Synthesis of the Alkoxo(hydrido)-clusters $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OR)]$ [R = Me, Et, Pr^n, or Bu^n] catalysed by Dinuclear Carbonyl Iron Complexes

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The use of dinuclear carbonyl iron complexes, namely $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ and $[Fe_2(CO)_4(PPh_3)_2(SMe)_2]$, as catalysts in reactions of CO replacement by the weak nucleophilic molecules ROH (R = Me, Et, Pr^n, or Bu^n) allows the isolation of the novel series of derivatives $[Ru_3(\mu\text{-}H)(CO)_{10}(\mu\text{-}OR)]$, previously inaccessible by thermal routes.

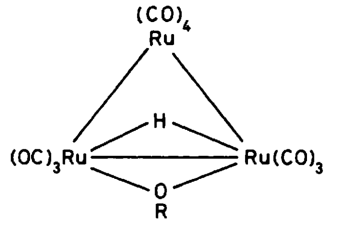
Derivatives of formula $[Os_3H(CO)_{10}(OR)]$ (R = H, alkyl, or aryl) are well known products of the reactions between $[Os_3(CO)_{12}]$ and alcohols at elevated temperatures;[1] marked improvements in their yields have been obtained *via* the 'lightly stabilized' intermediates $[Os_3(CO)_{10}L_2]$ (L = cyclo-octene or acetonitrile) which have good leaving groups.[2]

No synthetic route to the analogous ruthenium derivatives has yet been reported since the normal thermal activation of $[Ru_3(CO)_{12}]$ in the presence of alcohols invariably affords only small amounts of $[Ru_4H_4(CO)_{12}]$ and $[Ru_4H_2(CO)_{13}]$ along with extensive decomposition.[3] However interest in obtaining such compounds as molecular models has grown since several papers, dealing with $[Ru_3(CO)_{12}]$ chemisorbed on silica, indicate the formation of $[Ru_3H(CO)_{10}(O\text{–}Si{\leqslant})]$ grafted to the inorganic support.[4]

Recently we and others described the ability of $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$,[5] $[Fe_2(CO)_6(SMe)_2]$,[6] and other binuclear systems in promoting the substitution of CO groups by PR_3 and $P(OR)_3$ ligands in a variety of metal carbonyl clusters. In order to test the viability of this approach in reactions other than simple CO replacement by usual Lewis bases, we undertook a study of the reaction between $[Ru_3(CO)_{12}]$ and the weak nucleophiles ROH (R = Me, Et, Pr^n, or Bu^n) in the presence of binuclear iron complexes as catalysts.

Results and Discussion

The catalysts used in the reactions were $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (**1**), $[Fe_2(CO)_6(SMe)_2]$ (**2**), and $[Fe_2(CO)_4(PPh_3)_2(SMe)_2]$ (**3**). Both (**1**) and (**3**) proved able to promote the formation of complexes $[Ru_3H(CO)_{10}(OR)]$ (R = Me, Et, Pr^n, or Bu^n), whose characterization was possible on the basis of i.r., ^1H n.m.r., and mass spectra (Table). In particular their i.r. spectra are very similar to those of the analogous Os derivatives, all bands being shifted to lower frequences by 3—7 cm^{-1} for the Ru complexes.



R = Me, Et, Pr^n, or Bu^n

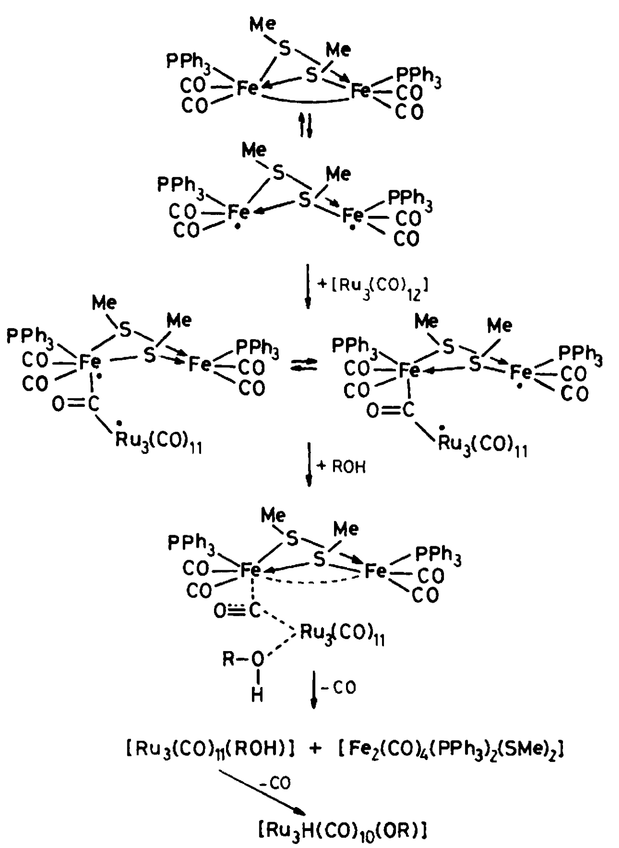
It is worth commenting that the high-field resonances of $[Ru_3H(CO)_{10}(OMe)]$ (δ −11.90 p.p.m.) and $[Ru_3H(CO)_{10}(OEt)]$ (δ −11.97 p.p.m.) correspond exactly to those found by Lewis and co-workers[7] in the ^1H n.m.r. hydride region of mixtures arising from the carbonylation of $RuCl_3$ in methanol and ethanol respectively. At that time Lewis and co-workers suggested that these resonances were likely to be associated to ruthenium carbonyl hydrido clusters having methoxo or ethoxo groups.[7]

Isoelectronic ruthenium complexes, namely $[Ru_3H(CO)_{10}X]$ (X = Cl, Br, or I), have been reported by Kaesz and co-workers[8] through a very different pathway. On the other hand, reactions in the presence of (**2**) did not afford any detectable formation of $[Ru_3H(CO)_{10}(OR)]$ products but invariably gave rise to the same hydrido complex, whose spectral data clearly indicate it to be $[Ru_3H(CO)_{10}(SMe)]$.[9] It is likely that in this case the binuclear iron derivative interacts with the alcohol affording in solution the MeSH species, which promptly reacts

Table. Spectroscopic data and yields

Compound	ν(CO)^a/cm^{-1}	δ(^{1}H)^b/p.p.m.	M^{+c}	Yield (%) *d*	Yield (%) *e*
$[Ru_3H(CO)_{10}(OMe)]$	2 105w, 2 065vs, 2 057s, 2 026vs, 2 013m, 2 010s, 1 995m	3.37 (s, 3), −11.90 (s, 1)	618	7	—
$[Ru_3H(CO)_{10}(OEt)]$	2 106w, 2 067vs, 2 058s, 2 028vs, 2 025vs, 2 014m, 2 012s, 1 994m	3.35 (q, 2), 1.19 (t, 3), −11.97 (s, 1)	632	15	5
$[Ru_3H(CO)_{10}(OPr^n)]$	2 106w, 2 067vs, 2 058s, 2 027vs, 2 025vs, 2 014m, 2 009s, 1 993m	3.25 (t, 2), 1.55 (m, 2), 0.34 (t, 3), −12.01 (s, 1)	646	30	12
$[Ru_3H(CO)_{10}(OBu^n)]$	2 106w, 2 067vs, 2 058s, 2 028vs, 2 025vs, 2 014m, 2 010s, 1 993m	3.29 (t, 2), 1.53 (m, 2), 1.24 (m, 2), 0.88 (t, 3), −12.02 (2, 1)	660	40	18

[a] In n-hexane. [b] In $CDCl_3$ at 25 °C. [c] Followed by stepwise loss of 10 CO. [d] With $[Fe_2(CO)_4(PPh_3)_2(SMe)_2]$ as catalyst. [e] With $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ as catalyst.



Scheme.

with $[Ru_3(CO)_{12}]$ to form the $[Ru_3H(CO)_{10}(SMe)]$ cluster. The crossover species $[Fe_2(CO)_6(SMe)(OR)]$ and $[Fe_2(CO)_6(OR)_2]$ might be formed in this way, but we were unable to detect them.

On going from (**2**) to (**3**), the presence of two phosphine ligands strengthens the chalcogen bridge bonds so that replacement of a SMe group by OR is no longer possible. The stabilization of the iron–sulphur bonds has been suggested by theoretical calculations, which indicate that a higher electronic charge (in our case brought about by the better σ donor, phosphine ligand) causes an increase in the iron to sulphur back-bonding interaction.[10] Furthermore the bulky PPh_3 ligand causes an overall flattening of the complex, which in turn favours the homolytic cleavage of the metal–metal bond.

We think that the biradical species $[Fe(CO)_2(PPh_3)(SMe)]_2^{\bullet\bullet}$ is generated by thermal activation and is the actual catalyst for CO substitution in the $[Ru_3(CO)_{12}]$ substrate.[6] In analogy to the previously reported mechanism, we suggest that the pathway leading to species $[Ru_3H(CO)_{10}(OR)]$ takes place according to the Scheme.The $[Ru_3H(CO)_{10}(OR)]$ yields follow the order Me < Et < Pr^n < Bu^n which provides further support to the suggested mechanism, as the important step related to the formation of the $[Ru_3(CO)_{11}(ROH)]$ adduct is clearly related to the nucleophilicity of the alcohol employed, which shows the same order of the product yields. The formation of the final compound $[Ru_3H(CO)_{10}(OR)]$ is accounted for by a simple internal oxidative–addition coupled with the extrusion of a CO ligand through a well established pathway in the chemistry of metal carbonyl clusters.

In conclusion we consider that the use of binuclear transition-metal carbonyl complexes as catalysts could provide a route to the low-temperature chemistry of $[Ru_3(CO)_{12}]$, thus allowing the isolation of novel products inaccessible under more drastic experimental conditions.

Experimental

Complex $[Fe_2(\eta^5\text{-}C_5H_5)_2(CO)_4]$ (**1**) was purchased from Strem Chemicals Ltd. while $[Fe_2(CO)_6(SMe)_2]$[11] (**2**) and $[Fe_2(CO)_4(PPh_3)_2(SMe)_2]$[12] (**3**) were prepared by the published procedures or modification thereof.

All reactions were routinely brought about in double-necked flasks under N_2 and the $[Ru_3(CO)_{12}]$ to catalyst molar ratio was always 10:1.

In a typical run $[Ru_3(CO)_{12}]$ (320 mg, 0.5 mmol) and a suitable amount of the catalyst (0.05 mmol) in cyclohexane (150 cm^3) were heated and stirred. When all the $[Ru_3(CO)_{12}]$ had dissolved, an excess of the appropriate alcohol (*ca.* 2 cm^3) was added and the reactant solution was refluxed and checked by t.l.c. and i.r. spectroscopy. The reaction was complete typically in 3 h. After filtration, the excess alcohol and solvent were removed under reduced pressure, and the residue, dissolved in chloroform, was separated by t.l.c. (eluant light petroleum) to give three compounds. The faster moving band (yellow-orange) corresponded to $[Ru_3H(CO)_{10}(OR)]$ and the other two yellow bands were identified as $[Ru_4H_4(CO)_{12}]$ (*ca.* 5%) and unreacted $[Ru_3(CO)_{12}]$. T.l.c. work-up also showed other products, in very low yields, which have not been characterized.

^1H N.m.r. spectra were recorded on a JEOL GX-270/89 spectrometer, i.r. spectra on a 580 B Perkin-Elmer instrument with Data Station, and mass spectra on a Kratos A.E.I. M.S. 12 spectrometer using electron impact, direct inlet, and an ionizing potential of 70 eV.

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