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XXXV *. REACTIONS OF SOME RUTHENIUM CLUSTER COMPLEXES WITH HYDROGEN: CLEAVAGE OF ELEMENT–CARBON BONDS

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Summary

Hydrogenation (20 atm, 80°C, 2 h) of trinuclear $Ru_3(CO)_{12-n}L_n$ (L = tertiary phosphine or phosphite; $n = 1$–3) resulted in aggregation to give mixtures of $H_4Ru_4(CO)_{12-n}(L)_n$ ($n = 0$–4), but $Ru_3(CO)_{10}(L–L)$ (L–L = dppm, dpam) gave $Ru_3(\mu\text{-H})(\mu_3\text{-PhECH}_2\text{EPh}_2)(CO)_9$ (E = P, As, respectively) and $Ru_3(\mu\text{-H})_2(\mu_3\text{-PPh})(CO)_8(PMePh_2)$, and $Ru_3(\mu\text{-H})(\mu_3\text{-SBu}^t)(CO)_9$ gave $Ru_3(\mu\text{-H})_2(\mu_3\text{-S})(CO)_9$ by cleavage of P–C, As–C, or S–C bonds. Both types of reaction occurred with $Ru_3(CO)_{10}(dppe)$ and $[Ru_3(CO)_{11}]_2(\mu\text{-dppe})$.

The facile conversion of $Ru_3(CO)_{12}$ to $Ru_4(\mu\text{-H})_4(CO)_{12}$ by reaction with hydrogen in refluxing octane [1] has few parallels in the reactions of other ruthenium complexes. Hydrogenation of $Ru_3(CO)_{11}(CNBu^t)$, for example, affords $Ru_4(\mu\text{-H})_4(CO)_{12-n}(CNBu^t)_n$ ($n = 0$–2) together with $Ru_3(\mu\text{-H})(\mu_3\text{-HC=NBu}^t)(CO)_9$, the latter being formed by addition of hydrogen to the isocyanide ligand and the cluster core [2]. Similar reactions of $Ru_3(CO)_8(L–L)_2$ (L–L = dppm, dpam) afforded the bis-dephenylated complexes $Ru_3(\mu\text{-H})_2(\mu_3\text{-PhECH}_2\text{EPh}_2)_2(CO)_6$ (E = P or As, respectively) [3]. The ready availability of an extensive series of Group 5-donor ligand-substituted ruthenium carbonyls [4] prompted a more detailed investigation of their reactions with hydrogen under relatively mild conditions.

Cyclohexane solutions of complexes $Ru_3(CO)_{12-n}L_n$ (L = tertiary phosphine or phosphite, $n = 1$–3) react with hydrogen (20 atm, 80°C, 2 h) to give mixtures of the tetranuclear hydrido clusters $Ru_4(\mu\text{-H})_4(CO)_{12-n}(L)_n$, which can be readily separated by preparative TLC (Kieselgel GF_{254} (Type 60), developed with hexane/

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* For Part XXXIV, see ref. 15.

acetone mixtures). Table 1 summarises the results obtained for L = PPh_3, $PPh(OMe)_2$ and $P(OMe)_3$; complexes containing other tertiary phosphines and phosphites behaved similarly. The reactions are characterised by the ready formation of polysubstituted complexes, even when the precursor is monosubstituted, together with an apparent reluctance to form the tetrasubstituted derivatives, $Ru_4(\mu\text{-}H)_4(CO)_8(L)_4$, even when the trinuclear complex contained one ligand on each metal atom (cf. the X-ray structure of $Ru_3(CO)_9(PMe_3)_3$ [5]).

Consideration of the results presented in Table 1 indicates that these apparently simple reactions are in reality quite complex, and that even a qualitative rationalisation of the reaction products requires that

(i) facile rearrangement/redistribution reactions occur between these complexes (this has been confirmed by separate experiments);
(ii) ligands L can be readily displaced by CO (and perhaps H_2), and vice versa;
(iii) the final product ratios may be affected by the size of the ligand L (no tri- or tetra-substituted cluster hydride was obtained for L = PPh_3);
(iv) the Ru–Ru bonds are cleaved by oxidative addition of H_2 (no products formed by degradation of the tertiary phosphine or phosphite ligands were identified in any reaction).

These reactions were initially studied as possible routes to selectively substituted $H_4Ru_4(CO)_{12\text{-}n}(L)_n$ complexes; although some of the required complexes were obtained, these reactions are experimentally less convenient than the radical-ion catalysed substitutions reported earlier [6].

Extension of the hydrogenation reactions to complexes containing bidentate tertiary phosphines or arsines might be expected to give different results if fragmentation of the cluster was prevented by the bidentate ligand. As found previously with $Ru_3(CO)_8(L\text{–}L)_2$ (L–L = dppm, dpam) [3], the major reaction products obtained from $Ru_3(CO)_{10}(L\text{–}L)$ ((**1**) and (**2**)) were the dephenylated complexes $Ru_3(\mu\text{-}H)(\mu_3\text{-}PhECH_2EPh_2)(CO)_9$ ((**3**) and (**4**), respectively), obtained in 75% (E = P) and 65% yields (E = As). These complexes can also be formed by sequential addition of

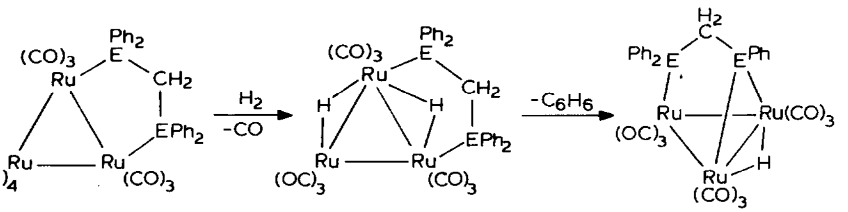
TABLE 1

COMPLEXES FORMED FROM $Ru_3(CO)_{12\text{-}n}L_n$ AND H_2 [a]

Precursor, $Ru_3(CO)_{12\text{-}n}L_n$		Product, $H_4Ru_4(CO)_{12\text{-}n}(L)_n$					Remarks
L	n	$n = 0$	$n = 1$	$n = 2$	$n = 3$	$n = 4$	
PPh_3	1	4.9	67.0	7.8	n.d.	n.d.	[b]
	2	1.7	62.8	10.8	n.d.	n.d.	
	3	n.d.	n.d.	64.3	n.d.	n.d.	
$PPh(OMe)_2$	1	4.4	69.9	5.2	1.2	n.d.	[c]
	2	n.d.	34.2	43.9	10.4	n.d.	
	3	n.d.	2.2	28.1	21.5	n.d.	
$P(OMe)_3$	1	7.2	57.8	3.9	n.d.	n.d.	[d]
	2	0.6	16.9	57.1	3.0	n.d.	
	3	n.d.	n.d.	15.0	14.0	3.3	

[a] Standard conditions: cyclohexane solution (2.5 mg ml^{-1}); 20 atm H_2, 80°C, 2 h. [b] Complexes $H_4Ru_4(CO)_{12\text{-}n}(PPh_3)_n$ identified from literature [12] and authentic samples. [c] Complexes $H_4Ru_4(CO)_{12\text{-}n}\{PPh(OMe)_2\}_n$ identified by independent synthesis [14]. [d] Complexes $H_4Ru_4(CO)_{12\text{-}n}\{P(OMe)_3\}_n$ identified from literature [13] and independent synthesis.

H^- and H^+ to the same precursors [7]. Oxidative addition of H_2 to the Ru_3 complexes is followed by P–C bond cleavage and elimination of benzene (eq. 1), the μ_3-bridging ligands preventing both break-up and condensation of the clusters, as expected.



(1)

(1, E = P;
2, E = As)

(3, E = P;
4, E = As)

Cleavage of a second P–C bond occurred after prolonged reaction, both **1** and **3** giving $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$ (**5**) after two days (ν(CO) (cyclohexane) 2077s, 2044vs, 2008vs, 1998(sh), 1996vs, 1980m cm^{-1}; ^1H NMR: δ ($CDCl_3$) 7.27–8.18 (m, 15H, Ph), 2.14 (d, J(PH) 7.7 Hz, 3H, Me), −18.71 (d, J(HP) 12.9 Hz, 1H, RuH), −18.91 (d, J(HP) 12.0 Hz, 1H, RuH). This unusual reaction is a net conversion of the dppm ligand to benzene, coordinated phenylphosphinidene and $PMePh_2$ mediated by the cluster.

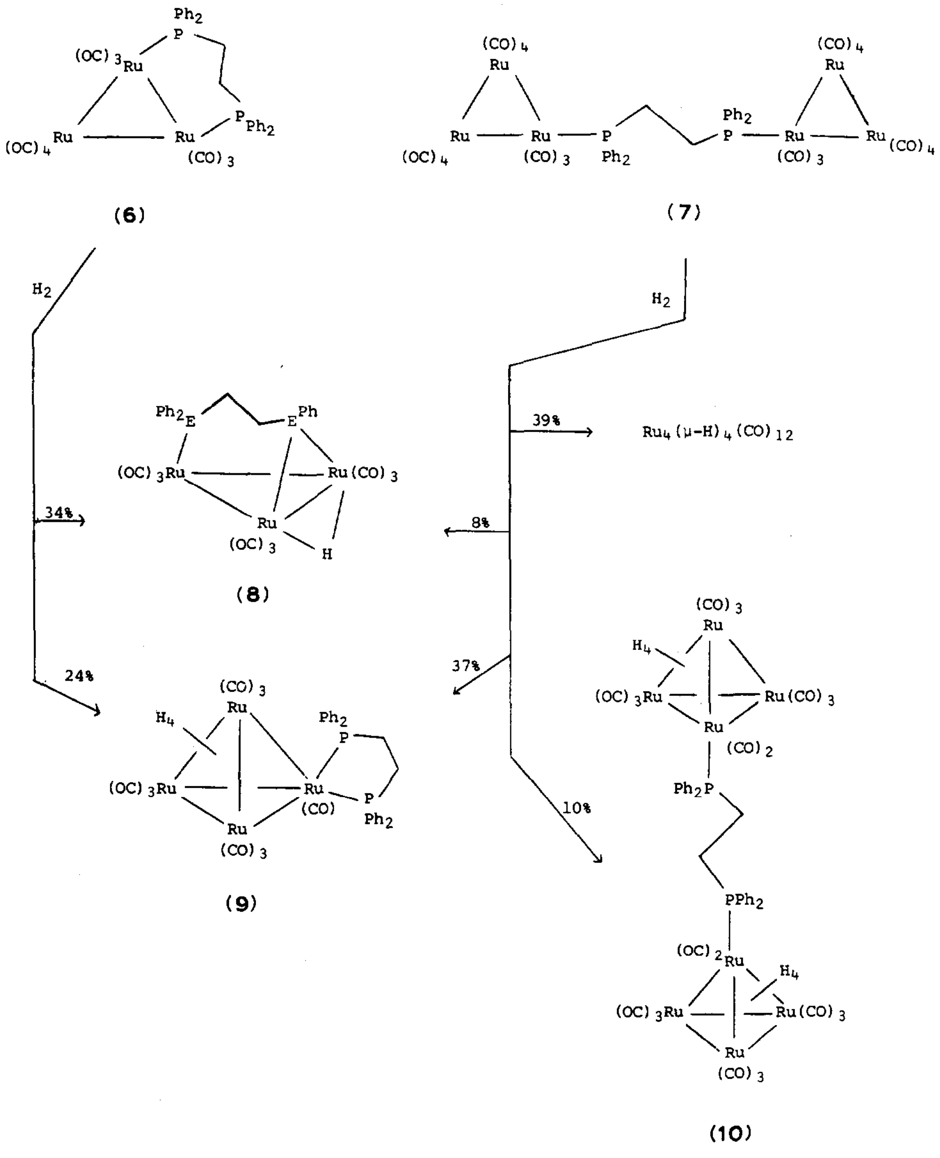
In contrast again, the complexes $Ru_3(CO)_{10}$(dppe) (**6**) and $[Ru_3(CO)_{11}]_2(\mu$-dppe) (**7**) afford mixtures of tri- and tetra-nuclear compounds **8**–**10** (Scheme 1). A route to the tetranuclear complex **8** could involve conversion of the precursor to an intermediate containing an η^1-dppe ligand, which would be expected to react in a similar way to the other complexes containing monodentate ligands described above, and also observed with **7**.

This element–carbon bond cleavage reaction is also exhibited by Group 6 donor ligands. The reaction between $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_9$ and hydrogen afforded $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$, a not-unexpected result since cleavage of the C–S bond by heating $Ru_3(\mu\text{-}H)(\mu\text{-}SEt)(CO)_{10}$ in concentrated sulphuric acid has been described previously [8]. Hydrogenation of $Ru_3(\mu\text{-}H)(\mu_3\text{-}SBu^t)(CO)_7$(dppm) also results in C–S, but not C–P, bond cleavage, giving the complex $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_7$(dppm) as the sole product. Others have also remarked that such reactions are common with sulphur-containing ligands [9], although they are apparently not well documented.

The facile loss of small molecules formed by element–carbon bond cleavage and combination of the resulting fragment with a hydrogen atom on the metal cluster is also demonstrated by pyrolysis of $Ru_4(\mu\text{-}H)_4(CO)_{10}$(dppm) (toluene, 105°C, 1.5 h), which afforded $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_{10}$ (ν(CO) 2075m, 2056s, 2024 vs, 1996m, 1981m, 1898w, 1843m cm^{-1}; RuH at δ −17.95, s(br), 1H, −19.74, s(br), 2H). Other recent examples of similar reactions have been noted, including the synthesis of sulphido-osmium clusters by pyrolysis of $Os_3(\mu\text{-}H)(\mu\text{-}SPh)(CO)_{10}$ [10] and of the mixed-metal complex $MnRu(\mu\text{-}PPh_2)(CO)_6(PPh_3)_2$ by reaction of $[Mn(CO)_5]^-$ with $RuCl_2(PPh_3)_3$ [11].

It is interesting to find that the formation of tetranuclear clusters is prevented in the presence of an actual or potential μ_3-bridging ligand, further pointing to the utility of such ligands in the preservation of such clusters in the presence of hydrogen. Our results also indicate the readiness with which these bidentate or

SCHEME 1. Reactions of $Ru_3(CO)_{12}$-dppe complexes with H_2.



bridging ligands fragment under those conditions. Full details of these experiments will be presented elsewhere.

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