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Double oxidative addition of C–H bonds on a triruthenium cluster complex; synthesis and characterization of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)=C(H)\}(CO)_9$ and $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)N(Me)C(H)\}(CO)_9$ *

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Abstract

Titration of $Ru_3(\mu\text{-}H,\mu\text{-}O{=}C(CH_3))\}(CO)_{10}$ (**1**) with $LiCH_3$ in diethyl ether at −30 °C leads to its instantaneous conversion into $[Li][Ru_3\{\eta^1\text{-}C(O)CH_3\}\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9]$. Alkylation with $C_2H_5OSO_2CF_3$ at 25 °C leads after 48 h to $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)\}(CO)_9$ (**3**) in 80% yield; acetaldehyde is obtained as a by-product. Use of $LiCD_3$ in the first step of this sequence gives unlabeled acetaldehyde and the trinuclear product $Ru_3\{\mu\text{-}D_2,\eta^2,\mu_3\text{-}C(OEt){=}C(D)\}(CO)_9$. Starting with $Ru_3\{\mu\text{-}H,\mu\text{-}C(O)CD_3\}(CO)_{10}$ and $LiCH_3$, the reaction gives $CD_3C(O)H$ and no deuterium incorporation into the triruthenium product.

Under an atmosphere of CO, acetaldehyde is still eliminated from the initial alkylation product but oxidative addition is prevented; IR spectroscopy indicates that a new complex is present, but this has eluded characterization owing to its rapid conversion to **3** under conditions used in attempts to isolate or purify it.

Reaction of **1** with LiPh or $LiCMe_3$ followed by alkylation with $C_2H_5OSO_2CF_3$ also gives **3**, along with the corresponding aldehyde RC(O)H. Reaction of **1** with $HNMe_2$ followed by alkylation with $C_2H_5OSO_2CF_3$ gives $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)N(Me)C(H)\}(CO)_9$ (45% yield).

Introduction

Earlier [2] we reported the synthesis of a Fischer-type carbene group on a triosmium cluster complex, $Os_3\{1\text{-}\eta^1\text{-}C(OR')R\}\{\mu\text{-}H,\mu\text{-}O{=}CMe\}(CO)_9$, which was

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* Dedicated to Professor Luigi Sacconi.

** Taken in part from the Dissertation of C.M. Jensen [1a].

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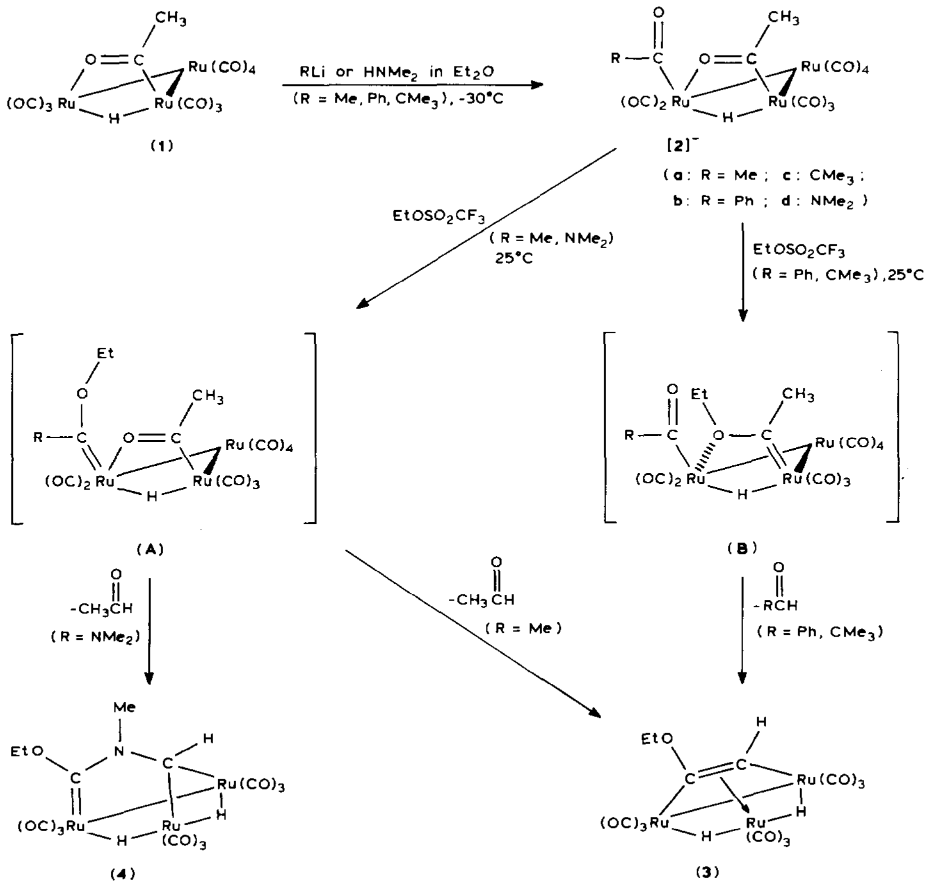
accomplished by alkylation of the salt, $[Li][Os_3\{C(O)R\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9)]$. Treatment of the analogous triruthenium salts (R = CH_3, C_6H_5, $C(CH_3)_3$, and $N(CH_3)_2$) with $C_2H_5OSO_2CF_3$, by contrast, results in transformations beyond the initial alkylation [1]. Characterization of the products obtained in these reactions as well as elucidation of the reaction pathway through isotopic labeling are described in full in this paper.

Results

The formation of the products **3** and **4** of double C–H oxidative-addition is summarized in Scheme 1. Characteristic infrared absorptions in the carbonyl stretching region for the new products and the anions from which they are derived are given in Tables 1 and 2. The postulated intermediates **A** and **B** in Scheme 1 are considered in the Discussion section.

Titration of $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_{10}$ (1) with $LiCH_3$ at −30°C. The titration of **1** [3] is carried out in dry, freshly distilled diethyl ether with a solution of $LiCH_3$ (1.6 *N* in diethyl ether). This leads instantaneously to $[Li][Ru_3(\eta^1$-



SCHEME 1.

Table 1

IR spectral data for new compounds

Compound	IR ^{a} (cm^{-1})
$Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)\}(CO)_9$ (**3**) ^{b}	2108w, 2080s, 2056vs, 2040s, 2034w, 2018m, 2013w, 2008m, 1995w, 1988vw
$Ru_3\{\mu\text{-}D_2,\eta^2,\mu_3\text{-}C(OEt){=}C(D)\}(CO)_9$ (**3**-d_3)	2106w, 2078s, 2053vs, 2040s, 2033w, 2018m, 2013w, 2006m, 1991w, 1988vw
$Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}^{13}C(H)\}(CO)_9$ (**3**-^{13}C)	2107w, 2080s, 2056vs, 2040s, 2033w, 2018m, 2013w, 2008m, 1995w, 1988vw
$Ru_3(\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)N(Me)C(H)\}(CO)_9$ (**4**)	2103w, 2065s, 2051vs, 2024s, 2015s, 2003m, 1999m, 1981w,
$Ru_3\{1,2\text{-}\mu\text{-}O{=}CCD_3;\ 1,2\text{-}\mu\text{-}H\}(CO)_{10}$ (**1**-d_3)	2105w, 2068vs, 2055vs, 2030s, 2018s 2009m, 2004m, 1989w, 1509w (μ-acyl)
$Ru_3\{C(OC_2H_5)CH_3\}(CO)_{11}$ (**5**)	(Et_2O) 2069w, 2035s, 2010vs, 2000s, 1989m

^{a} In hexane unless stated otherwise. ^{b} Compare with absorptions reported for $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OMe){=}C(Me)\}(CO)_9$, cyclohexane; 2015m, 2076s, 2054vs, 2038s, 2030m, 2012s, 2004s, 1998w, 1988w cm^{-1} [17].

$C(O)(CH_3\}(\mu\text{-}H,\mu\text{-}O{=}C(CH_3))\}(CO)_9]$ ([**Li**][**2a**]); its ^1H and ^{13}C NMR spectra are shown in Fig. 1.

The presence of a high field signal (−14.46 ppm) in the ^1H NMR spectrum indicates that nucleophilic alkylation rather than deprotonation has occurred. Despite the thermodynamic acidity of cluster-bonded hydrogen atoms [4], these prove to be removed only slowly, as observed in earlier work on hydridotriosmium cluster complexes [2]. By contrast, only deprotonation is observed in treatment of **1** with CH_3Li at room temperature (see Experimental section).

The presence of two distinct methyl resonances in Fig. 1, both for ^1H (2.70 and 2.41 ppm) and for ^{13}C (266.3 and 249 ppm), indicates that the two different types of

Table 2

IR spectral data for $[Li][Ru_3\{C(O)R\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}O{=}C(R')\}(CO)_9]$

Compound	IR ^{a} (cm^{-1})
$[Li][Ru_3\{C(O)CH_3\}\{1,2\text{-}\mu\text{-}H;\text{-}1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9)]$ [**Li**][**2a**]	2075m, 2033s, 2008s, 1999vs, 1968m, 1932m, 1571w (η^1-acyl), $CHCl_3$ 1424 (μ-acyl)
$[Li][Ru_3\{C(O)CH_3\}\{1,2\text{-}\mu\text{-}H;1,2\text{-}\mu\text{-}\text{-}O{=}C(CD_3)\}(CO)_9)]$ ([**Li**][**2a-O=C(CD$_3$)**])	2075m, 2032s, 2007s, 1999vs, 1965m, 1931m, 1571w (η^1-acyl)
$[Li][Ru_3\{C(O)CD_3\}\{1,2\text{-}\mu\text{-}H;\text{-}1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9)]$ ([**Li**][**2a**-d_3])	2075m, 2033s, 2008s, 1999vs, 1966m, 1932m, 1565w (η^1-acyl)
$[Li][Ru_3\{C(O)^{13}CH_3\}\{1,2\text{-}\mu\text{-}H;\text{-}1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9)]$ ([**Li**][**2a**-^{13}**C**])	2075m, 2033s, 2008s, 1999vs, 1965m, 1931m, 1568w (η^1-acyl)
$[Li][Ru_3\{C(O)C_6H_5\}\{1,2\text{-}\mu\text{-}H;\text{-}1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9]$ ([**Li**][**2b**])	2070m, 2024s, 2000vs, 1964m, 1927w, 1579w (η^1-acyl)
$[Li][Ru_3\{C(O)CMe_3\}\{1,2\text{-}\mu\text{-}H;\text{-}1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9)]$ ([**Li**][**2c**])	2076m, 2034s, 2008vs, 1966m, 1942m, 1565w (η^1-acyl)
$[Li][Ru_3\{C(O)NMe_2\}\{1,2\text{-}\mu\text{-}H;\text{-}1,2\text{-}\mu\text{-}O{=}C(Me)\}(CO)_9)]$ ([**Li**][**2d**])	2087m, 2042s, 2006vs, 1964m, 1939m, 1529w (η^1-acyl)

^{a} All spectra in Et_2O (unless stated otherwise).

acyl groups do not exchange on the NMR time scale; experiments with ^{13}C and deuterium labelled complexes presented below, indicate that there is also no exchange during longer periods. Possible reasons for this are presented in the Discussion section. Use of Li^{13}CH$_3$ in the first step of Scheme 1 gives rise to the regiospecifically ^{13}C-labeled product, $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}^{13}C(H)\}(CO)_9$ (**3**-*^{13}C*), presumably through a regiospecifically labelled anion $[Ru_3\{\eta^1\text{-}C(O)^{13}CH_3\}\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9]^-$ ([**2a**-*^{13}C*]$^-$), which is consistent with the non-exchange of acyl groups indicated in the NMR spectra of the anion [**2a**$^-$] (Fig. 1). Formation of regiospecifically labeled product establishes that the non-exchange of acyl groups persists outside the NMR time scale, and must also persist in intermediates **A** or **B** shown in Scheme 1.

The non-exchange of acyl groups is further confirmed through a second labeling experiment. The regiospecifically-labeled starting material $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(^{13}CH_3)\}(CO)_{10}$ (**1**-*^{13}C*), was synthesized from $Ru_3(CO)_{12}$ and Li^{13}CH$_3$. When this is treated with un-labeled LiCH$_3$, followed by alkylation, the trinuclear product **3** contains no ^{13}C.

Alkylation of [**Li**][**2a**]; *formation of* $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)\}(CO)_9$, *(3).* The solution of [**Li**][**2a**] is warmed to room temperature and treated with two equivalents of $C_2H_5OSO_2CF_3$ [5]. The IR spectrum shows no initial change, and 48 h stirring is required for complete disappearance of the absorptions of [**2a**$^-$]. Monitoring of the reaction by GC reveals that an essentially quantitative amount of acetaldehyde formed. Upon completion of the reaction, the solvent is removed and the solid residue extracted with 30 ml of pentane. Evaporation of the orange-red pentane extract gives orange crystals of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)\}(CO)_9$ (**3**), in 80% yield. This sequence is summarized by the route **1/2a/A-3** in Scheme 1. The overall molecular formula of **3** is established by the parent ion multiplet in the mass spectrum (see Experimental Section, below). Similar alkylation of [**Li**][**2a**-*^{13}C*] gives $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}^{13}C(H)\}(CO)_9$ (**3**-*^{13}C*).

Characterization of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)\}(CO)_9$ *(3).* The ^{1}H NMR spectrum of **3** is shown in Fig. 2. The resonances of an intact ethyl group are recognized as the triplet and quartet, respectively. Instead of a singlet of intensity 3 expected in the region for an α-methyl group of a carbene [6], a singlet of intensity 1 corresponding to a vinyl proton and a singlet of intensity 2 corresponding to two (rapidly averaging) metal hydrides are observed (see Fig. 2). It is apparent that the methyl group of the Fischer-carbene in intermediate **A** has undergone double oxidative addition onto the cluster framework giving rise to the structure shown in Scheme 1. This is one of three possible tautomers and is the one consistent with all the spectroscopic data, as shown in the Discussion section below; ^{13}C NMR spectra of **3** and **3**-*^{13}C* are shown in Fig. 3. The upper trace shows a specifically enhanced intensity of the resonance at 74.2 ppm, assigned as =*C*H of the C(OEt)–CH group the *C*(OEt)= resonance of this group appears as the doublet centered at 218 ppm. The coupling constant shown has a value intermediate between that observed for carbon–carbon double and carbon–carbon triple bonds, as shown in the insert, Fig. 3. The ^{13}C–^{1}H coupling constant in *C*H is observed in the ^{1}H and the off-resonance decoupled ^{13}C NMR spectra of **3**-*^{13}C*, Fig. 4; the values of 158 and 159 Hz, are close to that for $^{13}C_{sp^2}$-H, as indicated in the insert, Fig. 4.

The appearance of the signals in the carbonyl region of the ^{13}C NMR spectrum at room temperature reflects some exchange processes; a limiting spectrum is

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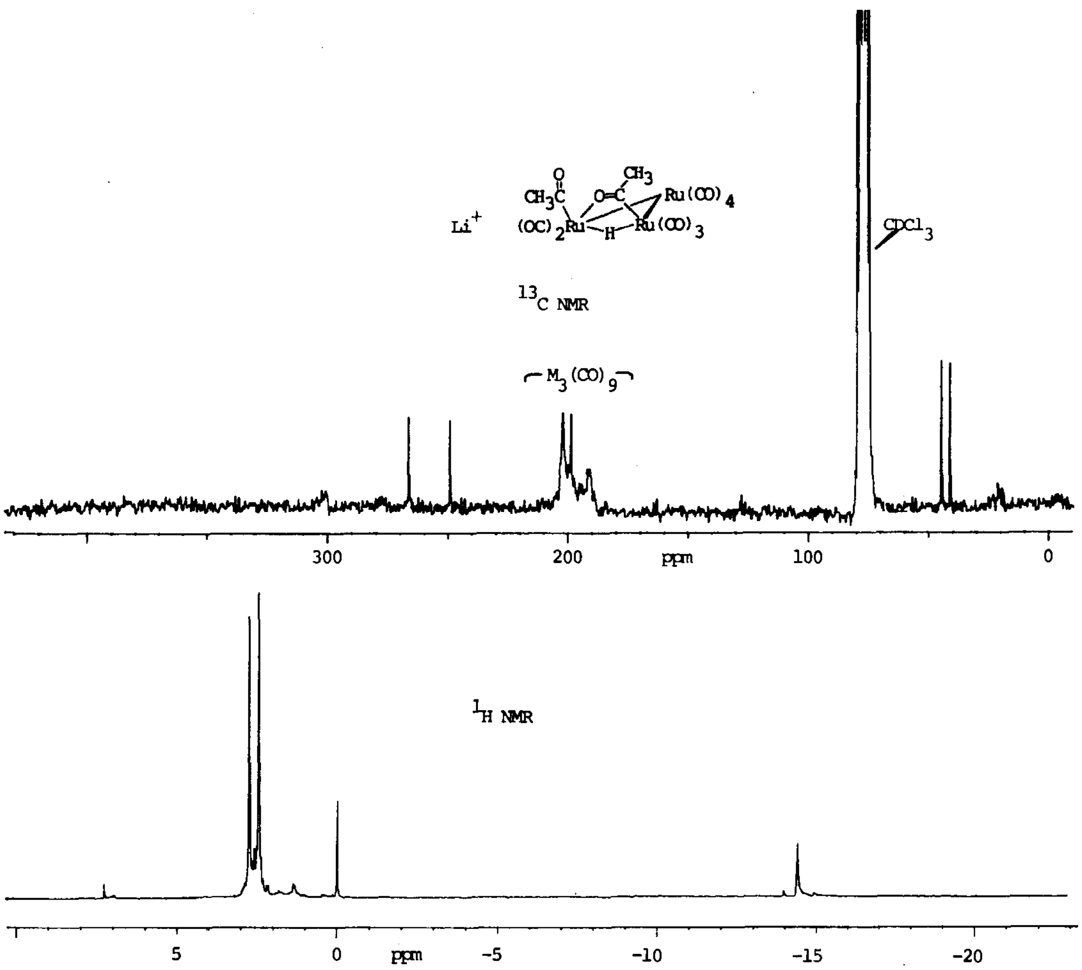

Fig. 1. NMR spectra for [Li][Ru_3{C(O)CH_3}{1,2-μ-H;1,2-μ-O=C(Me)}$(CO)_9$)] (**[Li][2a]**). Upper scan, {^{1}H}^{13}C, in C_6D_6, 25 °C, δ, ppm, (rel. int.): 266.3 (1), 249.1 (1); CO region, 202.0 (1), 198.4 (4), 190.9 (3), 189.1 (1); 47.5 (1), 41.0 (1). Lower scan, ^{1}H, in $CDCl_3$, δ, ppm (mult., rel. int.): 2.70 (s,3); 2.41 (s,3); −14.46 (s,1).

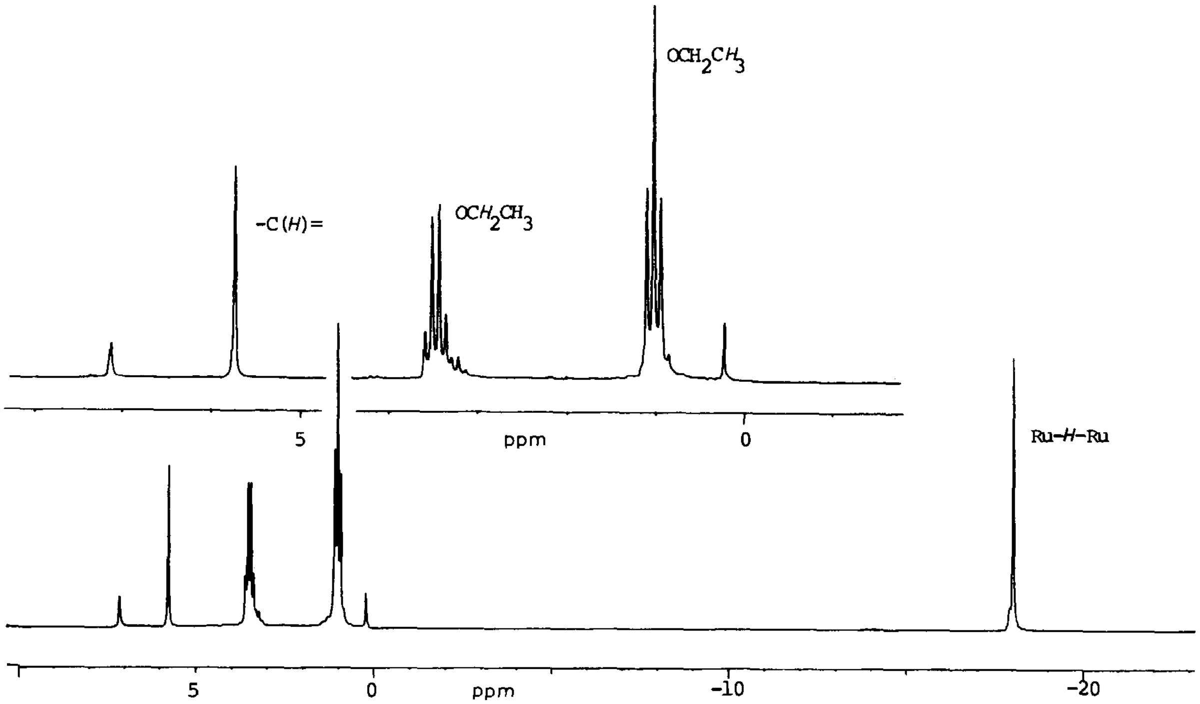

Fig. 2. ^{1}H NMR spectrum of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)\!=\!C(H)\}(CO)_9$ (**3**) in C_6D_6, δ, ppm (mult., rel. int.): 5.75 (s,1), 3.49 (q,2), 1.03 (t,3), −17.98 (s,2) Ru−*H*−Ru.

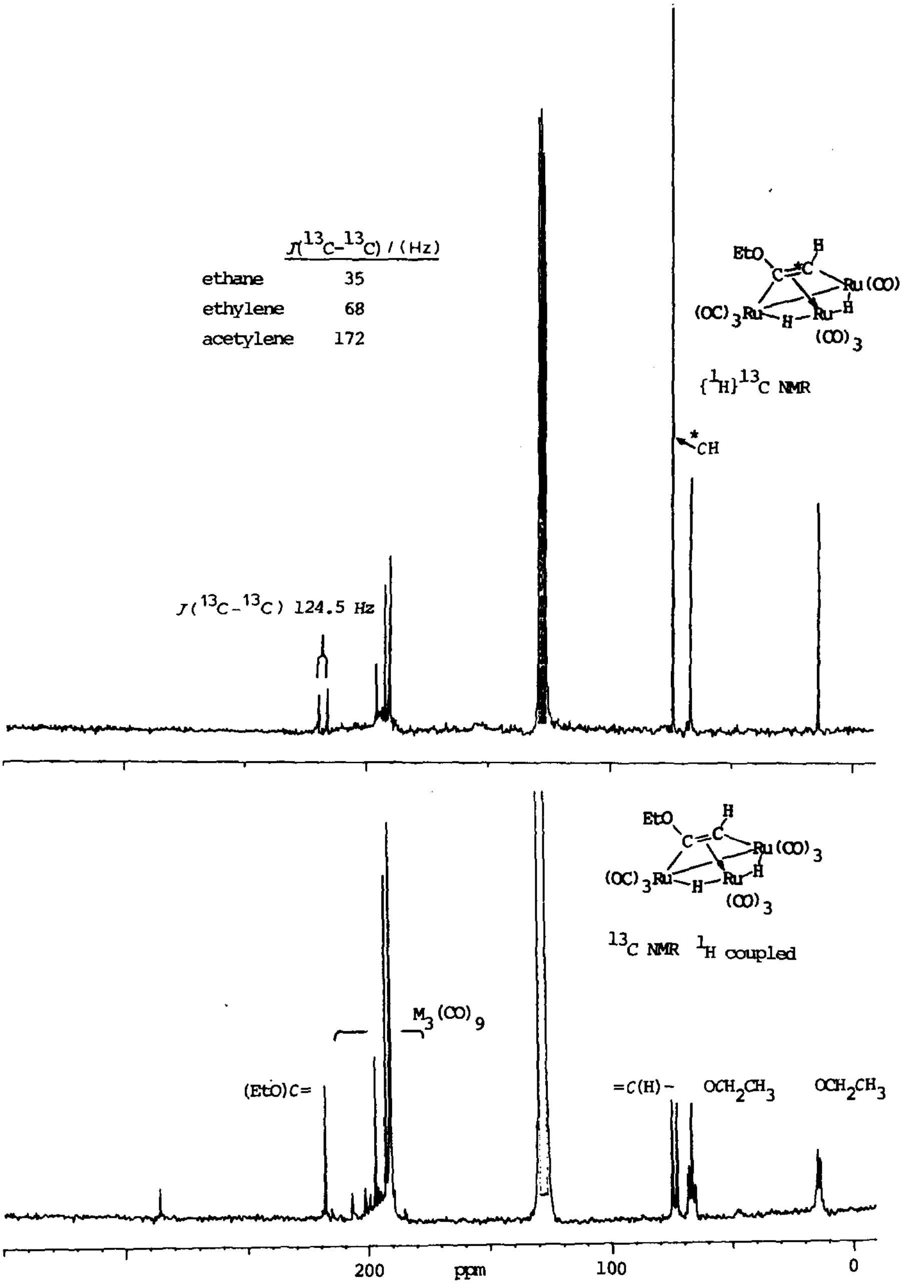

Fig. 3. ^{13}C NMR spectra. Upper scan, for Ru$_3${μ-H$_2$,η^2,μ$_3$-C(OEt)=^{13}C(H)}(CO)$_9$ (3-^{13}C) in C$_6$D$_6$, ^{1}H-decoupled, δ, ppm (rel. int.): 218 (1) (J(^{13}C–^{13}C) 125 Hz); CO region, 197.0 (1), 192.6 (2), 190.6 (6); 74.2 (51), 67.0 (1), 14.2 (1). Lower scan, for Ru$_3${μ-H$_2$,η^2,μ$_3$-C(OEt)=C(H)}(CO)$_9$ (3) in C$_6$D$_6$, off-resonance decoupled, δ, ppm (mult.): 218.0(s), (CO region, 197.0(s), 192.6(s), 190.6(s)), 74.2(d), 67.0(t), 14.2(q). For CO region at −90 °C, see Experimental.

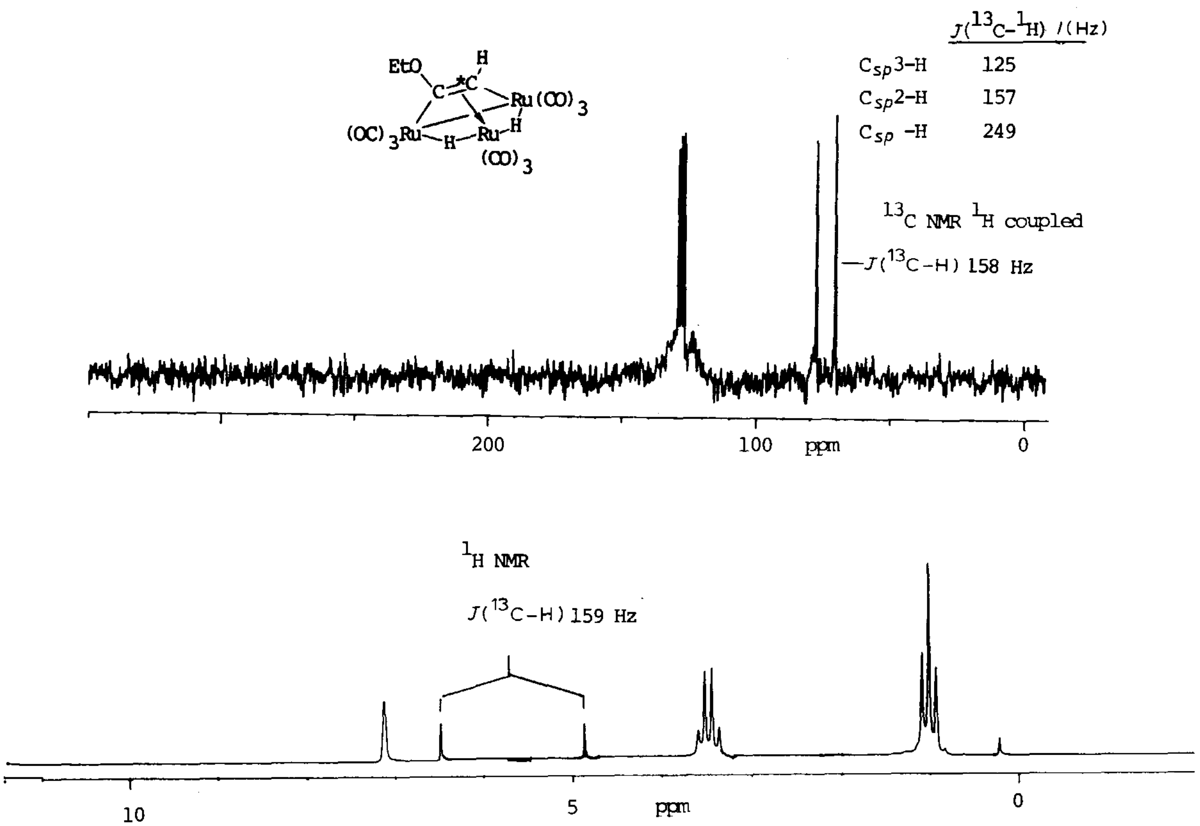

Fig. 4. NMR spectra of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}^{13}C(H)\}(CO)_9$ ($3\text{-}^{13}C$). Upper scan, ^{13}C (^1H-Coupled) in C_6H_6, 74.2 ppm (doublet, $J(^{13}C\text{-}H)$ 158 Hz). Lower scan, ^1H in C_6D_6, δ, ppm (mult., rel. int.): 5.75 (d, $J(^1H\text{-}^{13}C)$ 158 Hz, 1), 3.49 (q,2), 1.03 (t,3); not shown in the Figure: -17.98 (s,2) Ru–H–Ru.

obtained at −90 °C (see Experimental). This contains nine resonances of equal intensity, one for each of the nine carbonyl groups.

Deuterium labeling. Use of $LiCD_3$ in the first step of Scheme 1 gives the trinuclear product $Ru_3\{\mu\text{-}D_2,\eta^2,\mu_3\text{-}C(OEt)=C(D)\}(CO)_9$ (**3**-d$_3$). This formulation is deduced from a combination of ^1H and ^2H NMR spectra in which the ethoxy resonances are seen only in the ^1H NMR (see Experimental) and the vinyl and hydride resonances appear only in the ^1H NMR spectrum (Fig. 5). The mass spectrum of the acetaldehyde produced in this experiment is virtually identical with that of a sample of unlabeled acetaldehyde (Fig. 6A and B), showing no masses higher than 44 nor any formyl fragments of mass higher than 29 beyond the naturally occurring ^{13}C satellite peaks in acetaldehyde.

Alternatively, the deuterium label is placed in the bridging acyl group, $Ru_3\{\mu\text{-}H,\mu\text{-}C(O)CD_3\}(CO)_{10}$ (**1**-d_3), by use of $LiCD_3$ in synthesis of the starting material. Titration of **1**-d_3 with $LiCH_3$ in the first step of Scheme 1 results in no deuterium incorporation in the triruthenium product. The mass spectrum of the acetaldehyde produced in this experiment (Fig. 6C) contains a large parent ion at m/e 47 along with intense formyl (m/e 29) and acylium (m/e 46) fragment peaks. The appearance of these peaks along with only traces of m/e 30 (formyl-d) and m/e 48 (parent-d_4) peaks demonstrates that the acetaldehyde obtained > 95% $HC(O)CD_3$.

Alkylation of $[Li][Ru_3\{\eta^1\text{-}C(O)C_6H_5\}\{\mu\text{-}H,\mu\text{-}O=C(CH_3)\}(CO)_9]$ *[Li][**2b**], and* $[Li][Ru_3\{\eta^1\text{-}C(O)C(CH_3)_3\}\{\mu\text{-}H,\mu\text{-}O=C(CH_3)\}(CO)_9][Li]$*[**2c**].* The reaction of **1** with LiPh and $LiCMe_3$ has also been investigated (see Scheme 1); in these cases the corresponding lithium salts of the η^1-acyl anions [**2b**]$^-$ or [**2c**]$^-$ are obtained. Alkylation of either salt with $C_2H_5OSO_2CF_3$ results in the formation of **3**, along with the corresponding aldehyde RC(O)H. Experimental evidence suggests alkylation via [**B**] rather than [A] in Scheme 1; this is discussed in the next section.

Isolation and characterization of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)NMeC(H)\}(CO)_9$ *(**4**).* Dimethylamine rather than RLi may be used in the first step of Scheme 1. Alkylation of the ion thus formed, [**2d**]$^-$, gives deep orange cyrstals of **4**. The overall molecular formula of **4** is established by the parent ion multiplet in the mass spectrum (see Experimental). The structure of this derivative is deduced by the features in the NMR spectra (Fig. 7). The singlet ^1H resonance of intensity 2 at −16.56 ppm indicates the presence of two rapidly exchanging bridging hydrogen atoms on the trinuclear cluster. The singlet of intensity 1 at 6.78 ppm is in the region expected for an α-proton of a μ-carbene group. For comparison, note the following resonances: for $Os_3\{\mu\text{-}H_2,\mu\text{-}CH_2\}(CO)_{10}$ at 6.12 and 4.32 ppm, [8a]; for $Os_3\{\mu\text{-}CO,\mu\text{-}CH_2\}(CO)_{10}$ at 6.47 and 7.75 ppm, [8b]; and for $Os_3\{\mu\text{-}H_2,\mu\text{-}CHSiMe_3\}(CO)_{10}$ at 8.72 ppm [9].

Confirmation of the groupings shown in Fig. 7 was derived from the off-resonance decoupled ^{13}C NMR spectrum of **3** (see caption to Fig. 7). The appearance of only one resonance in the extreme low field region (252.3 ppm) of the ^{13}C NMR spectrum signifies there is only one terminal carbene carbon in this derivative. This resonance is unaffected in the off-resonance decoupled experiment and can thus be assigned as the (di-heterocarbene) carbon atom. Both the μ-carbene and the $N\text{-}CH_3$ carbon atom resonances may be expected at approximately 40 ppm. For comparison, note the following ^{13}C resonances of bridging methylene groups: for $Os_3\{\mu\text{-}H_2,\mu\text{-}CH_2\}(CO)_{10}$ at 25.8 ppm [8a], and for $Os_3\{\mu\text{-}CO,\mu\text{-}CH_2\}(CO)_{10}$ at 62.5 ppm [8b]. The off-resonance decoupled spectrum provides differentiation between the

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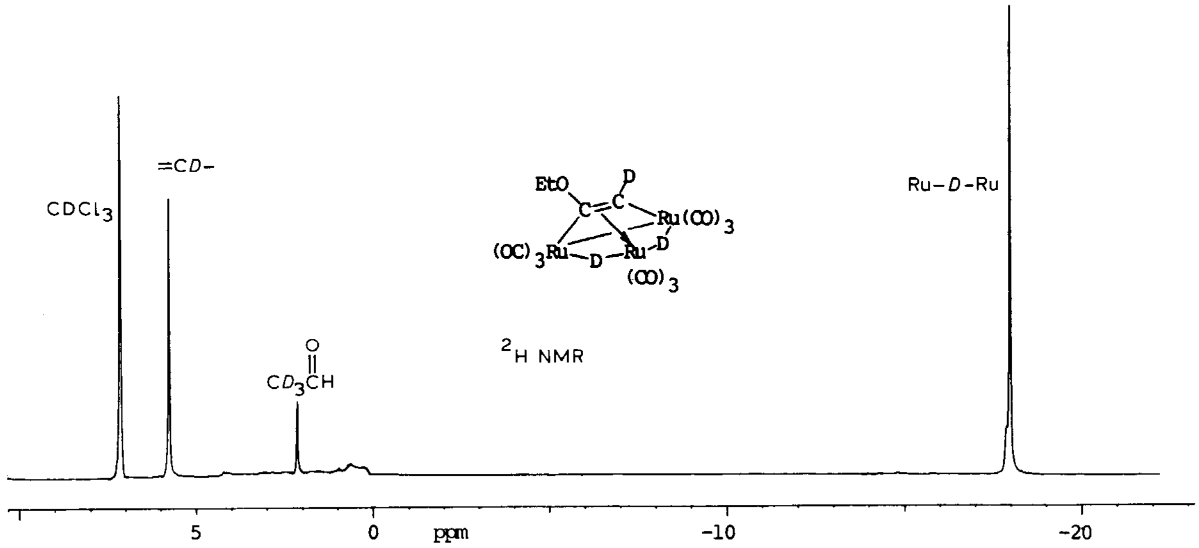


Fig. 5. ^{2}H NMR of $Ru_3\{\mu\text{-}D_2,\eta^2,\mu_3\text{-}C(OEt){=}C(D)\}(CO)_9$, (3-$d_3$), $CHCl_3$ solution, δ (referenced to $CDCl_3$ 7.25), ppm: 6.07 (s,1), 2.17 ($CD_3C(O)H$), −18.00 (s,2).

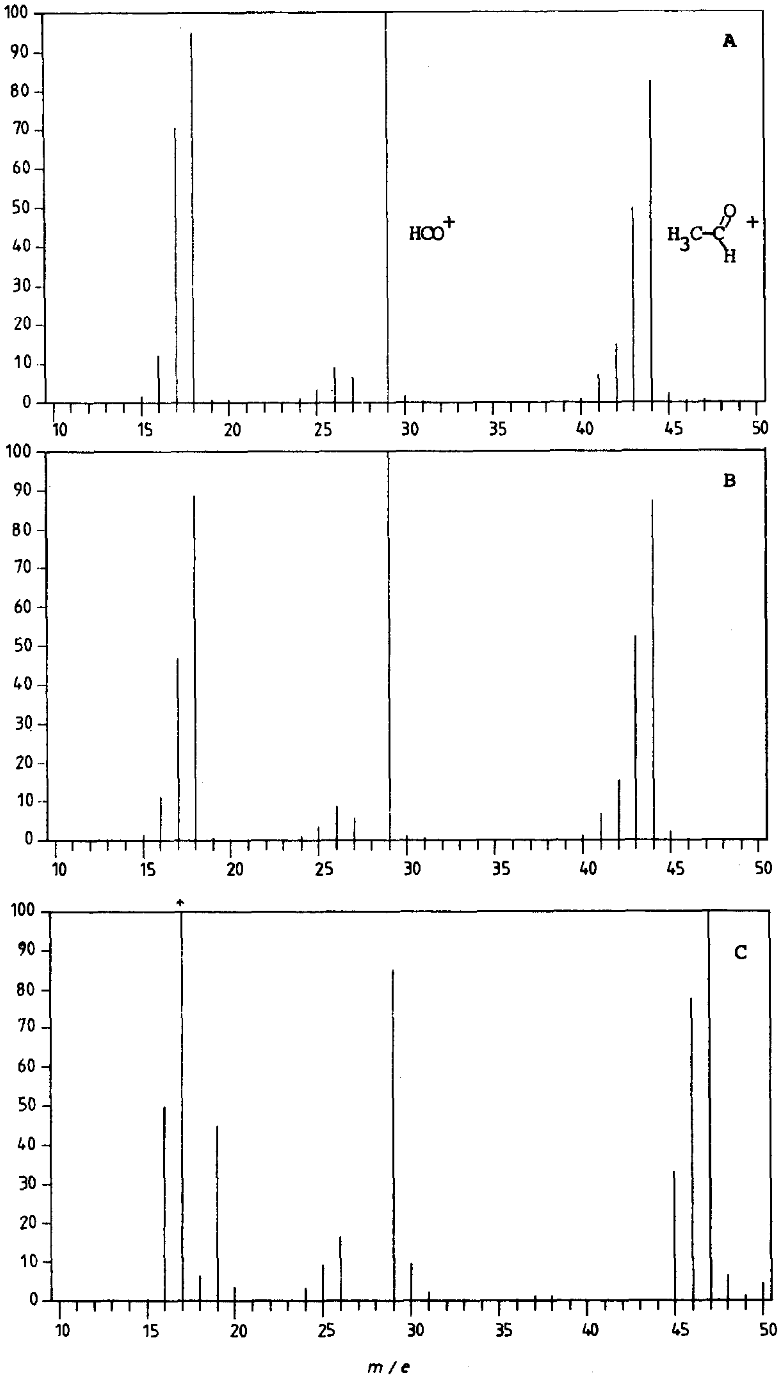


Fig. 6. Mass spectra of acetaldehyde. A, Standard reference. B, Acetaldehyde obtained in the alkylation of $[\mathrm{Li}][\mathrm{Ru}_3\{\eta^1\text{-C(O)CD}_3\}\{\mu\text{-H},\mu\text{-O{=}C(CH}_3)\}(\mathrm{CO})_9]$. C, Acetaldehyde obtained in the alkylation of $[\mathrm{Li}][\mathrm{Ru}_3\{\eta^1\text{-C(O)CH}_3\}\{\mu\text{-H},\mu\text{-O{=}C(CD}_3)\}(\mathrm{CO})_9]$.

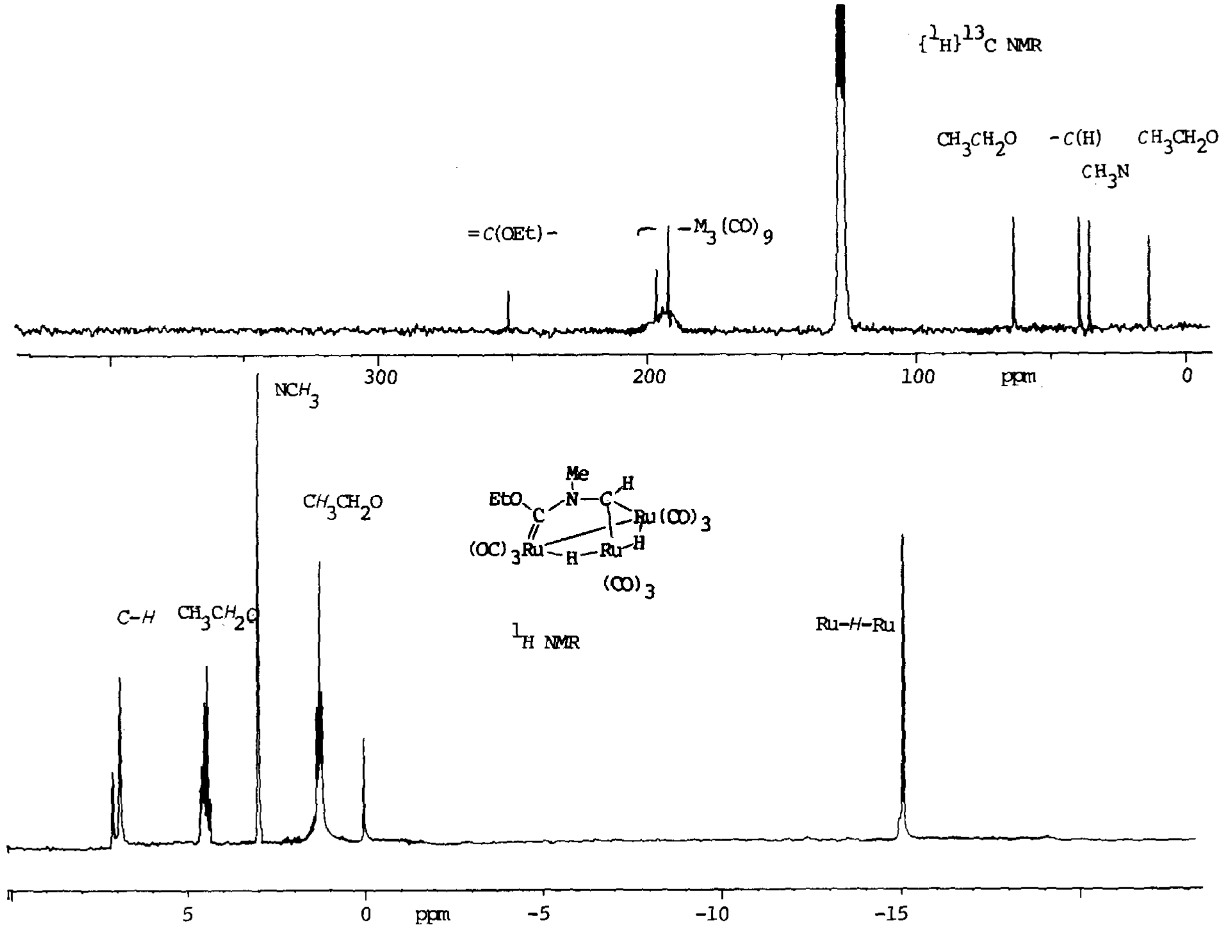
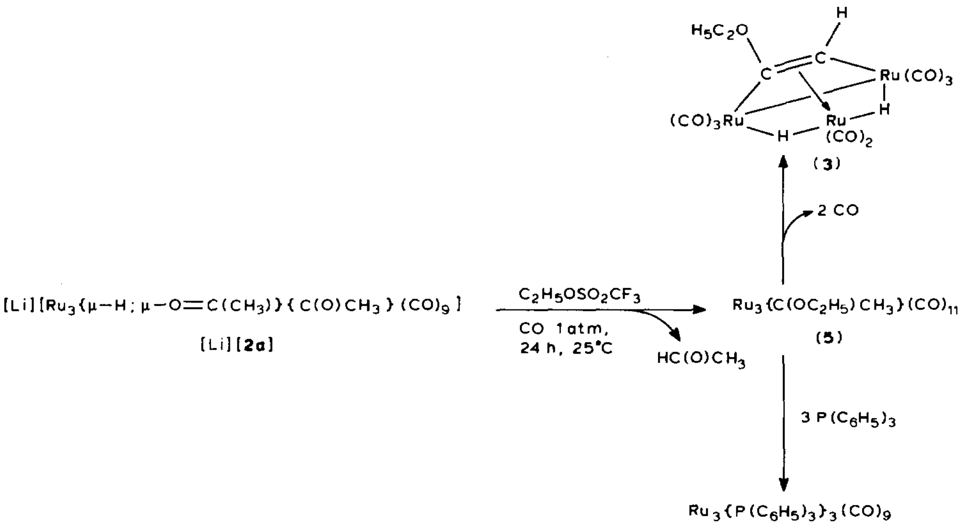


Fig. 7. NMR spectra of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)N(Me)C(H)\}(CO)_9$, (4). Upper scan, {^{1}H}^{13}C in C_6D_6, δ (ppm) (mult., determined under off resonance ^{1}H-decoupling, rel. int.): 252.3 (s,1); CO region, 196.4 (s,3), 191.6 (s,6); 64.7 (t,1); 39.9 (d,1); 37.2 (q,1); 14.1 (q,1). Lower scan, ^{1}H in C_6D_6, δ (ppm) (mult., rel. int.): 6.98 (s,1); 4.42 (q,2); 3.02 (s,3); 1.18 (t,3); −14.97 (s,2).



SCHEME 2.

two resonances in this region: the first appears as a doublet while the second appears as a quartet (see caption Fig. 7).

Competition between the double C–H oxidative addition process and external reagents

Aromatic hydrocarbons. It was decided to carry out the alkylation of **2** in the presence of C_6H_5F or $C_6H_5CF_3$ to see whether C–H activation of these could compete with the intramolecular double oxidative addition, and so parallel studies on mono-nuclear complexes [10] in which it was observed that certain intramolecular C–H oxidative additions are slower than C–H addition of external hydrocarbon. In the competition experiments, the C_6H_5F is added just before alkylation of [Li][**2a**]; IR spectra taken at various intervals show that the absorptions of [**2a**]$^-$ are progressively replaced by those of **3**, with no bands from any other compounds evident. Similar results are obtained in the presence of $C_6H_5CF_3$.

Carbon monoxide. Performing the alkylation of [Li][**2a**] under an atmosphere of CO results in formation of a highly unstable species **5** (Scheme 2), whose IR spectrum differs greatly from that of **3**. A nearly stoichiometeric amount of acetaldehyde is also obtained. Removal of the CO from the solution of **5** results in the rapid conversion of **5** to **3**. Addition of an excess of triphenylphosphine to a solution of **5** results in the instantaneous formation of $Ru_3(CO)_9(P(C_6H_5)_3)_3$ [11].

Discussion

Origin of eliminated aldehyde, alternate site of O-alkylation, and, non-exchange between η^1- and μ-acyl groups

The regio-specifically labeled products derived from isotopic labeling experiments (see Fig. 6 and related text) reveal that there is no exchange between the two different acyl groups in the intermediate anion [**2a**]$^-$. The exchange pathway would require conversion of the μ-acyl group in the η^1,μ isomer into an η^1-acyl group.

$[\eta^1,\mu]^-$ $[\eta^2,\eta^1]^-$

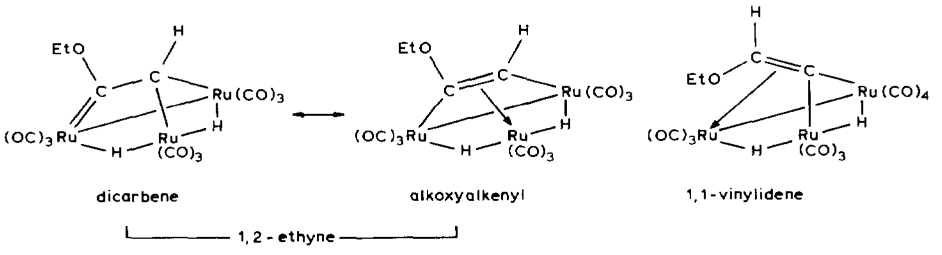
However, the coordinative unsaturation thus created must draw the original η^1-acyl group into η^2-bonding, cf. $Ru(PPh_3)_2(I)\{\eta^2\text{-}C(O)Me\}$ [12]. This η^2,η^1 tautomeric form of the bis-acyl anion would explain the non-interconversion of the two acyl groups. This tautomer could also account for alkylation of the originally bridging acyl group in **[2b]**$^-$ or **[2c]**$^-$, where the newly formed acyl group, RC(O), R = Ph or CMe_3, is deactivated towards O-alkylation. In the case of the t-butyl derivative **[2c]**$^-$ it is steric hindrance which directs alkylation to the oxygen of the originally bridging acyl group. Similar direction of the alkylation occurs in **[2b]**$^-$ owing to deactivation of the oxygen atom in the phenacyl group. For related circumstances in which an η^1-form of a coordinated acyl group may be of importance, see the reports of O-alkylation of $[Fe_3\{\mu_3\text{-}O{=}CMe\}(CO)_9{}^-]$ [13], or of the protonation of a μ-acyl group in $Cp_2Zr(\eta^2\text{-}O{=}CMe)Mo(CO)_3Cp$ [14].

Absence of H/D exchange in double C–H oxidative addition products

The deuterium labeling experiments described above indicate that there is no scrambling of cluster-bonded hydrogen atoms formed in the double oxidative addition or the eliminated aldehyde. This must be formed (and eliminated) in all likelihood in a step preceding the double oxidative addition.

Bonding representation for the C_2 fragment in $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)\}(CO)_9$ (3)

For the double oxidative addition product, two isomeric forms are possible for the C_2 fragment, namely 1,2-ethyne-{1-(OEt),2-H} or 1,1′-vinylidene-{2-(OEt),2′-H} [6a].



The vinylidene form can be ruled out on the basis of the NMR spectra: the coordinated C_2 fragment is represented by ^{13}C resonances at 74.2 and 218.0 ppm. The resonance at 74.2 ppm is established as that of the =C(H) group by its appearance as a doublet in the off-resonance decoupled spectrum, lower part Fig. 3.

If the ethoxy group were also attached to this carbon it would, by analogy to that in ethyl vinyl ether, be expected to resonate at least 100 ppm further downfield. Furthermore, if the vinylidene isomer had been obtained the μ-carbene carbon would be expected to resonate at approximately 45 [7] rather than at the value observed 218.0 ppm.

The 1,2-ethyne-{1-(OEt),2-H} fragment arising from the double oxidative addition may be represented by two resonance forms, a dicarbene or an alkoxyalkenyl form; the NMR data are more consistent with the latter. The $^{13}C-^{1}H$ coupling constants of 158 Hz and 159 Hz observed in the ^{1}H and the ^{1}H-coupled ^{13}C spectra respectively (Fig. 4) reflect *sp*^{2} hybridization at *C*H in the C_2 fragment [15]. The magnitude of the C–C coupling shown in Fig. 3 (124.5 Hz) indicates a bond order somewhere between two and three in the C_2 group, [15], data for comparison are tabulated in the figure. This is what would be expected for the alkoxy-alkenyl representation. Compound **3** is thus seen to be a heteroatom substituted homolog of the ethyne complexes observed previously in the reactions of olefins [7] * or acetylenes [16] with $Ru_3(CO)_{12}$. The structure of a close analog, $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OMe){=}C(Me)\}(CO)_9$ (isolated as one of the products in the hydrogenation of $Ru_3\{\mu\text{-}H,\eta^3,\mu_3\text{-}C(H)C(H)C(OMe)\}(CO)_9$) has recently been reported [17]. The C(Me)–C(OMe) separation is 1.402(8) Å, somewhat longer than that for an alkene (C=C 1.34 Å), in the range usually associated with coordinated alkenes cf. ref. 17.

Conclusion

Products **3** or **4** are the result of the double oxidative addition of a methyl group occurring after reductive elimination of an aldehyde (an overall four-electron donor) on the metal cluster complex. Both of these processes occur at the unprecedentedly mild temperature of 25 °C. There are many examples of formation of double oxidative addition products but all occur at significantly higher temperatures. For example, tri-nuclear reaction intermediates containing double oxidatively added groups are postulated in the H/D exchange in amines catalyzed by $Ru_3(CO)_{12}$ and $Rh_6(CO)_{16}$ at 150 °C [18]. Another example of double oxidative addition is the complex $Os_3\{\mu\text{-}H\}_3\{\mu_3\text{-}C(H)\}(CO)_9$, obtained in the thermolysis of $Os_3\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9$ or $Os_3\{\mu\text{-}H,\mu\text{-}O(CH{=}CH_2)\}(CO)_9$ at 150 °C [19a], or in the thermolysis of $Os_3\{\mu\text{-}H,\mu\text{-}CH_3\}(CO)_{10}$ at 100 °C [19b]. Similarly, the complex $Os_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(R)P(R')_2\}(CO)_9$ is obtained in the thermolysis of $Os_3(CO)_{11}\text{-}P(R')_3$ at 150 °C [19c].

The higher temperatures required to achieve coordinative unsaturation on the metal cluster complexes in these other examples precluded possible observation at lower temperatures of double oxidative additions, which in the present work were shown to take place at ambient temperature. The results described here may provide clues to interpretation of two other observations in the literature, namely (a) the extensive transformation leading to the complex $Ru_3\{\mu_3\text{-}H,\mu,\eta^3\text{-}C(Ph)\text{-}C_6H_4\}(CO)_9$ [20] from the reaction of $Ru_3(CO)_{12}$ with LiPh, and (b) the dehydrogenation of triethylamine by $Os_3(CO)_{10}(NCCH_3)_2$ leading to $HOs_3\{\mu\text{-}{}^{-}CHCH{=}{}^{+}NEt_2\}(CO)_{10}$ in refluxing benzene [21].

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* For a review of other cluster complexes of these and related fragments see ref. 7b.

It is also significant that the oxidative addition is prevented under an atmosphere of CO. The coordinatively unsaturated intermediate(s) formed by the loss of aldehyde can obviously be intercepted by this nucleophile, although not by the aromatic hydrocarbons examined (C_6H_5X, X = F, or CF_3). The rate of the internal oxidative additions observed must thus fall somewhere between the rates of attack by these two types of external reagents.

Experimental

IR spectra were recorded on a Nicolet MX-1 FT-IR spectrometer. NMR spectra were recorded on a JEOL FX-90 FT NMR spectrometer. Gas chromatographic (GC) measurements were performed on a Hewlett-Packard 5880A GC using a flame ionization detector and a 10 m OV-101 column. GC/MS was performed on a Kratos MS-25 spectrometer; the intensities of ion multiplets derived from metal complexes were analysed by MASPAN [22]. The addresses of the vendors mentioned below are as follows: Aldrich Chemical Co., Milwaukee, WI 53233; Alpha Division, Ventron Co., Danvers, MA 01923; Mallinckodt Inc., St. Louis, MO 63134; EM Reagents, Cincinnati, OH 45212; Linde Division, Union Carbide Corp., New York, NY 10017; Air Products, Allentown, PA 18105; MSD Isotopes, Los Angeles, CA 90051. The analyses were performed by the Schwarzkopf Microanalytical Laboratory, Woodside, N.Y.

The following were purchased and used as received; silver trifluoromethanesulfonate, ethyl iodide, triphenylphosphine, methyl iodide-d_3, ruthenium(III) chloride trihydrate, phenyllithium (2.4 *M* in cyclohexane/diethyl ether 70/30), t-butyllithium (1.3 *N* in pentane, Aldrich); methyllithium (1.6 *M* in diethyl ether, low halide, Alpha), methanol, dichloromethane, 35–60 °C petroleum ether, (Mallinckrodt), dimethylamine (Linde), carbon monoxide (Air Products) and $^{13}CH_3I$ (MSD Isotopes). Diethyl ether and pentane (Mallinckrodt) were dried by reflux over potassium benzophenone ketyl and freshly distilled under nitrogen. Column chromatographic separations were carried out on a 20 × 2 cm column of 60 mesh silica gel (EM Reagents). All reactions were conducted under a nitrogen atmosphere using standard Schlenk techniques [23].

$Ru_3\{\mu\text{-H},\mu\text{-O=C(CH}_3)\}(CO)_{10}$ (**1**), $Ru_3\{\mu\text{-H},\mu\text{-O=C(CD}_3)\}(CO)_{10}$ (**1**-d_3) [3], $LiCD_3$, $Li^{13}CH_3$ [24] and ethyl trifluoromethanesulfonate, (ethyl triflate) [5], were prepared by published methods.

Preparation of $Ru_3(CO)_{12}$. A modification [25] of the procedure described by Eady and co-workers [26] was used in preparing $Ru_3(CO)_{12}$. A mixture of $RuCl_3 \cdot 3H_2O$ (25.4 g) and anhydrous methanol (fresh bottle with no further drying or deaerating) (300 ml) is pressurized to approximately 1000 psi (65 atm) with carbon monoxide in a 1-liter autoclave. This is heated at 125 °C with stirring. After 8 h the autoclave is cooled and slowly vented in a well-ventilated hood.

The crude orange crystalline dodecacarbonyltriruthenium is separated by filtration in air on a Buchner funnel. The crude product is extracted into dichloromethane (3.5–4 l) leaving a blue-black solid residue. This blue-black solid of which the amount varies is identified as RuO_2. Elemental analyses. Found: Ru, 76.30; Cl, 0.1. RuO_2, calcd.: Ru, 75.95, Cl, 0.0%. The solution is concentrated on a rotary evaporator at room temperature. Spectroscopically pure orange crystalline $Ru_3(CO)_{12}$ is isolated by filtration. Yields vary typically from about 70% (15.4 g) occasionally to as high as 92%. Elemental analyses. Found: C, 22.54. $Ru_3C_{12}O_{12}$, calcd.: C, 22.54%.

Preparation of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)\}(CO)_9$ (3). A solution of 0.500 g, (797 μmol) of **1**, in 500 ml of diethyl ether is titrated with 1.6 *N* diethyl ether solution of $LiCH_3$ at −30 °C. Spectroscopic data for the resulting salt, $[Li][Ru_3(\eta^1\text{-}C(O)CH_3)\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9]$ **[Li][2a]**, are presented in Tables 1 and 2, and in the caption to Fig. 1.

The solution of $[\mathbf{2a}]^-$ is warmed to 25 °C and treated with 2 equivalents of ethyl triflate (100 ml of a 16 m*M* diethyl ether solution). The solution is stirred for 48 h during which time the IR absorptions of $[\mathbf{2a}]^-$ are replaced by those of **3**. The diethyl ether is removed and the solid residue extracted with 30 ml of pentane. Evaporation of the pentane extract gives complex **3** in 80% yield (0.401 g). Elemental analyses. Found: C, 24.29; H, 1.55. $Ru_3C_{13}H_8O_{10}$ (**3**) calcd.: C, 24.88; H, 1.29%.

The mass spectrum of **3** consists of a parent ion multiplet with a maximum at *m/e* 629 followed by nine multiplets spaced 28 units apart confirming the formula weight and presence of nine carbonyl groups. MASPAN analysis [22] of the parent ion multiplet indicates this to be exclusively from the unfragmented dihydrido ion (*R* 3.0%). The fit between the observed and calculated spectra is shown in the upper portion of Fig. 8.

^1H NMR data for **3** are presented in Fig. 2. For comparison, the parameters of the close analog, $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OMe){=}C(Me)\}(CO)_9$, in $CDCl_3$ solution at −65 °C are, δ, ppm (mult., assignment): 3.70 (s, OCH_3); 2.26 (s, CH_3); −15.46 (d) and −19.94 (d) (RuH_A, H_B, J_{AB} 3.0 Hz) [17].

^{13}C NMR data for **3** are presented in Fig. 3. The ^{13}C $\{^1H\}$ NMR in the CO region at −90 °C, CD_2Cl_2 solution (10 mg of $Cr(acac)_3$ added) are, ppm (rel. int.): 200.9(1), 199.4(1), 196.7(1), 193.9(1), 191.2(1), 190.6(1), 189.3(1), 187.4(1), 185.6(1).

The acetaldehyde produced in this reaction was characterized by GC/MS, the mass spectrum showing peaks (with related abundance in parentheses) at *m/e*: 44 (83), 43 (50), 42 (15), and 29 (100), see Fig. 6. Comparison of the relative GC peak areas to those of a standard solution of acetaldehyde in diethyl ether indicate that a stoichiometric amount of acetaldehyde has been produced.

Deprotonation of $Ru_3\{1,2\text{-}\mu\text{-}H;\mu\text{-}O{=}CMe\}(CO)_{10}$ (1) with LiMe. A solution of 0.500 g, (797 μmol) of **1**, in 500 ml of diethyl ether is treated with one equivalent of $LiCH_3$ (0.50 ml of 1.6 *M* diethyl ether solution at 25 °C. The IR carbonyl absorbances (2250–1500 cm^{-1}) of the resulting solution are indentical to those of $[Li][Ru_3\{\mu\text{-}O{=}C(CH_3)](CO)_{10}]$ [3]: 2011(vs), 1986(vs), 1961(s), 1822(br,sh), 1798(w). The ^1H NMR spectrum of this product in $Et_2O\text{-}d_{10}$ contains only a singlet at 2.57 ppm and no resonances observed in the hydride region.

Preparation of $Ru_3\{\mu\text{-}D_2,\eta^2,\mu_3\text{-}C(OEt){=}C(D)\}(CO)_9$ (3-d_3). A solution of 0.500 g, (797 μmol) of **1**, in 500 ml of diethyl ether is titrated with 1.1 *N* diethyl ether solution of $LiCD_3$ at −30 °C. IR spectral data for the resulting salt, $[Li][Ru_3\{C(O)CD_3\}\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9]$, **[Li][2a-$d_3$]** are presented in Table 2. The solution is warmed to 25 °C and treated with 2 equivalents of ethyl triflate (100 ml of a 16 m*M* diethyl ether solution). The solution is stirred for 48 h during which time the IR absorptions of $[\mathbf{2a}\text{-}d_3]^-$ are replaced by those of **3-d_3**. The diethyl ether is removed and the solid residue extracted with 30 ml of pentane. Evaporation of the pentane extract gives the complex **3-d_3** in 50% yield (0.251 g). NMR data. ^1H in

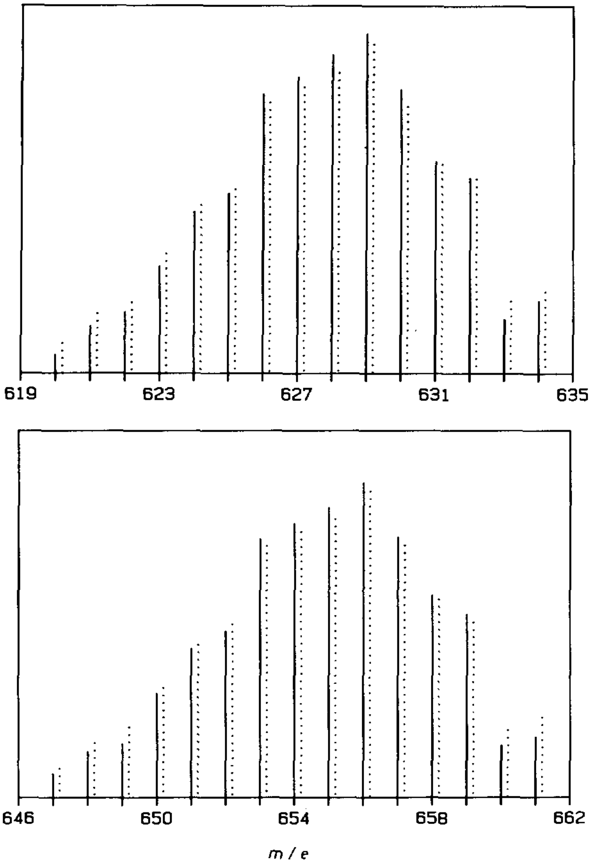

Fig. 8. Bar graphs of the observed (solid line) and calculated (dotted line) Mass spectra for parent ions; original data in ref. 1a. Top, $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}C(H)\}(CO)_9$ (3); *R* factor 3%. Bottom, $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)NMeC(H)\}(CO)_9$ (4); *R* factor 3%.

C_6D_6, ppm (mult., rel. int): 3.49(q,2), OCH_2CH_3; 1.03(t,3), OCH_2CH_3. For ^2H NMR, see Fig. 5.

The acetaldehyde produced in this reaction was characterized by GC/MS, which revealed ions at *m/e* (rel. int.): 44(88), 43(52), 42(15), and 29(100). No fragments consistent with deuterium incorporation were seen (Fig. 6B). Comparison of the relative GC peak areas with those of a standard solution of acetaldehyde in diethyl ether indicated that a stoichiometric amount of acetaldehyde had been produced.

Preparation of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt){=}^{13}C(H)\}(CO)_9$ *(3-*^{13}C*)*. A solution of 0.250 g, (399 μmol) of **1**, in 250 ml of diethyl ether is titrated with 1.1 *N* diethyl ether solution of $Li^{13}CH_3$ at −30 °C. The IR spectral data for the resulting salt, $[Li][Ru_3\{\eta^1\text{-}C(O)^{13}CH_3\}\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9]$ ([Li][**2a**-^{13}C]) are shown in Table 2. The solution is warmed to 25 °C and treated with 2 equivalents of ethyl triflate (50 ml of a 16 m*M* diethyl ether solution) and is stirred for 48 h during which time the IR absorptions of [**2a**-^{13}C]$^-$ are replaced by those of **3**-^{13}C. The diethyl ether is removed and the solid residue extracted with 30 ml of pentane. Evaporation of the pentane extract gives the complex **3**-^{13}C in 65% yield (0.163 g).

Reaction of $[Li][Ru_3\{\eta^1\text{-}C(O)CH_3\}\{\mu\text{-}H,\mu\text{-}O{=}C(CD_3)\}(CO)_9]$ *(*$[Li][2a\text{-}\mu\text{-}O{=}C(CD_3)]$*) with ethyl triflate.* A solution of 0.250 g (397 μmol) of **1**-d_3 in 250 ml of diethyl ether is titrated with a 1.6 *N* diethyl ether solution of $LiCH_3$ at −30 °C. The IR spectral data for the resulting salt, [**Li**][**2a**-μ-O=C(CD_3)] are presented in Table 2. The solution of [**Li**][**2a**-μ-O=C(CD_3)] is warmed to 25 °C and treated with 2 equivalents of ethyl triflate (50 ml of a 16 m*M* diethyl ether solution). The solution is stirred for 48 h during which time the IR absorptions of $[\mathbf{2a}\text{-}\mu\text{-}O{=}C(CD_3)]^-$ are replaced by those of **3**. The diethyl ether is removed and the solid residue extracted with 30 ml of pentane. Evaporation of the pentane extract gives the complex **3** in 75% yield (0.187 g).

The acetaldehyde produced in this reaction was identified as acetaldehyde-d_3, $HC(O)CD_3$ by its characteristic GC/MS *m/e* peaks (rel. area): 47(100), 46(78), 29(86), see Fig. 6C. The absence of a fragment at *m/e* 44 indicates that all of the acetaldehyde was labeled. The small peaks at *m/e* 30(8) and 48(5) are indicative of the presence of minor amounts of acetaldehyde-d_4. Comparison of the relative GC peak areas to those of a standard solution of acetaldehyde in diethyl ether indicated that a stoichiometric amount of acetaldehyde had been produced.

Reaction of $[Li][Ru_3\{\eta^1\text{-}C(O)C_5H_6\}\{\mu\text{-}H,u\text{-}O{=}C(CH_3)\}(CO)_9]$ *(*$[Li][2b]$*) with ethyl triflate.* A solution of 0.250 g (339 μmol) of **1** in 250 ml of diethyl ether is titrated with a 2.4 *N* cyclohexane/diethyl ether (70/30) solution of LiC_6H_5 at −30 °C. The IR spectral data for the resulting salt, [**Li**][**2b**], are shown in Table 2. The solution of [**Li**][**2b**] is warmed to 25 °C and treated with 2 equivalents of ethyl triflate (50 ml of a 16 m*M* diethyl ether solution). The solution is stirred for 72 h during which time the IR absorptions of $[\mathbf{2b}]^-$ are replaced by those of **3**. The diethyl ether is removed and the solid residue extracted with 30 ml of pentane. Evaporation of the pentane extract gives the complex **3** in 60% yield (0.150 g).

The benzaldehyde produced in this reaction was identified by its characteristic ions revealed by GC/MS at *m/e* (rel. area): 106(100), 105(96), 78(19), 77(97), 74(9), 52(13), 51(53), and 50(30). Comparison of the relative GC peak areas to those of a standard solution of benzaldehyde in diethyl ether indicated that a stoichiometric amount of the aldehyde had been produced.

Reaction of $[Li][Ru_3\{\eta^1\text{-}C(O)CMe_3\}\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9]$ *(*$[Li][2c]$*) with ethyl triflate.* A solution of 0.250 g (399 μmol) of **1** in 250 ml of diethyl ether is titrated with a 1.3 *N* pentane solution of $LiCMe_3$ at −30 °C. The IR spectral data for the resulting salt, [**Li**][**2c**] are shown in Table 2. The solution is warmed to 25 °C and treated with 2 equivalents of ethyl triflate (50 ml of a 16 m*M* diethyl ether solution) The solution is stirred for 120 h during which time the IR absorptions of $[\mathbf{2c}]^-$ are replaced by those of **3**. The diethyl ether is removed and the solid residue extracted with 30 ml of pentane. Evaporation of the pentane extract gives the complex **3** in 40% yield (0.099 g).

The 2,2-dimethylpropanol produced in this reaction was identified by comparison of its GC retention time to that of an authentic sample. Comparison of the relative GC peak areas with those of a standard solution of 2,2-dimethylpropanol in diethyl ether indicated that a stoichiometric amount of the aldehyde had been produced.

Preparation of $Ru_3\{\mu\text{-}H_2,\eta^2,\mu_3\text{-}C(OEt)N(Me)C(H)\}(CO)_9$ *(4).* Dimethylamine is bubbled through a solution of 250 g, (399 μmol) of **1**, in 250 ml of diethyl ether at −30 °C. After 10 minutes the IR absorbances of **1** have disappeared and are replaced by those of the salt, $[Li][Ru_3(\eta^1\text{-}C(O)NMe_2)\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9]$ (**[Li][2d]**) (see Table 2). The solution of **[Li][2d]** is warmed to 25 ° C and treated with 4 equivalents of ethyl triflate (100 ml of a 16 m*M* diethyl ether solution). The solution is stirred for 48 h during which time the IR absorptions of **[2d]**$^-$ are replaced by those of **3**. The diethyl ether is removed and the solid residue extracted with 30 ml of pentane. The pentane extract is concentrated to 3 ml and placed on a 20 × 2 cm column of silica gel. Eluting with petroleum ether gives rise to two fractions. The first is $Ru_3(CO)_{12}$ (0.020 g, 8% yield) and the second is **4** (0.118 g, 45% yield).

Elemental analyses. Found: C, 25.65; H, 1.17, N, 2.14. $Ru_3C_{14}H_{11}O_{10}N$ (**4**) calcd.: C, 25.61; H, 1.69; N, 2.13%.

The mass spectrum of **4** gave the parent ion multiplet with a maximum at *m/e* 656 followed by nine multiplets spaced 28 units apart confirming the formula weight and the presence of nine carbonyl groups. MASPAN analysis [22] of the parent ion multiplet shows it to be exclusively from the unfragmented dihydrido ion (*R* 3%). The observed and calculated spectra are shown in the lower trace of Fig. 8.

Reaction of $[Li][Ru_3\{\eta^1\text{-}C(O)CH_3\}\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_9]$ *([Li][2a]) with ethyl triflate in the presence of either fluorobenzene or trifluoromethylbenzene.* A solution of 0.200 g of $Ru_3\{\mu\text{-}H,\mu\text{-}O{=}C(CH_3)\}(CO)_{10}$ (**1**) in 100 ml of diethyl ether at −30 ° C is slowly titrated with a diethyl ether solution of $LiCH_3$ (1.6 *N*). To the resulting solution of **[Li][2a]** is added 30 ml of fluorobenzene. Still at −30 ° C, a 16 m*M* solution of ethyl triflate in diethyl ether (40 ml, 2 equivalents) is added. The low temperature bath is removed and the solution warmed to 25 ° C with stirring during 48 h; the IR spectra taken at various intervals show that the absorptions of **[2a]**$^-$ are replaced by those of **3**, with no bands of other compounds evident. The diethyl ether is then removed and the solid residue extracted with 30 ml of pentane. Evaporation of the pentane extract gives the complex **3** in 78% yield (0.160 g). No bands from any other product are observed.

Similar results are obtained in the presence of 100 ml of trifluorotoluene.

Reaction of [Li][2a] with ethyl triflate under 1 atm of CO. A diethyl ether solution containing 479 μmol of **[Li][2a]** is prepared as described above and warmed to 25 ° C. After addition of 2 equivalents of ethyl triflate (60 ml of a 16 m*M* diethyl ether solution), the solution is placed under 1 atm of CO. After 16 h stirring the IR absorbances of **[2a]**$^-$ have completely disappeared, having been replaced by those of the highly unstable complex **5**. Removal of the CO from the solution of **5** results in complete conversion into **3** within 15 minutes. The diethyl ether is removed and the solid residue extracted with 30 ml of pentane. Evaporation of the pentane extract gives the complex **3** in 78% yield (0.232 g).

Reaction of 5 with triphenylphosphine. A 300 ml diethyl ether solution containing 479 μmol of **5**, prepared as described in the preceding paragraph, is treated with 3 equivalents of triphenylphosphine (0.376 g, 1437 μmol). There is an instantaneous color change from red to purple. The IR spectrum of the solution shows that quantitative conversion into $Ru_3(CO)_9(P(C_6H_5)_3)_3$ (**6**) has occurred. The diethyl ether is removed under reduced pressure and the residue taken up in benzene. The benzene extract is deposited on 1 cm^3 of silica gel and placed on a column of silica gel. Elution with diethyl ether gives a single, red-purple, fraction, **6** (0.437 g, 68% yield). For **6** in $CDCl_3$: ^1H NMR, 7.45(m) ppm; ^{31}P NMR, 36.8(s) ppm. The spectra were identical to those of a sample of the tris(triphenylphosphine) derivative prepared as described by Bruce et al. [11].

Fate of the carbene group in the reaction of $Ru_3\{C(OEt)Me\}(CO)_{11}$ *(5) with triphenylphosphine.* The formation of the tris(triphenylphosphine) derivative **6** in the reaction of **5** with triphenylphosphine is in contrast with the outcome of the reaction for monocenter Fischer-type carbenes, where substitution of phosphine for carbonyl groups is the primary reaction pathway [27]. Three fates of the carbene group have been considered:

(i) Refluxing of solutions of monocenter Fischer-type carbene complexes in decalin results in the dimerization of the carbene groups to difunctionalized olefins [27b,28]. Authentic samples of the difunctionalized olefin MeC(OEt)=C(OEt)Me were prepared and analyzed by GC/MS. The reaction of **5** with triphenylphosphine did not give any products with matching retention times.

(ii) Mono center Fischer-type carbene complexes will react at $-15\,^\circ C$ with phosphines at the carbene carbon to give phosphonium products which upon warming to room temperature undergo loss of a carbonyl group to give phosphine-substituted derivatives. If this cluster bound heteroatom carbene behaved more like an alkylidene carbene and reacted to form the free ylide, the ylide would undergo a Wittig type reaction with the acetaldehyde in solution and form 2-ethoxy-2-butene and phosphine oxide [27b,29]. Neither of these products was detected in the reaction mixture.

(iii) Monocenter Fischer-type carbene complexes undergo a shift of an α-proton in the presence of pyridine to give the corresponding unsaturated ether [27b,30]. If such a rearrangement took place in the reaction of **5** with triphenylphosphine, the resulting ethyl vinyl ether could not be detected by GC analysis in the presence of the diethyl ether solvent peak.

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