^{13}C Nuclear Magnetic Resonance Study of the Trinuclear Metal Carbonyls $M_3(CO)_{12}(M = Fe, Ru and Os)$ and some Related Compounds

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Summary Variable temperature ^{13}C n.m.r. spectra of the
carbonyls $M_3(CO)_{12}$ (M = Fe, Ru, and Os) and other
related compounds have been recorded; at least three
CO scrambling processes have been shown to operate
in these systems.

ALTHOUGH the molecular geometries of $Fe_3(CO)_{12}{}^1$ (1),
$Ru_3(CO)_{12}{}^2$ and $Os_3(CO)_{12}{}^3$ (2) in the crystalline state have
been determined with accuracy the structures adopted by
these molecules in solution remain uncertain. Gansow et

(1)

M = M' = Fe n = 0
M = Fe, M' = Ru n = 0
M = Fe, M' = Mn n = 1

(2)
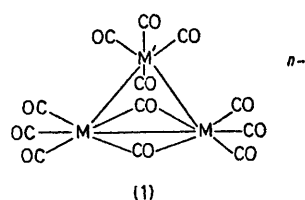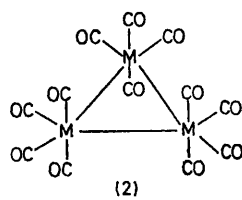
M = Ru or Os

$al.^4$, and Cotton[3,5] have shown conclusively that $Fe_3(CO)_{12}$
undergoes rapid CO scrambling in solution and Cotton and
Troup have predicted[1] and verified[5] that the activation

energy for this scrambling process is $\leqslant 5$ kcal mol^{-1}, thus
excluding the possibility that the predominant solution
structure may be obtained by recording a ^{13}C n.m.r. spec-
trum in the slow exchange limit.[†] I.r. studies indicate that
$Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ adopt the same geometry in solu-
tion as the solid. We now report variable temperature
^{13}C n.m.r. studies on $Os_3(CO)_{12}$ which support this view; also
^{13}C n.m.r. studies on other related trinuclear carbonyls.

At 100°C the ^{13}C n.m.r. spectrum of $Os_3(CO)_{12}$ shows a
single sharp absorption at $\delta 176 \cdot 4$. Upon cooling this signal
broadens and reaches a coalescence point at ca. 70°. On
further cooling to 10° the resonance is resolved into two
sharp lines ($\delta 182 \cdot 3$ and $\delta 170 \cdot 4$) of relative intensity
$1 : 1$ as expected for structure (2) possessing D_{3h} symmetry.[‡]
The other $M_3(CO)_{12}$ molecules examined, namely $RuFe_2$-
$(CO)_{12}$, $Ru_3(CO)_{12}$ and $[MnFe_2(CO)_{12}]^-$ show a single reson-
ance over a similar temperature range (see Table) implying
a lower rearrangement barrier. Because of the poor
solubility of these carbonyls we were unable to record these
spectra at temperatures lower than those shown in the
Table and their limiting spectra have not been measured.

On the basis of their i.r. spectra in solution, $Fe_2Ru(CO)_{12}{}^6$
and $Fe_2Mn(CO)_{12}^-{}^7$ molecules possess a structure similar to
that of $Fe_3(CO)_{12}{}^{-1}$ It is reasonable to assume, therefore,
that the scrambling of CO ligands over the trinuclear metal
skeleton occurs via pair-wise bridge–terminal interchange
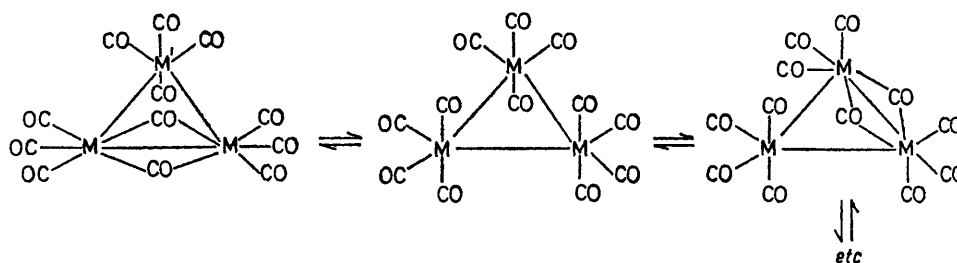of the type first postulated by Cotton[1] (Scheme 1).

[†] Cotton and Troup predict a coalescence temperature of less than $-160°$ which they confirmed by experiment.[5]

[‡] No ^{13}C ^{13}C coupling was resolvable (i.e., $J < 1$ Hz), although clearly observable (J ca. 77 Hz) in $Os_6(CO)_{18}$ of identical ^{13}C enrichment (unpublished data).
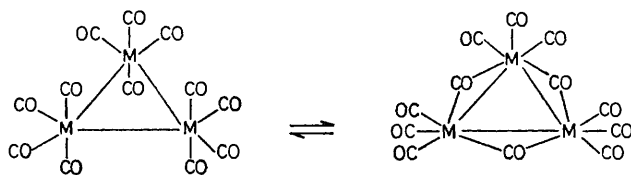
SCHEME 1

TABLE. ¹³C n.m.r. chemical shifts of the CO resonances in trinuclear carbonyl derivatives

Complex	Carbonyl[a]	Chemical shift δ p.p.m.[b]
Fe₃(CO)₁₂ −20—+40°	Av.	212·9
RuFe₂(CO)₁₂ −30—+40°	Av.	206·4
Ru₃(CO)₁₂ −50°—+40°	Av.	199·7
Os₃(CO)₁₂ + 100°	Av.	176·4
+10°[d](Tc ca. 70°)	T axial (2) equatorial (2)	182·3(1), 170·4(1)
[MnFe₂(CO)₁₂]⁻ −85—+40°	Av.	223·3
Ru₃(CO)₁₀(NO)₂ −50—+40°	Ru(CO)₄, T Ru(CO)₃, T	198·4 (4)[c] 196·6 (4), 182·8(2)
[HFe₃(CO)₁₁]⁻ +40°	Av.	221·0
−30°	B.	259·8 (1)
(Tc ca. 0°)	Av.	214·8 (10)

[a] All spectra recorded for isotopically enriched [¹³CO] samples (ca. 70%) in presence of Cr(acac)₃; Av = average, T = terminal, B = bridging; [b] Relative intensities in parenthesis. Chemical shifts were measured relative to the internal solvent resonance and are reported in p.p.m. (from Me₄Si) using the following conversions: $\delta_{Me_4Si} = \delta_{CH_2Cl_2} - 54·2$ p.p.m., $\delta_{Me_4Si} = \delta_{CHCl_3} - 77·2$ p.p.m. All chemical shifts were found to be reproducible to within ± 0·1 p.p.m.; [c] This resonance is assigned to the Ru(CO)₄ unit by analogy with Ru₃(CO)₁₂; [d] Spectrum unchanged down to +10°.

In contrast, in the crystalline state the M₃(CO)₁₂ molecules (M = Ru or Os) have structures without CO bridging groups (2). For these, rearrangement could occur via either or both of the following mechanisms:


M₃ = Ru₃ or Os₃

SCHEME 2

(i) Scrambling through the intermediacy of an asymmetric bridged species of the type shown for Fe₃(CO)₁₂ (Scheme 1) or the more symmetrical three CO-bridged species (Scheme 2).

(ii) Interconversion CO_ax ⇌ CO_eq via a simple twist mechanism about an individual metal atom which does not necessitate the transfer of CO groups from one metal atom to another. Thus, structure (2a) can be converted to structure (2b) by bending the CO–M–CO equatorial angle

to 180°, and decreasing the CO–M–CO angle to 120° followed by the rotation of the M(CO)₄ unit by 90°. (Scheme 3).

Both mechanisms are viable and apparently have similar rates. Mechanism (i) is clearly allowed from Cotton's[1,6] observations on Fe₃(CO)₁₂ and our observations on Fe₂Ru-(CO)₁₂. The latter exhibits one signal over the temperature range (−30—+40°) indicating that CO scrambling over the
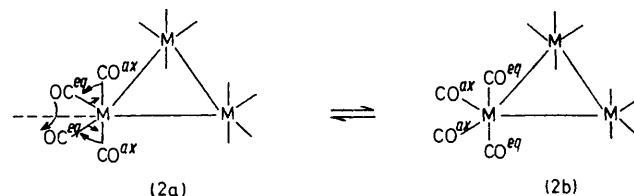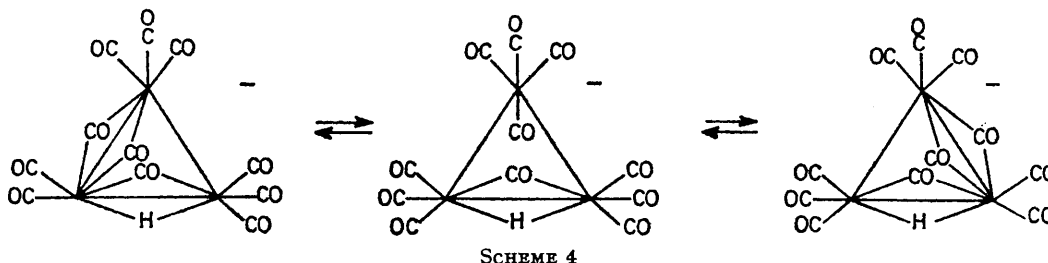

SCHEME 3

RuFe₂ cluster is occurring since localised scrambling about the Ru(CO)₄ unit according to mechanism (ii) together with terminal-bridge CO exchange over the Fe₂(CO)₈ unit would lead to two time averaged signals of relative intensity 1:2. However, neither our observations nor those of Cotton permit the differentiation of the two possible types of CO bridge–terminal exchange [mechanism (i)]. The plausibility of mechanism (ii) follows from our study of Ru₃(CO)₁₀-(NO)₂ (3). This molecule is reported[8] to have a structure related to that of Fe₃(CO)₁₂ involving two bridging NO ligands. The Ru(CO)₄ unit within this structure possesses a geometry identical to that in Ru₃(CO)₁₂. In the tempera-

M = Ru or Os

(3)   (4)
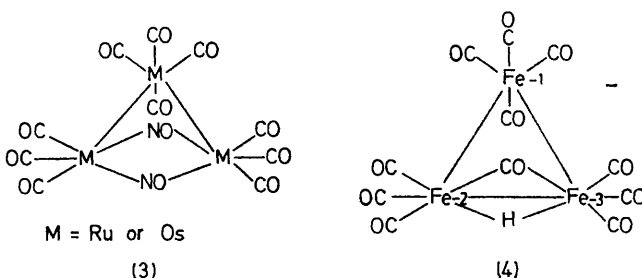
ture range −50°—+40° the ¹³C n.m.r. remains unchanged exhibiting three signals with relative intensity 4:4:2. This corresponds to structure (3); the equivalence of the axial and equatorial CO groups on the Ru(CO)₄ unit (see Table) indicating that localised CO scrambling must be occurring via mechanism (ii) since, because the two Ru(CO)₃ units are observed to be rigid, CO-bridged intermediates cannot be available to the molecule. The higher barrier to interconversion within the Ru(CO)₃ units is in keeping with earlier observations of Ru(CO)₃[9] and Fe(CO)₃[10] species. Stereochemical non-rigidity involving axial–equatorial

interchange has also been observed with Fe(CO)₄(AuPPh₃)₂. This molecule exhibits only one ¹³CO resonance over a wide temperature range. In contrast Fe(CO)₄Br₂ is rigid exhibiting two resonances over the same range.§

The anion [HFe₃(CO)₁₁]⁻ possesses a structure in the solid closely related to that of Fe₃(CO)₁₂[11] (4). At −30° in solution

Any mechanism involving the formation of single bridges would not maintain electroneutrality throughout the anion. However, unlike mechanism (i) discussed above this corresponds to an oscillation rather than a complete migration of CO groups. Thus two CO bridges are formed first between Fe-1 and Fe-2, then Fe-1 and Fe-3 and the process is
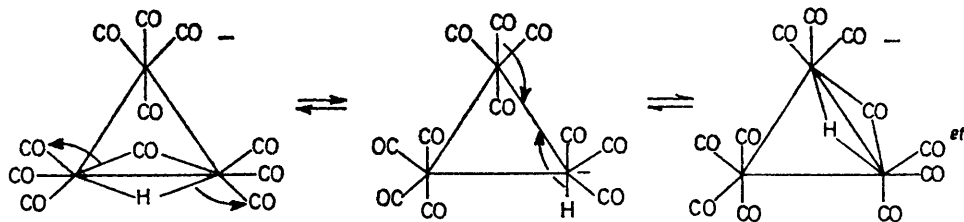

Scheme 4

two signals are observed. One of intensity 1 falls in the bridging region at δ 259·8 and the other of intensity 10 at δ 214·8 p.p.m. At higher temperatures (ca. +40°) one resonance at δ 221·0 p.p.m. is observed. These observations lead to two conclusions. First, in the slow exchange

repeated. In the high temperature limit total scrambling of CO ligands occurs presumably via an intermediate containing only terminally bonded CO groups (Scheme 5) a process which, not unexpectedly, has a higher rearrangement energy.

Scheme 5

limit, ten of the eleven CO ligands are undergoing a scrambling process (δ 214·8) whilst the eleventh bridging CO group is static. Bridge–terminal exchange is therefore of the type shown in Scheme 4 and must occur via the pair-wise opening and closing of bridges.

§ These spectra will be discussed in a full report of this work.

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[9] See e.g., A. J. Canty, B. F. G. Johnson, J. Lewis, and J. R. Norton, J.C.S. Chem. Comm., 1972, 1331.
[10] See e.g. L. Kruczynski and J. Takats, J. Amer. Chem. Soc., 96, 932; G. Rigatti, G. Boccalon, A. Ceccon, and G. Ciaconnetti, J.C.S. Chem. Comm., 1972, 1165.
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