1.59, H_b]
		0.91 [1 H, m, $J(H_bH_{b'})$ = 0.45, $J(H_bH_{a'})$ = −1.17, H_b]	0.92 (9 H, s, Bu^t)
^{13}C NMR data[d]		213.7 (CO, 370 K)	200.7 (CO, 363 K)
		217.3, 212.8 (apical and basal CO, 213 K)	203.7, 199.3 (apical and basal CO, 248 K)
		80.01 [J(CH) = 158, C_b]	80.02 (C_b)
		77.70 [J(CH) = 166, C_a]	73.66 (C_a)
		33.32 (CMe_3)	32.77 (CMe_3)
		31.04 [J(CH) = 126, Bu^t]	31.75 (Bu^t)

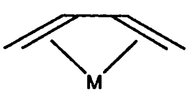
[a] Analytical data given as found (required). Parent ions, with the appropriate isotope pattern, were observed in the mass spectra of complexes **1** and **2**. [b] Light petroleum solution. [c] In C_7D_8 solution (295 K), data given as: chemical shift (δ) (relative intensity, multiplicity, J/Hz, assignment). Assignments of the resonances of complex **1** at δ 4.67 and 0.91 to H_a and H_b made on the basis of T_1 relaxation measurements (1.44 and 3.17 s respectively). This is supported by H $\cdots$ H distances obtained from structural data ($H_a \cdots H_a$ 1.83, $H_b \cdots H_b$ 2.30 Å). Coupling constants taken from iterative simulation using WIN DAISY.[7] [d] Assignments assisted by ^{13}C–^1H correlation spectroscopy.

Table 2 Fractional atomic coordinates (× 10^4) for complexes **1** and **2**

	M = Fe **1**			M = Ru **2**		
Atom	*X/a*	*Y/b*	*Z/c*	*X/a*	*Y/b*	*Z/c*
M	2107.2(11)	5082.1(7)	2111.1(5)	2158.1(2)	5100.9(1)	2116.0(1)
O(1)	5600(7)	7576(4)	1907(3)	3626(4)	3598(2)	213(2)
O(2)	3588(7)	3664(4)	294(3)	5734(3)	7708(2)	1963(2)
O(3)	4206(8)	4091(5)	3760(3)	4475(4)	4106(3)	3797(2)
C(1)	4209(9)	6622(5)	1996(4)	3041(4)	4155(2)	911(2)
C(2)	2952(8)	4193(5)	989(4)	4377(4)	6765(2)	2022(2)
C(3)	3376(8)	4473(6)	3122(4)	3626(4)	4471(3)	3176(2)
C(4)	−227(10)	1139(6)	1921(5)	2912(6)	7615(3)	4781(3)
C(5)	−1765(12)	1707(6)	293(5)	1901(6)	8809(3)	3406(3)
C(6)	−3956(9)	1307(6)	1785(6)	−722(6)	7754(4)	4549(3)
C(7)	−1677(9)	1920(6)	1500(4)	1150(4)	7597(2)	3973(2)
C(8)	−957(8)	3454(5)	2045(4)	379(3)	6161(2)	3241(2)
C(9)	−1106(7)	4580(5)	1554(4)	−51.8(3)	5951(2)	2185(2)
C(10)	−389(8)	5959(5)	2149(4)	−1227(3)	4572(2)	1579(2)
C(11)	445(7)	6157(5)	3215(3)	−999(3)	3458(2)	2064(2)
C(12)	1242(9)	7570(5)	3951(4)	−1727(4)	1924(2)	1494(2)
C(13)	2060(13)	8821(6)	3406(5)	−1773(6)	1739(3)	296(2)
C(14)	3015(12)	7557(7)	4760(5)	−315(5)	1156(3)	1922(3)
C(15)	−655(12)	7751(8)	4512(6)	−3991(4)	1304(3)	1755(3)



A



B

complexes, whereas late transition metals with π-acceptor ligands tend to form 'diene' complexes. The values of Δ = −0.12 Å for compound **1** and −0.15 Å for the anion $[Co(\eta^4\text{-}C_4H_4Bu^t{}_2)_2]^-$ are unusually large, and indicate that the bulky Bu^t groups of 1,4-di-*tert*-butylbuta-1,3-diene 'push away' the external carbon atoms of the butadiene ligand from the metal atom.

The quality of the X-ray data allowed the location and isotropic refinement of the hydrogen atoms bonded to the butadiene fragment [H(8) to H(11)] for both complexes **1** and **2**. While H(9) and H(10) lie in the plane defined by the butadiene skeleton, H(8) and H(11) are bent away from the metal atoms, to reduce steric crowding and minimise the H $\cdots$ H repulsions.

We have examined the fluxional behaviour of complexes **1** and **2** in solution using variable-temperature ^{13}C NMR spectroscopy. At low temperatures (below 240 K) the spectra show two sharp peaks of relative intensities 1 : 2 in the carbonyl region (assigned to the apical and two basal carbonyls), Table 1. The two singlets broaden, coalesce and sharpen again as the temperature is raised, so that one sharp peak is observed at high temperatures (above 350 K). Such behaviour indicates that a fluxional exchange process occurs which interchanges the three carbonyl ligands. Intramolecular rearrangement processes in five-co-ordinate $[M(CO)_3(diene)]$ complexes have been investigated by Cotton, Takats and co-workers using NMR spectroscopy,[11h,14,15] and recently by Grevels, Turner and co-workers[3] using IR spectroscopy. While the detailed mechanism of carbonyl exchange is not known, studies of single enantiomers of $[Fe(CO)_3(\eta^4\text{-}RCHCHCHCHR')]$ complexes establish that the interconversion process does not involve transfer of a metal atom from one diene face to another (*via* an η^2-diene intermediate or a modified 'envelope shift' mechanism, for example).[16] Turnstile rotation of the $Fe(CO)_3$ unit, or diene rotation (which amounts to the same motion), is likely.[15]

Twelve spectra of complex **1** (measured between 213 and 370 K) and nine of **2** (between 248 and 363 K) were investigated using line-shape analysis in both the high- and low-temperature regions. For equilibrium (1), where sites **C** and **D** are not

$$C \underset{k_D}{\overset{k_C}{\rightleftharpoons}} D \qquad (1)$$

equally populated, the rate constants, k, for exchange in the low-

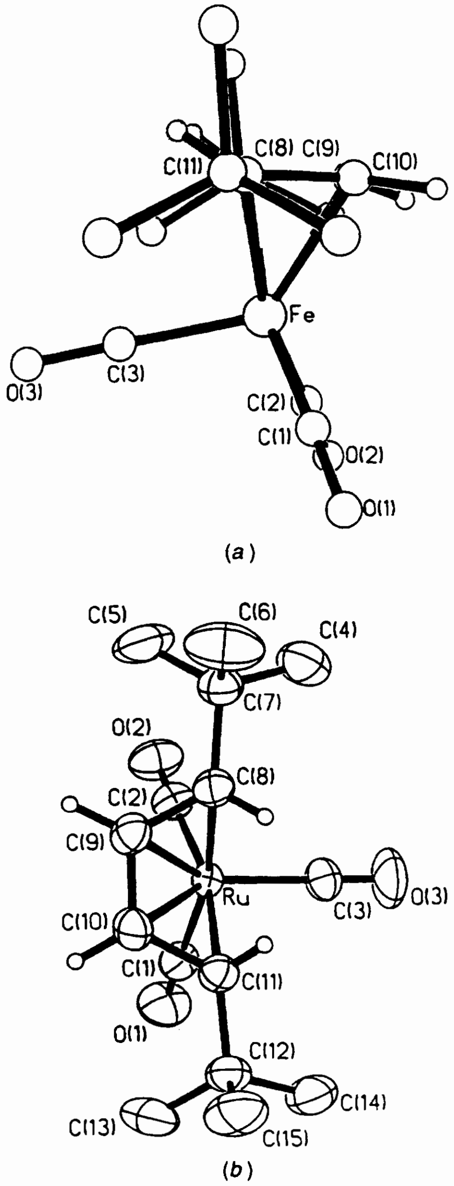


Fig. 1 Molecular structures of complexes **1** (*a*) and **2** (*b*) (50% thermal ellipsoids)

Table 3 Selected bond lengths (Å) and angles (°) for complexes **1** and **2**

	1	**2**
M–C(1)	1.797(5)	1.902(3)
M–C(2)	1.793(5)	1.920(2)
M–C(3)	1.798(6)	1.927(3)
M–C(8)	2.192(4)	2.254(3)
M–C(9)	2.076(5)	2.190(3)
M–C(10)	2.073(6)	2.197(2)
M–C(11)	2.191(5)	2.261(2)
C(1)–O(1)	1.151(6)	1.131(3)
C(2)–O(2)	1.140(7)	1.125(3)
C(3)–O(3)	1.143(8)	1.122(4)
C(8)–C(9)	1.419(8)	1.409(3)
C(9)–C(10)	1.423(6)	1.414(3)
C(10)–C(11)	1.425(7)	1.418(4)
C(1)–M–C(2)	87.7(2)	88.3(1)
C(1)–M–C(3)	100.4(2)	97.2(1)
C(2)–M–C(3)	99.3(3)	97.9(1)
C(2)–M–C(8)	94.4(2)	96.7(1)
C(2)–M–C(9)	97.4(2)	99.7(1)
C(1)–M–C(10)	97.6(2)	99.6(1)
C(1)–M–C(11)	95.7(2)	96.1(1)
C(9)–M–C(10)	40.1(2)	37.6(1)
C(8)–M–C(11)	79.1(2)	75.6(1)

Table 4 Some Δ values for selected metal diene complexes *

Compound	Δ	Ref.
$[Zr(C_5H_5)_2(\eta^4\text{-}C_4H_{10})]$	0.30	11(*a*)
$[Hf(\eta^4\text{-}C_6H_{10})(PMe_3)_2]$	0.18	11(*b*)
$[TaCl_2(C_5H_5)(\eta^4\text{-}C_4H_6)]$	0.17	11(*c*)
$[Mo(\eta^4\text{-}C_6H_{10})_3]$	0.15	11(*d*)
$[Rh(C_5Ph_5)(\eta^4\text{-}C_8H_{12})]$	−0.05	11(*e*)
$[Mo(\eta^4\text{-}C_4H_6)_2(PMe_3)_2]$	−0.06	11(*f*)
2	−0.06	This work
$[Fe(CO)_3(\eta^4\text{-}C_4H_6)]$	−0.08	11(*g*)
$[Ru(CO)_3(\eta^4\text{-}C_8H_8)]$ **6**	−0.08	11(*h*)
$[Mn(CO)(\eta^4\text{-}C_4H_6)_2]$	−0.09	11(*i*)
$[Co(\eta^5\text{-}C_8H_{13})(\eta^4\text{-}C_4H_6)]$	−0.10	11(*j*)
1	−0.12	This work
$[Fe(CO)_3(\eta^4\text{-}C_8H_8)]$ **5**	−0.13	11(*l*)
$[Co(\eta^4\text{-}C_4H_4Bu^t_2)_2]^-$	−0.15	6

* Δ = average(M–C_{int}) − average(M–C_{ter}).

temperature region are given by equations (2) and (3) where *w*

$$k_C = \pi w_C = k_D/2 \qquad (2)$$

$$k_D = \pi w_D \qquad (3)$$

is the excess linewidth of each peak at half-height (in Hz). The high-temperature region is governed by expression (4) where

$$k_C = 8\pi(\Delta\delta)^2/27w_C = k_B/2 \qquad (4)$$

$\Delta\delta = \nu_C - \nu_D$ (equation applicable for the specific case of **1** and **2**).[17] Plots of ln *k* and ln(*k*/*T*) against T^{-1} for **1** and **2** yield straight lines, Fig. 2, from which the activation parameters E_a, $\Delta H^\ddagger$ and $\Delta S^\ddagger$ are derived, Table 5. The calculated values of $\Delta G^\ddagger{}_{298}$ are included in Table 5. The values of E_a of 44.6 and 52.6 kJ mol^{-1}, for **1** and **2** respectively, are the largest reported for simple 1,3-diene complexes of the $M(CO)_3$ fragment. Trends in activation parameters have been accounted for previously by ascribing metallacyclopentene character to the $[M(CO)_3(\text{diene})]$ species; the increasing σ^2,π nature resulting from increased electron acceptance by the diene ligand (*e.g.* cycloheptatriene is both a better donor and acceptor ligand than is butadiene) gives some 'six-co-ordinate' character to the complex, and implies a greater barrier to carbonyl interconversion.[15] There is no crystallographic evidence to support this postulate. Indeed, comparison of the Δ values of $[M(CO)_3(\eta^4\text{-}C_8H_8)]$ (C_8H_8 = cyclooctatetraene) complexes **5** and **6** with **1** and **2** (Table 4) suggests that the latter pair will have activation parameters similar to, or slightly smaller than, those of the former. In fact the values of E_a and $\Delta H^\ddagger$ are *ca.* 10 and *ca.* 15 kJ mol^{-1} higher. We also note that the barrier to carbonyl exchange in the formally six-co-ordinate $[M(CO)_3(\eta^6\text{-}C_7H_8)]$ (M = Cr or Mo) complexes is comparable to that of the five-co-ordinate $[Fe(CO)_3(\eta^4\text{-}C_7H_8)]$ complex (all have E_a values in the region of 46–50 kJ mol^{-1}).[18]

Assuming the mechanism for carbonyl-site exchange involves a cyclic rotation of the carbonyl groups, with simultaneous flexing of the $M(CO)_3$ tripod, **E** is a likely intermediate in the exchange process;[15] the ease with which the diene can span its two co-ordination sites during the exchange is likely to have a large impact on the ease with which the carbonyl interconversion takes place. Fig. 3 illustrates that there is indeed a correlation between the diene 'bite angle' θ_1 (defined as the angle subtended at the metal centre by the midpoints of the diene C=C bonds) and the activation barrier E_a for several $[M(CO)_3(\text{diene})]$ complexes (E_a, as opposed to $\Delta G^\ddagger$, has been

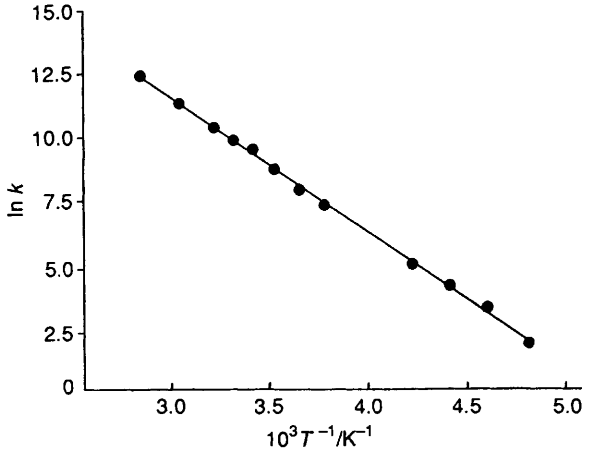


Fig. 2 Straight-line plot of ln *k vs.* $1/T$ for complex **1**

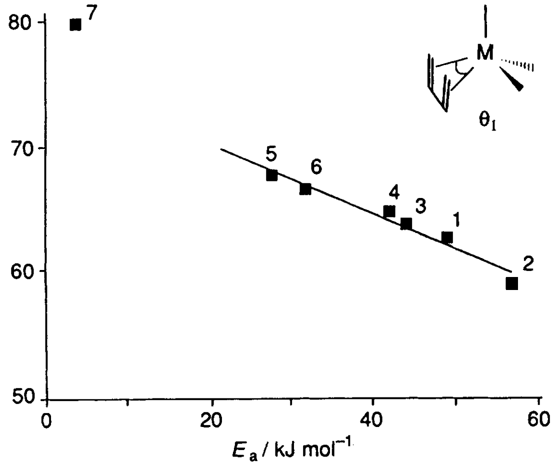
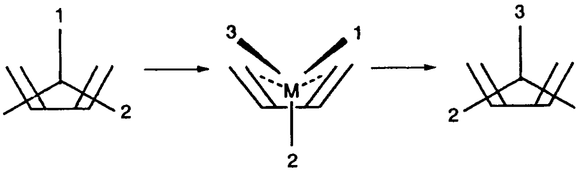


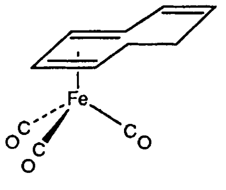
Fig. 3 Plot of diene bite angle θ_1 *vs.* activation parameter E_a for a range of [M(CO)$_3$(η^4-diene)] complexes [M = Fe; diene = cycloheptatriene **3**, butadiene **4**, cyclooctatetraene **5** or cycloocta-1,5-diene **7**: M = Ru, diene = cyclooctatetraene **6**]. The crystal structure of **3** has not been determined; θ_1 taken from azepine analogue



E

Table 5 Activation parameters for the carbonyl-scrambling process in complexes **1** and **2**

	1	**2**
E_a/kJ mol^{-1}	44.6 ± 1.2	52.6 ± 0.9
$\Delta H^‡$/kJ mol^{-1}	42.2 ± 1.3	50.0 ± 0.9
$\Delta S^‡$/J K^{-1} mol^{-1}	−29.8 ± 0.5	−30.5 ± 0.3
$\Delta G^‡_{298}$/kJ mol^{-1}	51.1	59.1



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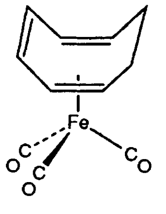

G

employed because it is the experimentally determined parameter which is most consistently reported). It can be seen that as θ_1 increases, *i.e.* as the diene's bite becomes bigger, the barrier to carbonyl exchange decreases. An approximately linear relationship is observed regardless of the metal atom centre. The inference is that the capacity of the diene to 'breathe' is intimately involved in the dynamic process.

It is tempting to suggest that complexes containing 1,4- or 1,5-diene ligands have very small barriers to carbonyl exchange because they have larger θ_1 values. The cycloocta-1,5-diene complex [Fe(CO)$_3$(η^4-C$_8$H$_{12}$)] **7** (θ_1 = 80.0°) has been shown to undergo CO site exchange on the IR time-scale,[1] implying that E_a < 10 kJ mol^{-1}. However, other factors (*e.g.* the C$_2$-symmetric diene present in **7**) may account for the unusually low activation parameters, and we are not presently in a position unambiguously to eliminate these possibilities.

The cycloocta-1,3,5-triene complex [Fe(CO)$_3$(η^4-C$_8$H$_{10}$)] **8** exhibits dynamic behaviour on the NMR time-scale[15] such that E_a = 40.2 kJ mol^{-1} and $\Delta H^‡$ = 42.7 kJ mol^{-1}. These parameters fall nicely between those for the cycloheptatriene complex **3** and the cyclooctatetraene complex **5**, and are very different for those for **7**. On this evidence we conclude that the 1,3,5-C$_8$H$_{10}$ ligand is 1,3-bound as in **F** and not 1,5 as in **G**.

There are undoubtedly other factors which contribute to the barrier to carbonyl exchange. Consider the trienone complex [Fe(CO)$_3$(η^4-C$_7$H$_6$O)] [C$_7$H$_6$O = cyclohepta-2,4,6-trien-1-one(tropone)]. With a bite angle of 65.8°[18] we predict an activation enthalpy of *ca.* 40 kJ mol^{-1}. In fact the measured value is 49.8 kJ mol^{-1}, some 10 kJ mol^{-1} higher.[15] Kruczynski and Takats[15] comment that the relatively low-lying lowest unoccupied molecular orbital (brought about by the CO group of the tropone) makes tropone a significantly better π acceptor, and with a Δ value of −0.07 Å for the η^4-tropone ligand there are some crystallographic data to support this. The scope of two-dimensional correlations (such as E_a with θ_1) to account for trends in fluxional behaviour is clearly not limitless, but they seem to be of value when comparing structurally similar compounds.

Conclusion

The syntheses, crystal structures and solution dynamic behaviour of [M(CO)$_3$(η^4-C$_4$H$_4$Bu$^t_2$)] (M = Fe or Ru) are summarised. The structures show that the molecules adopt square-pyramidal geometries in the solid state. The activation barriers to carbonyl exchange are the largest known for simple 1,3-diene complexes of iron and ruthenium. A correlation between the diene 'bite' angle θ_1 and E_a is noted and used to account for the trend in activation parameters in a range of [M(CO)$_3$(diene)] complexes.

Experimental

All manipulations of air- and moisture-sensitive materials were carried out using standard vacuum and Schlenk techniques or in a dry-box under an atmosphere of nitrogen. All solvents were dried and purified by refluxing over a suitable drying agent, followed by distillation under a nitrogen atmosphere. Toluene was dried over molten sodium, light petroleum (40–60 °C) over sodium–potassium alloy (NaK$_{2.2}$) and tetrahydrofuran over molten potassium. Chromatography was performed on columns of silica (Fluka) under a nitrogen atmosphere.

Nuclear magnetic resonance spectra were recorded using Bruker ACF-250 and Bruker ACP-400 spectrometers. Spectra were referenced using the resonances of residual protons in the deuteriated solvents. The variable-temperature unit was calibrated from a second thermocouple inserted in a dummy sample. Temperatures were accurate to ±2 K. Infrared spectra

Table 6 Crystal data for $[M(CO)_3(\eta^4\text{-}C_4H_4Bu^t_2)]$ (M = Fe **1** or Ru **2**)[a]

	1	**2**
(*a*) Crystal parameters		
Formula	$C_{15}H_{22}FeO_3$	$C_{15}H_{22}O_3Ru$
M	306.2	351.4
a/Å	6.548(2)	6.648(3)
b/Å	10.158(6)	10.137(4)
c/Å	13.016(16)	12.879(6)
α/°	99.04(3)	99.47(4)
β/°	93.20(3)	93.40(4)
γ/°	106.63(3)	106.80(3)
U/Å^3	814.6	814.3
Crystal dimensions/mm	0.15 × 0.14 × 0.21	0.19 × 0.43 × 0.71
Colour	Yellow	Colourless
D_c/g cm^{-3}	1.248	1.433
μ(Mo-Kα)/mm^{-1}	0.93	0.96
Transmission (minimum, maximum)	0.86, 0.90	0.75, 0.87
T/K	230	240
(*b*) Data collection		
Data collected (h,k,l)	7, ± 12, ± 15	8, ± 12, ± 14
Reflections collected	3126	4099
Independent reflections	2862	3776
Independent observed reflections [$F_o \geqslant 4\sigma(F_o)$]	2238	3560
Variation in standards	< 0.01	< 0.02
(*c*) Refinement		
R[b]	0.052	0.027
R'[c]	0.069	0.028
Δ/σ_{max}	0.01	0.01
$\Delta\rho$/e Å^{-3}	0.56	0.42
N_o/N_v[d]	11.9	19.3
Goodness of fit	1.39	0.81
Weighting scheme, w^{-1}	$\sigma^2(F) + 0.0011F^2$	$\sigma^2(F) + 0.002F^2$

[a] Data collected on a Siemens R3m diffractometer; graphite-monochromated Mo-Kα radiation (λ = 0.710 73 Å); $2\theta_{max}$ = 50 (**1**) or 55° (**2**); three standards every 197. Anisotropic thermal parameters used for all non-H atoms. Hydrogen atoms were given fixed isotropic thermal parameters, U = 0.05 Å^2. Most hydrogen atoms were inserted at calculated positions and fixed; the four hydrogen atoms on the diene skeleton [H(8)–H(11)] were located in the difference map and their positions refined. Details in common: triclinic, space group $P\bar{1}$; Z = 2. [b] $R = \Sigma|F_o - F_c|/\Sigma F_o$. [c] $R' = \Sigma(|F_o - F_c|w^{\frac{1}{2}})/\Sigma(F_o w^{\frac{1}{2}})$. [d] N_o = Number of observations, N_v = number of variables.

were measured using a Perkin-Elmer 1720X FTIR spectrometer, mass spectra [electron impact (EI) and chemical ionisation (CI)] using a Kratos MS80 spectrometer. Microanalyses were made using a Leeman Labs CE440 analyser.

Preparations.—$[Fe(CO)_3(\eta^4\text{-}C_4H_4Bu^t_2)]$ **1**. A mixture of $C_4H_4Bu^t_2$ (0.5 g, 3.0 mmol) and $[Fe_2(CO)_9]$ (1.0 g, 2.75 mmol) in light petroleum (50 cm^3) was heated under reflux for 1 h. The solvent was removed *in vacuo*. The green residue was extracted with light petroleum (30 cm^3) and the solution filtered. The solution was concentrated, and complex **1** purified by chromatography on silica. Elution with light petroleum gave, upon removal of solvent, 0.22 g (26%) of a yellow powder. The complex may be further purified by sublimation at 30 °C, 10^{-3} mmHg (m.p. 44–46 °C).

$[Ru(CO)_3(\eta^4\text{-}C_4H_4Bu^t_2)]$ **2**. A mixture of $C_4H_4Bu^t_2$ (0.09 g, 0.52 mmol) and $[Ru_3(CO)_{12}]$ (0.1 g, 0.16 mmol) in toluene (20 cm^3) was heated to 140 °C for 92 h in a sealed ampoule. The solvent was removed *in vacuo*. The red residue was extracted with light petroleum (30 cm^3) and the solution filtered. Removal of solvent gave 0.08 g (44%) of a pale yellow powder. Complex **2** may be further purified by sublimation at 40 °C, 10^{-3} mmHg (m.p. 79–81 °C).

Crystal-structure Determinations.—Crystallographic data for complexes **1** and **2** are summarised in Table 6. Suitable single crystals were grown by slow sublimation, glued to quartz fibres, coated in Nujol and cooled in the cold nitrogen gas stream of the diffractometer. Encasing the crystal in frozen oil prevented aerial oxidation for the duration of the data collection. The data were corrected for Lorentz, polarisation and absorption effects (by the Gaussian method). The iron atom of **1** was located by the Patterson method and the light atoms by successive Fourier syntheses. The solution of **1** was used for the refinement of the structure of **2**, with the iron atom replaced by ruthenium.

All computing was carried out with the SHELXTL PLUS[20] program on a DEC Micro-Vax II computer. Final non-hydrogen atomic coordinates are given in Table 2, with selected bond lengths and angles of Table 3.

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

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