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Synthesis and reactions of edge double-bridged trinuclear cluster complexes of ruthenium or osmium

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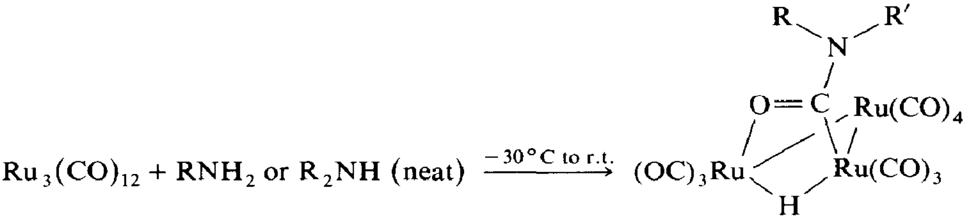
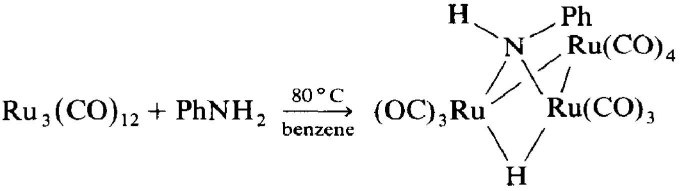
Introduction

It is a pleasure to contribute to this Mond Centennial Volume an account of the work of my group and that of others in the area defined in the title. We were led to such studies by the initial observation of Rosemarie Szostak [1] of the reaction of $Ru_3(CO)_{12}$ with a primary or secondary alkylamine, (eq. 1). The unprecedented mild conditions and the product obtained in this transformation caught us by surprise, relative to an earlier observation by Sappa and Milone [2] shown as eq. 2.



(1)

(R′ = R or H)



(2)

With a base of low nucleophilicity like $PhNH_2$, loss of CO must be the first step which necessitates the higher temperature in reaction 2. By contrast, direct attack at carbon of a coordinated CO is observed with bases of higher nucleophilicity as in reaction 1, with a lower barrier in the first step. These observations led us to a general investigation of the reactions of a variety of nucleophiles with $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$, in which efforts we were eventually joined by several other capable groups.

A summary of the various anions that are encountered in this work and which

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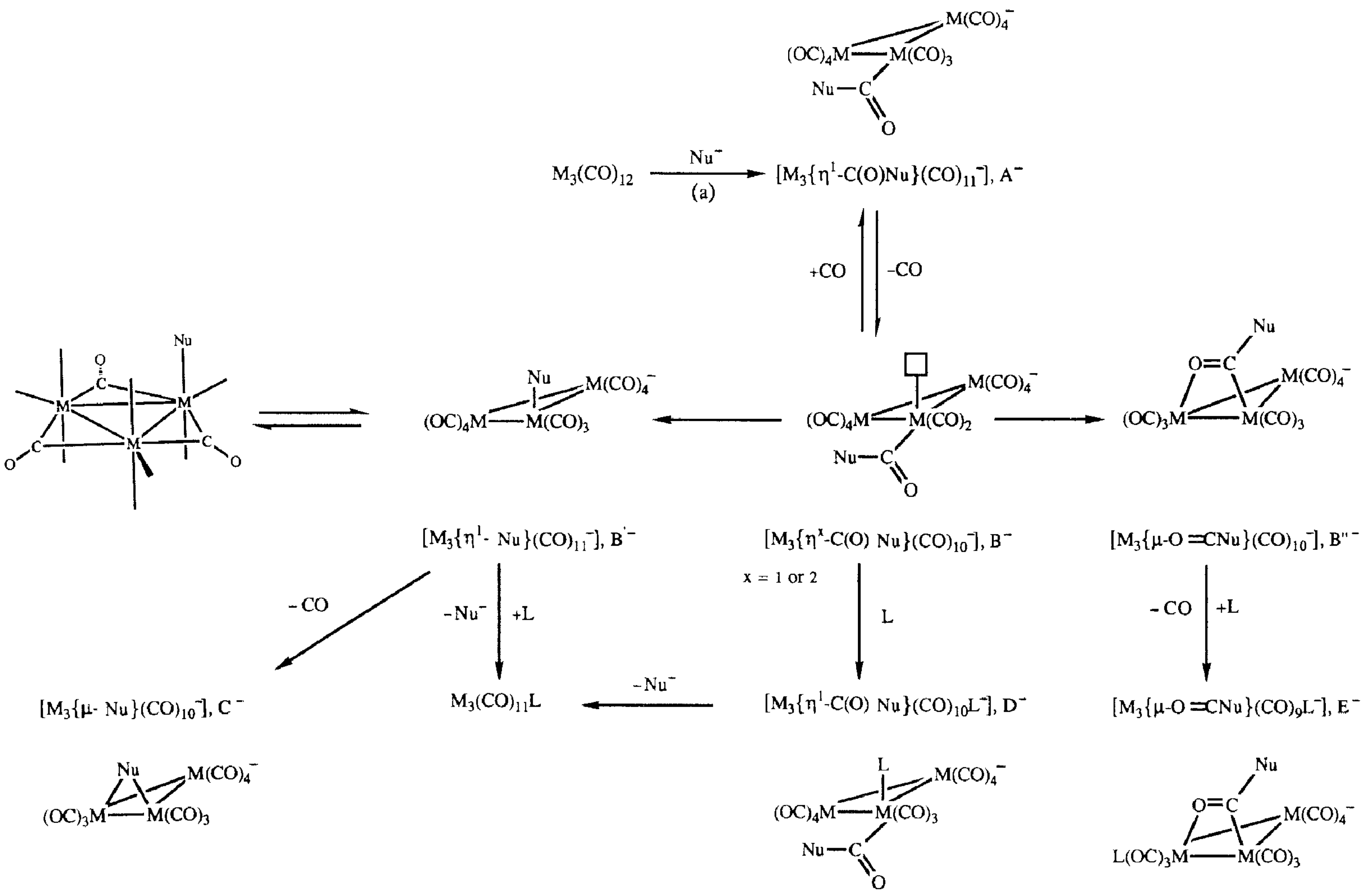

Scheme 1. Anions traversed or isolated in the reaction of $M_3(CO)_{12}$, M = Ru or Os, with nucleophiles. Acidification of end products like $[B'']^-$, $[C]^-$, or $[E]^-$ gives edge double bridged species containing the {μ-H,μ-Nu} or the {μ-H,μ,η^2-O=CNu} groups.

defines the scope of this account is given in Scheme 1; the transformations are discussed below. Acidification of end products $[B'']^-$, C^-, or E^- give edge double-bridged complexes, containing the groups $\{\mu\text{-H},\mu\text{-Nu}\}$ or $\{\mu\text{-H},\mu\text{-O=C(Nu)}\}$, hence the title of this account. A reaction scheme like the one presented below was published in a general review of the reactions of metal cluster complexes [3]. A comprehensive review of the nucleophilic activation of carbon monoxide has also appeared [4].

Formation of adducts between nucleophiles and $M_3(CO)_{12}$ (M = Ru or Os); Activation of the trinuclear cluster complexes

We were able to observe the simple adduct of a nucleophile only in complexes of $Os_3(CO)_{12}$, see $[M_3\{\eta^1\text{-C(O)Nu}\}(CO)_{11}^-]$, A^-, in Scheme 1 (M = Os; Nu = NMe_2, or CH_3) [5,6]. The carbonyl groups are fluxional in these complexes, but we obtained a limiting ^{13}C NMR for the Li^+ salt of $[Os_3\{\eta^1\text{-C(O)CH}_3\}(CO)_{11}^-]$ at −85 °C [6]. This was assigned as the equatorial isomer from the pattern of seven resonances appearing in the intensity ratio 2/4/1/1/1/1/1 (expected, 2/2/2/1/1/1/1/1). Owing to the fluxionality in the system, this must surely be the thermodynamically stable species; we believe that the point of initial attack (the kinetic product) may well be attachment of the nucleophile at the carbon of an axial CO group; the carbon atom of this CO group, *trans* to another CO group, is expected to be more electrophilic than the carbon atom of an equatorial CO group, which is *trans* to an M–M bond. The unstable formyl complex $[Os_3\{\eta^1\text{-C(O)H}\}(CO)_{11}^-]$ was observed upon reaction of $K[BH(O\text{-i-Pr})_3)]$ with $Os_3(CO)_{12}$ [7]; a structure like that shown for A^- in Scheme 1 is believed to apply.

In sharp contrast, simple adducts of Nu^- with $Ru_3(CO)_{12}$ are much more fleeting owing to a high degree of labilization of coordinated CO in such complexes. This high lability is remarkable when compared to the relatively stable adducts with nucleophiles known for mononuclear complexes, such as $Mn(CO)_5C(O)OR$ (from the addition of OR^- to $[Mn(CO)_6^+]$) [8], or for higher nuclearity carbonyls (such as $[Rh_6(CO)_{15}C(O)Nu^-]$, Nu = NHR or OR, [9]). For example, NMR studies of the reaction of $Na[BH_4]$ with $Ru_3(CO)_{12}$ at −30 °C [10 *] show the presence of a formyl resonance for a species whose formula would be $[Ru_3\{\eta^1\text{-C(O)H}\}(CO)_{11}^-]$. However this quickly loses CO and undergoes H-shift upon warming to give the well known $[Ru_3[\mu\text{-H},\mu\text{-C(O)}\}(CO)_{10}^-]$. An alternative structure to A^- (Scheme 1) has been proposed for $[Ru_3\{\eta^1\text{-C(OH)H}\}(CO)_{11}^-]$, namely one in which the H-atom is terminally bonded to an $Ru(CO)_3$ group in an opened metal triangle: e.g. two bonded $Ru(CO)_4$ groups bridged by the $Ru(H)(CO)_3C(O)$ unit [11].

Simple adducts of OH^- or OR^- with $Ru_3(CO)_{12}$ have been observed by optical, IR and NMR spectroscopies [12,13]. ^{13}C NMR studies show that eleven of the CO groups in the anion $[Ru_3\{\eta^1\text{-C(O)OCH}_3\}(CO)_{11}^-]$ (as the $[N(PPh_3)_2^+]$ salt) are still exchanging rapidly at −105 °C [12c]. The unstable anion $[Ru_3\{\eta^1\text{-C(O)OH}\}(CO)_{11}^-]$ (as the $[Na^+]$ salt) has been observed by fast flow optical spectroscopy [12a,b]. Similar adducts ($Nu^- = RNH^-$ or R_2N^-) must be traversed in the reaction depicted as eq. 1; however we have not as yet made a concerted effort to observe these by spectroscopic means. In contrast, anions derived by CO loss from the first

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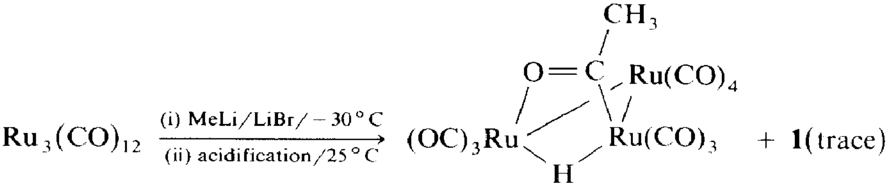
* Reference number with asterisk indicates a note in the list of references.

formed adduct as observed spectroscopically and in some cases, isolated; these are discussed below. It should be noted that labilization of CO in $Ru_3(CO)_{12}$ by nucleophiles is paralleled (but not equaled in reactivity enhancement) by that observed in mononuclear systems [14].

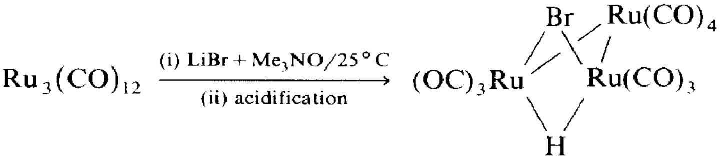
Reaction of $Ru_3(CO)_{12}$ with highly dissociated salts; catalysis of substitution reactions

Our work on the stepwise transformation of trinuclear clusters to edge double-bridged complexes $[B'']^-$ and E^- on Scheme 1 will be described below. Among other investigations of this kind, we carried out the transformation shown in eq. 3 [5]. We consistently observed a minor product which proved to be the complex $Ru_3\{\eta\text{-H},\mu\text{-Br}\}(CO)_{10}$, **1**, [15].



(3)

(50% yield)



(4)

(**1**, 30% yield)

Complex **1** was found to derive from the 22.5% of LiBr stabilizer present in commercial samples of MeLi employed in reaction 3. We could separately make this derivative by following the procedure indicated in reaction 4. At that time, Dr. G. Lavigne from the Laboratory of Coordination Chemistry in Toulouse was spending a period of residence at UCLA. Lavigne wished to follow the stepwise formation of **1** by looking for an intermediate adduct of Br^- with $Ru_3(CO)_{12}$. By a fortunate decision, he decided to use the $[N(PPh_3)_2{}^+]$ salt in order to observe the spectrum of the cluster anion in the absence of ion-pairing effects [16]. Not expecting a direct reaction, Lavigne put together $[N(PPh_3)_2]Br$ and $Ru_3(CO)_{12}$ in tetrahydrofuran solution, and paused to obtain a reference spectrum before adding Me_3NO. Much to everyone's surprise, the solution turned color within a few minutes and spectra indicated a nearly quantitative conversion to the salt $[N(PPh_3)_2][Ru_3\{\mu\text{-Br}\}(CO)_{10}]$; acidification leads to complex **1**, eq. 5 [17]. This remarkably easy transformation was paralleled by observations in other laboratories leading to a variety of $[Ru_3\{\mu\text{-Nu}\}(CO)_{10}{}^-]$ anions which are discussed in the next section.

$$Ru_3(CO)_{12} + [PPN]Br \xrightarrow{25\,^\circ C} [PPN][Ru_3\{\mu\text{-Br}\}(CO)_{10}] \xrightarrow{H^+} \underset{(\mathbf{1})}{Ru_3\{\mu\text{-H},\mu\text{-Br}\}(CO)_{10}} \quad (5)$$

Lavigne went on to discover that the highly dissociated salts in trace quantities will catalyze substitution reactions on $Ru_3(CO)_{12}$. Without catalyst, no reaction is observed between PPh_3 with $Ru_3(CO)_{12}$ at room temperature. Substitution is initiated upon heating to 60 ° C; however, the tri-substituted cluster $Ru_3(CO)_9L_3$ is the primary reaction product [18]. By contrast, the catalyzed reaction takes place at 25 ° C, and gives the mono-substituted product $Ru_3(CO)_{11}L$ in high yield [17].

$$Ru_3(CO)_{12} + PPh_3 \xrightarrow{[N(PPh_3)_2]Nu/25\,^\circ C} Ru_3(CO)_{11}(PPh_3) \tag{6}$$

The effect is also observed for salts of $[R_4N^+]$, and for the series of anions (in decreasing order of rate enhancement) $[Nu^-] = [CN^-], [CH_2CO_2^-] > F^- > Cl^- > Br^- > I^- > NO_2^-$ [17]. We believe the course of the catalyzed reaction is represented by the transformations B^- to D^- to $M_3(CO)_{11}L$, M = Ru, in Scheme 1. We do not find a similar catalytic effect for $Os_3(CO)_{12}$, this being due to the higher bond dissociation for Os–CO preventing the low temperature dissociation from a species like $[A^-]$ (Scheme 1). We believe that the catalytic effect depends on the labilization of CO by an $\{\eta^1\text{-C(O)Nu}\}$ group, and reversibility of the attachment of the nucleophile at carbon. This is true for $Nu^- =$ halides or oxygen containing species. For carbon or nitrogen-based nucleophiles attachment at carbon of coordinated CO is not easily reversible, and the course of the reactions follow towards species like $[B'']^-$ and E^- in Scheme 1 which are discussed below. Deactivation of the catalyst occurs by formation of species such as $[B']^-$ shown in Scheme 1 (and others such as seen for $Nu^- = CN^-$, discussed in the next section). As is well known, substitution reactions on cluster complexes may also be catalyzed by radical ion initiators [19].

After returning to France, Guy Lavigne together with co-workers in Toulouse have discovered that the catalysis of CO substitution is also effected by salts of various hydride-donating anions such as $[Ru_3\{\eta\text{-H}\}(CO)_{11}^-]$, $[HRu(CO)_4^-]$, and ["Selectride"] (Aldrich) [20]; the hydride donating properties of $[Ru_3\{\mu\text{-H}\}(CO)_{11}^-]$ are developed under an atmosphere of CO as has elegantly been demonstrated by Shore and co-workers [21].

The anions $[M_3(Nu)(CO)_{11}^-]$, $[M_3\{\mu\text{-Nu}\}(CO)_{10}^-]$, and related derivatives

In the absence of other ligands, the loss of CO from the first formed adduct with nucleophiles such as the halides leads to anions $[B']^-$ and C^-, shown in Scheme 1. The various equilibria which exist in the $Ru_3(CO)_{12}$/halide system have subsequently been investigated [22]. Anions $[B']^-$ and C^- (Scheme 1) are formed reversibly for $Nu^- = Cl^-$ or Br^-; for $Nu^- = I^-$, only species C^- is seen, which does not react with CO to give the corresponding nonacarbonyl, $[B']^-$ [22]; heating C^- gives tetranuclear cluster anions $[Ru_4(\mu\text{-X})(CO)_{13}^-]$ for $X^- = Cl^-$ or Br^-, which transformations can be reversed in the presence of CO. By contrast, heating $[Ru_3\{\mu\text{-I}\}(CO)_{10}^-]$ leads to $[Ru_3[\mu_3\text{-I}\}(CO)_9^-]$ [22].

Very recently, the isolation and structures of salts $[M_3(Nu)(CO)_{11}^-]$, M = Ru, $Nu^- = Cl^-$ [23] and M = Os, Nu = Br^- or I^- [24] have been reported. The structure depicted as $[B']^-$ is seen only for $[Os_3(Br)(CO)_{11}^-]$ [24]. That for $[Os_3(I)(CO)_{11}^-]$ contains the I atom in an equatorial position, while that for $[Ru_3(Cl)(CO)_{11}^-]$ [23] contains three equatorially bridging CO groups as shown to the left of $[B']^-$ in Scheme 1. In this section we should also mention the reaction of $Ru_3(CO)_{12}$ with a variety of other $[N(PPh_3)_2^+]$ salts, namely that of $[NO_2^-]$, $[N_3^-]$, or [acetate$^-$], yielding the salts of the anions $[Ru_3\{\mu\text{-}X\}(CO)_{10}^-]$, respectively, X = NO [25], NCO [26], or acetate [27]. With $[N(PPh_3)_2]CN$, $Ru_3(CO)_{12}$ gives a dimeric anion in which two Ru_3 triangles are linked by CN bridging groups: $[N(PPh_3)_2][Ru_6\{\mu\text{-}CN\}_2(CO)_{20}]$ [28]. The anion $[Ru_3\{\mu\text{-}NCO\}(CO)_{10}^-]$ is an active catalyst for olefin hydrogenation [26].

Formation of anions containing the $\{\mu,\eta^2\text{-}O = C(Nu)\}$ group; differences in structure and fluxionality for M = Ru vs. M = Os

In cases of a stable bond between the nucleophile and carbon of a coordinated CO, the loss of CO from the complex converts the $\{\eta^1\text{-}C(O)Nu\}$ group into complexes $[B'']^-$ containing the $\{\mu,\eta^2\text{-}O{=}C(Nu)\}$ group for Nu = R or NRR′, see Scheme 1 [5,29]. Dr. Andreas Mayr introduced us to the use of $C(NMe_2)_4$ which proved to be an excellent reagent providing a source of NMe_2^- anion while being converted into the guanidinium cation, $[C(NMe_2)_3^+]$ [29]. Reaction of $C(NMe_2)_4$ with $Os_3(CO)_{12}$, followed by loss of two CO groups, thus leads to the anion shown as $[B'']^-$, M = Os, in Scheme 1; this contains all terminal CO groups [29]. The same reaction with $Ru_3(CO)_{12}$ leads to an anion of the same stoichiometry, but whose structure contains bridging CO groups [5,29]. This is by now a familiar pattern first seen in the neutral diazene complexes $Ru_3[\mu,\eta^2\text{-}N_2C_4H_4\}\{\mu\text{-}C(O)\}_3(CO)_7$, [30], vs. $Os_3\{\mu,\eta^2\text{-}N_2C_4H_4\}(CO)_{10}$ [31].

The ^{13}C NMR of these anions was investigated by Dr. N.M. Boag, who observed a reversal Ru > Os of the usual barrier heights for fluxionality between complexes of these two metals. For the anion $[Ru_3\{\mu,\eta^2\text{-}O{=}CNMe_2\}\{\mu\text{-}C(CO)\}_3(CO)_7]^-$, a limiting spectrum is seen at −100 °C whose coalescence is not yet complete at +65 °C (the highest temperature accessible before decomposition) [5,29]. By contrast, for $[Os_3\{\mu,\eta^2\text{-}O{=}CNMe_2\}(CO)_{10}]^-$, a limiting ^{13}C NMR spectrum is not yet developed at −100 °C, whose coalescence into an averaged signal is observed at +26 °C. We have proposed that the reason for this reversal may derive from an energy lowering in the CO bridging form of the anionic complexes. This is the ground state for the tri-ruthenium anion, thus requiring a steeper barrier for tautomerism, presumably through an all-terminal isomer. The all-terminal isomer is the ground state for the tri-osmium anion; if a CO-bridged tautomer is the transition state for fluxionality, then the energy of such an anion is lowered [5,29].

CO substitution in anions or neutral complexes containing the $\{\mu,\eta^2\text{-}O{=}C(Nu)\}$ group

Anionic complexes containing the $\{\mu,\eta^2\text{-}O{=}C(Nu)\}$ group are very easily substituted, $[B'']^-$ to E^- in Scheme 1 [29]; upon acidification, the neutral derivatives $M_3\{\mu\text{-}H,\mu,\eta^2\text{-}O{=}CNMe_2\}(CO)_9L$ are obtained. The ligand is found attached to the metal to which the oxygen of the bridging O=CN(Nu) group is also attached [29]. The carbonyl groups are not rapidly exchanging sites in these edge double-bridged derivatives. We were able to assign ^{13}C resonances of the individual CO groups. In following ^{13}C-enrichment, we observed this to occur initially at the metal atom to which the oxygen of the bridging O=C(Nu) group was attached [32]. There are two possible origins for the labilization of substitution at this site: (i) a "*cis*-labilization" by the oxygen of the $\{\mu,\eta^2\text{-}O{=}CNu\}$ group, or (ii) a mechanism where a vacant site is created by "lift-off" at oxygen of the (μ,η^2-O=CNu) group in $[\mathrm{B}'']^-$. This would create an isomer of the species $[\mathrm{B}^-]$ (Scheme 1) in which the $\{\eta^2\text{-C(=O)Nu}\}$ group is attached to an $\mathrm{M(CO)_3}$ center, while the vacancy created would be at the adjacent $\mathrm{M(CO)_3}$ group. The entering ligand would thus be accommodated at the site where it is observed in the final product while at the same time the $\{\eta^1\text{-C(=O)Nu}\}$ group would assist in the dissociation of a CO group (possibly at the $\mathrm{M(CO)_3}$ site where it is attached). The final product would be obtained when tautomerism of terminally bonded groups brought the vacancy to a position where the $\{\eta^1\text{-C(=O)Nu}\}$ group could become a bridging group again, i.e. $\{\mu,\eta^2\text{-O=CNu}\}$ group, as observed in the final product. By contrast, for substitutions on the derivatives $\mathrm{M_3\{\mu\text{-H},\mu\text{-C=NMe_2}\}(CO)_{10}}$ (M = Ru, with L = $\mathrm{PR_3}$, $\mathrm{AsPh_3}$, or $\mathrm{SbPh_3}$; M = Os, L = $\mathrm{AsPh_3}$) [33], initial attachment of L is observed at the unbridged $\mathrm{M(CO)_4}$ group. This kinetic product is seen to convert to an isomer in which L is substituted on a metal along the double-bridged edge.

When substitution reactions on $\mathrm{Ru_3\{\mu\text{-H},\mu,\eta^2\text{-O=CNMe_2}\}(CO)_{10}}$ were attempted with ethylene, we observed formation of bis-acyl complexes; this and related work on complexes derived from successive alkylation/oxidation of the parent $\mathrm{M_3(CO)_{12}}$ carbonyls (M = Ru or Os) has recently been reviewed [34] and is not discussed in detail here. Suffice it to say that trinuclear starting complexes of ruthenium are fragmented in this reaction giving di-nuclear bis-acyl complexes [35]; by contrast, the tri-nuclearity of the starting materials for complexes of osmium is maintained in the bis-acyl products [36]. We have recently been able to intercept the adduct $\mathrm{Os_3\{1,2\text{-}\mu\text{-H},1,2\text{-}\mu\text{-O=C(Me)}\}\{1\text{-}\eta^2\text{-CH_2=CH_2}\}(CO)_9}$, in which the ethylene is coordinated to the same metal atom to which the oxygen of the bridging {O=C(Me)} group is attached [36b].

We also investigated the reactions of acetylenes with the edge double-bridged cluster complexes which are described elsewhere [37,38]; again in this work there is evidence that the initial attachment of the acetylene is that as observed for ethylene above.

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References

1 R. Szostak, C.E. Strouse and H.D. Kaesz, J. Organomet. Chem., 191 (1980) 243.
2 E. Sappa and L. Milone, J. Organomet. Chem., 61 (1973) 383.
3 H.D. Kaesz and G. Lavigne, Chap. 4 in H. Knözinger, B.C. Gates, and L. Guczi (Eds.), Metal Clusters in Catalysis, Elsevier, Amsterdam, 1986, p. 43–88.
4 P.C. Ford and A. Rokicki, Adv. Organomet. Chem., 28 (1988) 139.
5 A. Mayr, Y.C. Lin, N.M. Boag, and H.D. Kaesz, Inorg. Chem., 21 (1982) 1704.
6 C.M. Jensen, C.B. Knobler, and H.D. Kaesz, J. Am. Chem. Soc., 106 (1984) 5926.

7 (a) G.R. Steinmetz and G.L. Geoffroy, J. Am. Chem. Soc., 103 (1981) 1278; (b) G.R. Steinmetz, E.D. Morrison, and G.L. Geoffroy, ibid., 106 (1984) 2559.

8 (a) T. Kruck, M. Höfler, and M. Noack, Chem. Ber., 99 (1966) 1153; (b) cf. R.J. Angelici, Acc. Chem. Res., 5 (1972) 335.

9 P. Chini, S. Martinengo, and G. Giordano, Gazz. Chim. Ital., 102 (1972) 330.

10 R.C. Schoening, J.L. Vidal, and R.A. Fiato, J. Organomet. Chem., 206 (1981) C43; (b) the transient formyl complex [$Ru_3\{\eta^1\text{-}C(O)H\}(CO)_{11}{}^-$], has also been observed in the reaction of $Ru_3(CO)_{12}$ with $LiEt_3BH$ at −78 °C (J.A. Partin and M.G. Richmond, J. Organomet. Chem., 353 (1988) C13).

11 M.W. Payne, D.L. Leussing, and S.G. Shore, J. Am. Chem. Soc., 109 (1987) 617.

12 (a) M. Anstock, D. Taube, D.C. Gross, and P.C. Ford, J. Am. Chem. Soc., 106 (1984) 3696; (b) D.C. Gross and P.C. Ford, ibid., 107 (1985) 585; (c) D.J. Taube, A. Rokicki, and P.C. Ford, Inorg. Chem., 26 (1987) 526.

13 D.L. Darensbourg, R.L. Gray, and M. Pala, Organometallics, 3 (1984) 1928.

14 (a) D.E. Morris and F. Basolo, J. Am. Chem. Soc. 90 (1968) 2536; (b) J.D. Atwood and T.L. Brown, ibid., 97 (1975) 3380; 98 (1976) 3155, and 3160; (c) M.A. Cohen and T.L. Brown, Inorg. Chem., 15 (1976) 1417; (d) D.L. Lichtenberger and T.L. Brown, J. Am. Chem. Soc., 100 (1978) 366; (e) T.L. Brown and P.A. Bellus, Inorg. Chem., 17 (1978) 3726.

15 (a) N.M. Boag, C.E. Kampe, Y.C. Lin, and H.D. Kaesz, Inorg. Chem., 21 (1982) 1706; (b) C.E. Kampe, N.M. Boag, C.B. Knobler, and H.D. Kaesz, ibid., 23 (1984) 1390.

16 K.-P. Schick, N.L. Jones, P. Sekula, N.M. Boag, J.A. Labinger, and H.D. Kaesz, Inorg. Chem., 23 (1984) 2204.

17 G. Lavigne and H.D. Kaesz, J. Am. Chem. Soc., 106 (1984) 4647.

18 J.P. Candlin and A.C. Shortland, J. Organomet. Chem., 16 (1969) 289.

19 M.I. Bruce, J.G. Matisons, and B.K. Nicholson, J. Organomet. Chem., 247 (1983) 321.

20 G. Lavigne, N. Lugan, and J.-J. Bonnet, Inorg. Chem., 26 (1987) 2347.

21 J.C. Bricker, C.C. Nagel, A.A. Bhattacharyya, and S.G. Shore, J. Am. Chem. Soc., 107 (1985) 377.

22 S-H. Han, G.L. Geoffroy, B.D. Dombek, and A.L. Rheingold, Inorg. Chem., 27 (1988) 4355.

23 T. Chin-Choy, W.T.A. Harrison, G.D. Stucky, N. Keder, and P.C. Ford, Inorg. Chem., 28 (1989) 2028.

24 J.L. Zuffa, S.J. Kivi, and W.L. Gladfelter, Inorg. Chem., 28 (1989) 1888.

25 R.E. Stevens and W.L. Gladfelter, Inorg. Chem., 22 (1983) 2034.

26 (a) J.L. Zuffa, M.L. Blohm and W.L. Gladfelter, J. Am. Chem. Soc., 108 (1986) 552; (b) J.L. Zuffa and W.L. Gladfelter, ibid., 108 (1986) 4669.

27 D.L. Darensbourg, M. Pala, and J. Walker Organometallics, 2 (1983) 1285.

28 G. Lavigne, N. Lugan, and J.-J. Bonnet, J. Chem. Soc. Chem. Commun., (1987) 957.

29 A. Mayr, Y.C. Lin, N.M. Boag, C.E. Kampe, C.B. Knobler, and H.D. Kaesz, Inorg. Chem., 23 (1984) 4640.

30 F.A. Cotton, B.E. Hanson, and J.D. Jamerson, J. Am. Chem. Soc., 99 (1977) 6588.

31 F.A. Cotton and B.E. Hanson, Inorg. Chem., 16 (1977) 2820.

32 C.E. Kampe and H.D. Kaesz, Inorg. Chem., 23 (1984) 4646.

33 M.R. Shaffer and J.B. Keister, Organometallics, 5 (1986) 561.

34 C.M. Jensen, Y.-J. Chen, C.B. Knobler and H.D. Kaesz, New J. Chem., 12 (1988) 649.

35 C.E. Kampe, N.M. Boag and H.D. Kaesz, J. Mol. Catal., 21 (1983) 297.

36 (a) C.M. Jensen, Y.-J. Chen, and H.D. Kaesz, J. Am. Chem. Soc., 106 (1984) 4046; (b) Y.-J. Chen, C.B. Knobler, and H.D. Kaesz, Polyhedron, 7 (1988) 1891.

37 N.B. Boag, W.J. Sieber, C.E. Kampe, C.B. Knobler, and H.D. Kaesz, J. Organomet. Chem., 355 (1988) 385.

38 H.D. Kaesz, Z. Xue, Y.-J. Chen, C.B. Knobler, W. Krone-Schmidt, W.J. Sieber and N.M. Boag, Pure & Appl. Chem., 60 (1988) 1245.