Coordination Chemistry Reviews, 76 (1987) 1–43
Elsevier Science Publishers B.V., Amsterdam – Printed in The Netherlands

SOME REACTIONS OF RUTHENIUM CLUSTER CARBONYLS UNDER MILD CONDITIONS

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(Received 6 January 1986)

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ABBREVIATIONS

bipy	2,2′-bipyridyl
Cy	cyclohexyl
diars	phenylene-1,2-bis(dimethylarsine), $C_6H_4(AsMe_2)_2$-1,2
dpae	1,2-bis(diphenylarsino)ethane, $AsPh_2CH_2CH_2AsPh_2$
dpam	bis(diphenylarsino)methane, $CH_2(AsPh_2)_2$
dppa	1,2-bis(diphenylphosphino)acetylene, $PPh_2C{\equiv}CPPh_2$
dppe	1,2-bis(diphenylphosphino)ethane, $PPh_2CH_2CH_2PPh_2$
dppm	bis(diphenylphosphino)methane, $CH_2(PPh_2)_2$
ebdp	*cis*-ethylene-1,2-bis(diphenylphosphine), $CH(PPh_2){=}CH(PPh_2)$
ETC	electron-transfer-catalysed
ffars	1,2-bis(dimethylarsino)tetrafluorocyclobutene, $C_4F_4(AsMe_2)_2$-1,2
ppn	bis(triphenylphosphine)iminium, $[N(PPh_3)_2]^+$
sp	styryldiphenylphospine, $C_6H_4(CH{=}CH_2)(PPh_2)$-1,2

0010-8545/87/$15.05

A. INTRODUCTION

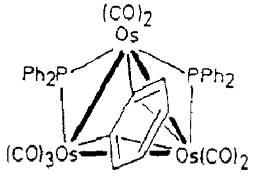
The chemistry of metal cluster complexes is a topic of much current interest, one reason being the expectation that a study of the reactions of small molecules coordinated to the metal cluster may shed some light on their similar reactions when chemisorbed on a metal surface [1]. Studies in this area have produced a multitude of intrinsically interesting molecules, whose unusual and intriguing structures have prompted many theoretical developments which even now are leading to a greater understanding of the properties of metals.

However, of the metal cluster carbonyls that are commonly used as precursors, those of Group 8 * have proved to be the more difficult to substitute under mild conditions. Whereas reactions of $Co_4(CO)_{12}$ [2,3] or $Rh_4(CO)_{12}$ [4–7], and where they have been studied, of $Rh_6(CO)_{16}$ [8,9], $Ir_4(CO)_{12}$ [10–14] or $Ir_6(CO)_{16}$ [15,16] proceed under mild conditions to give well-defined products, it is found that reactions of $Fe_3(CO)_{12}$ often lead to cluster break-up, while substitution of CO groups in $Ru_3(CO)_{12}$ occurs only at higher temperatures (ca. 80–100°C), and in $Os_3(CO)_{12}$ under even more vigorous conditions. Thus, the reactions of these three cluster carbonyls with PPh_3 are illustrative.

$$Fe_3(CO)_{12} + PPh_3 \rightarrow Fe(CO)_{5-n}(PPh_3)_n \qquad (n = 1 \text{ and } 2)$$

$$Ru_3(CO)_{12} + PPh_3 \rightarrow Ru_3(CO)_9(PPh_3)_3$$

$$Os_3(CO)_{12} + PPh_3 \rightarrow Os_3(CO)_{12-n}(PPh_3)_n \qquad (n = 1, 2 \text{ and } 3)$$
$$+ \text{six other cluster complexes } (\mathbf{1})\text{–}(\mathbf{6})$$



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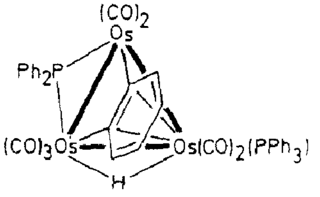

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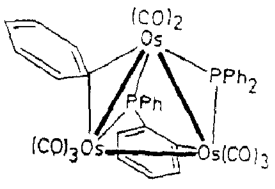

(3)

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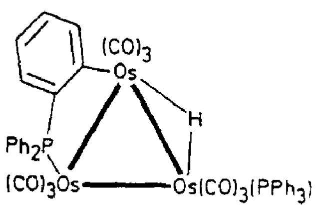
* In this article the periodic group notation is in accord with recent proposals by IUPAC and the American Chemical Society nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become Groups 1 and 2. The *d*-transition elements comprise Groups 3–12, and the *p*-block elements comprise Groups 13–18. The former Roman number designation is preserved in the last digit of the new numbering.



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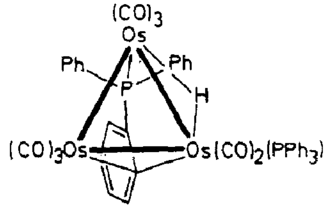

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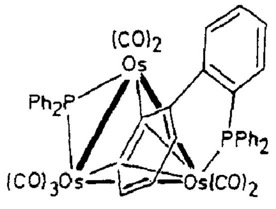
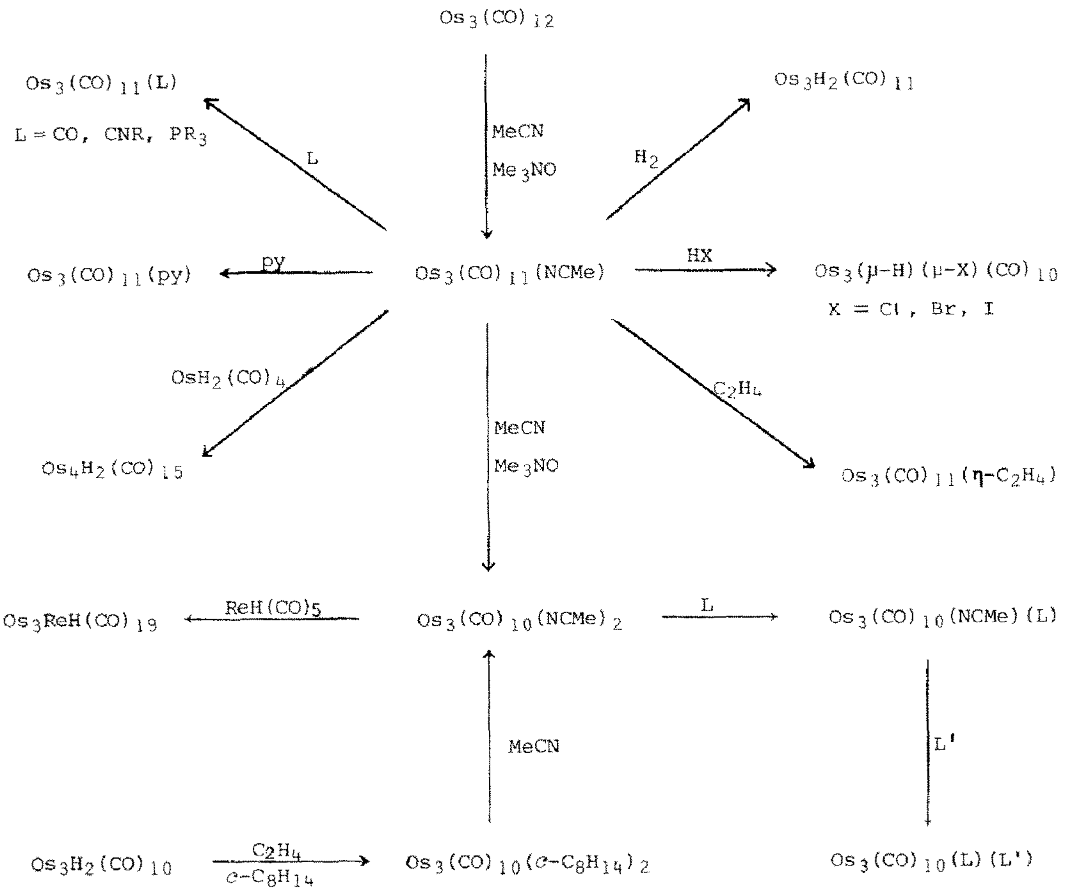


(6)

The reaction conditions are respectively, in refluxing tetrahydrofuran or dioxan [17], in refluxing benzene or cyclohexane [18–21], and in refluxing xylene [22–24]. In the case of $Ru_3(CO)_{12}$, the disubstituted complex can be obtained by carrying out the reaction in refluxing hexane, when the product precipitates [25], or under a CO atmosphere [26]; no general reaction conditions for the preparation of specifically substituted complexes were known before the studies reported below. The harsh conditions required for the reaction of the osmium congener result in further reaction of the initially formed products, with metallation and P–C bond cleavage reactions occurring with the complexed PPh_3 ligands to give complexes (**1**)–(**6**). A fourth, well-studied cluster complex, $Ru_4(\mu\text{-}H)_4(CO)_{12}$, proved to react with tertiary phosphines or phosphites with the production of all five complexes $Ru_4(\mu\text{-}H)_4(CO)_{12-n}(PR_3)_n$ ($n = 0$–4), which could only be separated with difficulty by extensive chromatography [27]. Only with $Ru_5C(CO)_{15}$ and $Ru_6C(CO)_{17}$ is it possible to prepare complexes specifically substituted with Group 15 donor ligands: reactions occur readily in CH_2Cl_2 solution at −40 and 0°C, respectively [28,29].

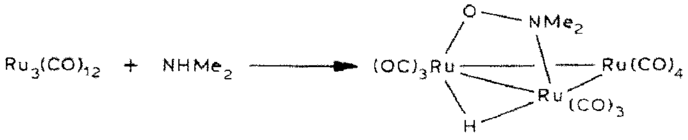
It was clearly evident that molecules coordinated to carbonyl clusters of the Group 8 metals were activated towards further reactions, which often occurred under the conditions used for the initial reaction: the complex mixtures of products reported in initial papers describing the reactions of the Ru and Os clusters particularly can now be seen to result from alteration of first-formed products. But how to study those first-formed products when the conditions for their formation were apparently harsher than those required for the alteration reactions?

The problem was solved for the osmium system by the discovery of the ready substitution of one or two CO ligands by acetonitrile when solutions of $Os_3(CO)_{12}$ in that solvent were treated with Me_3NO [30,31]. The bis-acetonitrile complex was also obtained from $Os_3(CO)_{10}(c\text{-}C_8H_{14})_2$ [32]. The acetonitrile ligands could then be substituted in turn by other molecules, such as ethylene, pyridine, tertiary phosphines and arsines, etc. (Scheme 1) by simply introducing them into the solutions of the $Os_3(CO)_{12-n}(NCMe)_n$ ($n = 1$ or 2) complexes.

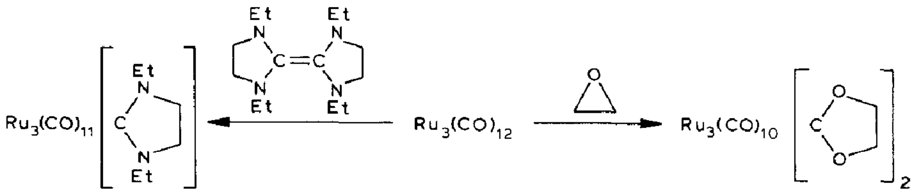


Scheme 1. Synthesis and some reactions of $Os_3(CO)_{12-n}(NCMe)_n$. Other substrates include: alkynes, methylenes (from diazoalkanes), aldehydes, α,β-unsaturated ketones, thiols, selenols, amines, amides, amidines, aldimines, thioamides, sulphur diimides, azides, diazonium salts, diazo esters, nitrogen heterocycles. See: K. Burgess, Polyhedron, 3 (1984) 1175.

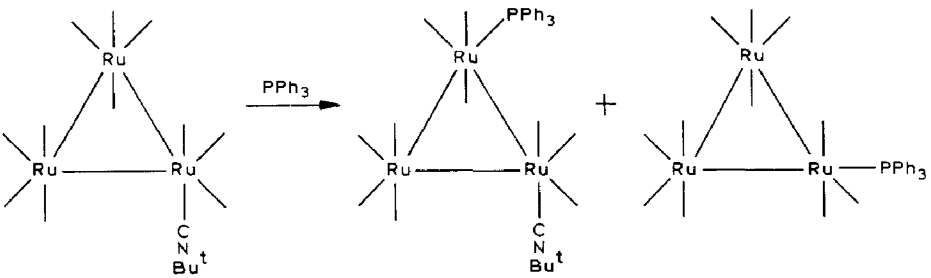
Unfortunately, the attempted extension of this approach to the ruthenium carbonyls resulted only in rapid decomposition, although recently the preparation, characterisation and some reactions of these potentially useful complexes have been described [33]. In only a few reactions of $Ru_3(CO)_{12}$ does ready substitution of CO by another ligand occur. Thus, with amines such as $NHMe_2$, reaction with coordinated CO (which, quite remarkably, occurs at −30°C) affords a μ-formamido ligand [34].



Carbene complexes have been obtained from reactions between an electron-rich olefin [35] or oxirane [36].



Reactions between $Ru_3(CO)_{12}$ and isocyanides, which take place in refluxing pentane, give high yields of the monosubstituted complexes $Ru_3(CO)_{11}(CNR)$ ($R = Bu^t$, Cy, C_6H_4OMe-4, etc.) [37]. Further reactions of these complexes with tertiary phosphines or arsines (L) then afforded relatively easily separable mixtures of $Ru_3(CO)_{11}(L)$ and $Ru_3(CO)_{10}(CNR)(L)$ [38].



In principle, the isocyanide in the latter complexes could be substituted in a second reaction with a second mole of L, although in practice substitution of CO is competitive, and such reactions often afford mixtures.

This was the situation in mid-1981, when Dr. Brian Nicholson, who was spending a sabbatical year in our laboratories, made us aware of the exciting results that were being obtained in the electron-transfer-catalysed (ETC) reactions of binuclear cobalt carbonyl–alkyne complexes with Group 15 donor ligands, including some remarkable stereospecific substitution reactions [39,40]. The possibility of applying these reactions to the long-sought specific synthesis of substituted cluster carbonyl derivatives was obvious. We first studied the substitution reactions of the three Group 8 cluster carbonyls with t-butyl isocyanide, using ca. 0.025 M solutions of sodium diphenylketyl in tetrahydrofuran as the electron transfer catalyst *. To our delight, we

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* Reproducible results are only obtained when the deep purple ketyl solution, obtained by stirring sodium with benzophenone in dry tetrahydrofuran for ca. 60 min under nitrogen, is used; the first-formed blue charge-transfer complex is not an efficient catalyst. The solution is stable for about 2 days, and may be regenerated by adding more benzophenone and stirring as above.

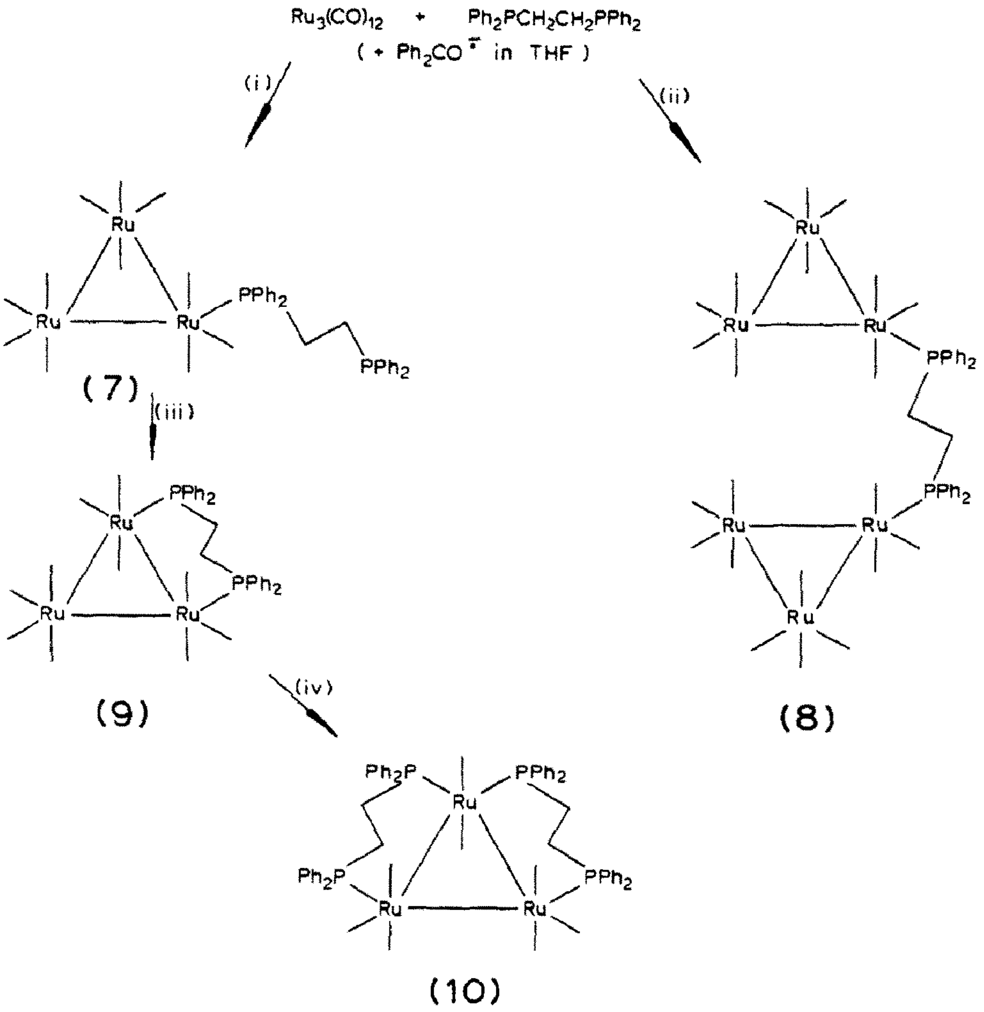
found that immediate substitution occurred at room temperature to give a virtually quantitative yield of the monosubstituted products. Examination of the similar reactions of PPh_3 showed that the mono-, di- and trisubstituted ruthenium complexes could be obtained in about 5 min by dropwise addition of the catalyst to stoichiometric mixtures of the cluster carbonyl and the ligand; again reactions occurred immediately and virtually quantitatively (as judged by TLC and IR examination of the reaction mixtures) [41].

We then asked John Matisons, who was completing his Ph.D. studies, to examine the scope of these reactions, and in a remarkably short period he had made and characterised some 75 known and new complexes from $Ru_3(CO)_{12}$ and a range of isocyanides, tertiary phosphines, phosphites, arsines and $SbPh_3$ [42]. We also briefly examined the reactions of other cluster carbonyls, and found that stoichiometric substitution occurred with such compounds as $Co_3(\mu_3\text{-CCl})(CO)_9$, $Rh_6(CO)_{16}$, and $Ru_4(\mu\text{-H})_4(CO)_{12}$. Most of these reactions have been reported in the original papers [41,42], and at the time of publication we became aware that we were not alone: the Otago group also reported application of this catalyst to the preparation of substituted derivatives of $Fe_3(CO)_{12}$, $Ru_3(CO)_{12}$, $Os_3(CO)_{12}$, $Co_3(\mu_3\text{-CPh})(CO)_9$ and $Ir_4(CO)_{12}$ [40].

B. SCOPE OF THE REACTION

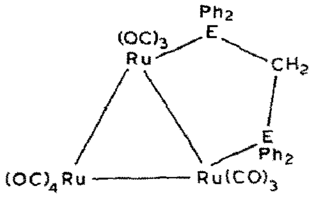
The mild conditions attendant upon these reactions allow the synthesis of cluster complexes which are otherwise sensitive to further reaction. Thus from the reaction between $Ru_3(CO)_{12}$ and $PPh_2CH_2CH_2PPh_2$ (dppe) under appropriate conditions (Scheme 2), it has proved possible to isolate $Ru_3(CO)_{11}(\eta^1\text{-dppe})$ (**7**) (with only one P atom coordinated), $\{Ru_3(CO)_{11}\}_2(\mu\text{-dppe})$ (**8**) (with one dppe ligand bridging two Ru_3 clusters), $Ru_3(CO)_{10}(\mu\text{-dppe})$ (**9**) and $Ru_3(CO)_8(\mu\text{-dppe})_2$ (**10**) (both having dppe bridging Ru–Ru bonds), all in good yield [43]. In the case of dppm, we were not able to detect the monodentate complex analogous to (**7**), but $Ru_3(CO)_{10}(\mu\text{-dppm})$ (**11**, E = P) was isolated in > 90% yield from stoichiometric reactions [42]. The corresponding thermal reaction in refluxing cyclohexane afforded the di- and tetra-CO-substituted derivatives together with small amounts of $Ru_3(\mu_3\text{-PPh})(\mu\text{-CHPPh}_2)(\mu\text{-dppm})(CO)_7$; the latter was obtained in higher yield from a reaction in xylene at 130°C [44]. However, the generally less reactive $Os_3(CO)_{12}$ system did afford the monodentate complex, and a subsequent kinetic study of its slow conversion to $Os_3(CO)_{10}(\mu\text{-dppm})$ showed that bridge formation is an associative process (S_N2 or I_a) [45].

Similarly, while the ETC reaction between $Ru_3(CO)_{12}$ and *o*-styryldiphenylphosphine (sp) gave the chelate complex $Ru_3(\mu\text{-}\eta^2,P\text{-}CH_2\text{=}CH\text{-}$



Scheme 2. Reactions of $Ru_3(CO)_{12}$ and dppe. Conditions (i) Ru_3/dppe = 1/1, 40 °C, minimum catalyst, 5 min; (ii) Ru_3/dppe = 2/1, 40 °C; (iii) Ru_3/dppe = 1/1, 40 °C, excess catalyst, 10 min; (iv) Ru_3/dppe = 1/2, 25 °C, excess catalyst, 15 min.

$C_6H_4PPh_2)(CO)_{10}$ [46], the *P*-bonded complex, $Os_3(CO)_{11}(sp)$, was obtained from the thermal reaction between sp and $Os_3(CO)_{11}(NCMe)$ [47].



(11) E = P or As

TABLE 1

Substituted cluster carbonyls prepared by $Na^+[Ph_2CO]^-$ catalysed reactions

Ligand	n	Yield (%) [a]	ν(CO) (cm^{-1})	Refs.
From $Fe_3(CO)_{12}$				
$CNBu^t$	1	53	2082m, 2039s, 2031s, 2012s, 1996m	41,48
PPh_3	1	60	2083m, 2031s, 2009s, 1979w, 1825w	41,40
$P(OMe)_3$	1	75 (at −30°C)		40
$P(OC_6H_4Me\text{-}4)_3$	1	25	2089w, 2065w(sh), 2049s, 2038s, 2018s, 1996w, 1959m	41
From $Fe_2Ru(CO)_{12}$				
PPh_3	1	50	2090w, 2035vs, 2015s, 2000m, 1990m, 1980m, 1840w, 1805w	49
$P(OMe)_3$	1	90	2100w, 2040s, 2025s, 2010s, 1990s, 1970m, 1942w, 1840w, 1805w	49
From $FeRu_2(CO)_{12}$				
PPh_3	1	80 [b]	2095m, 2040s, 2025vs, 1975m	49
	2	90	2080m, 2015s, 1995s, 1985m, 1945m, 1940w	49
$P(OMe)_3$	1	80 [b]	2095m, 2045s, 2025vs, 2005s, 1995s, 1970m	49
	2	90	2020w, 2005vs, 1995vs, 1975s, 1960m, 1890w	49
From $Ru_3(CO)_{12}$				
$CNBu^t$	1	78 (86)	2093m, 2047s, 2040s, 2016s, 1998m, 1995m	41,42
	2	61 (41)	2065m, 2020vs, 2007(sh), 1996m, 1990s, 1986s	41,42
CNCy	1	89 (80)	2090m, 2048m, 2038vs, 2032s, 2024m, 2011m, 2003m, 1994(sh)	42
(*R*)-(+)-CNCHMePh	1	32	2095m, 2047s, 2041s, 2022m, 2006m, 2001m	42
$CNCH_2SO_2C_6H_4Me\text{-}4$	2	87	2095w, 2069m, 2022vs, 2005m, 1996m, 1990s, 1982s	42
NCMe	1	65		40
$PHPh_2$	1	n.g.	2096w, 2045vs, 2028s, 2014vs, 1993w, 1985w, 1975(sh), 1959(sh)	50,51
$PHPh[CH_2CH_2Si(OEt)_3]$	1	n.g. [c]		51
PMe_3	1	75 (15)	2086w, 2066(sh), 2056m, 2040s, 2023s, 2011vs, 1990(sh), 1978(sh), 1943m	42
	2	60 (60)	2076m, 2046w, 2019vs, 1998vs, 1976s, 1955m	42
	3	76 (90)	2044w, 2015(sh), 1997(sh), 1975vs, 1943s	41.42
PMe_2Ph	1	76 (3)	2096m, 2044s, 2028s, 2016s, 2000w, 1987w	42
PPh_3	1	81 (37)	2097m, 2047s, 2031(sh), 2026(sh), 2017s, 2001w, 1986w	41,42
	2	96 (76)	2072w, 2060w, 2047m, 2034(sh), 2024s, 1990s, 1968s, 1950m	41,42

	3	85 (98)	2044m, 1978(sh), 1967(br)	41,42
$P(C_6H_4Me\text{-}2)_3$	1	37	2099m, 2045s, 2030s, 2016vs, 2000m, 1989m, 1955(sh)	42
$P(C_6H_4Me\text{-}4)_3$	1	79	2098m, 2063m, 2048s, 2032ms, 2017vs, 2001m, 1989m, 1977(sh), 1955m	42
	3	87 (88)	2039vw, 2017vw, 1977(sh), 1965s	42
$PPh_2(C_6H_4CH{=}CH_2\text{-}2)$	1	74	2094s, 2039s, 2026vs, 2015vs, 1999m, 1991w, 1976m, 1959w	47
$PPh_2\{CH_2CH_2Si(OEt)_3\}$	1	n.g.		29
PCy_3	1	89 (42)	2099m, 2082m, 2047m, 2026s, 2016vs, 1996s, 1985s, 1970m, 1945m	42
	2	55 (80)	2077s, 2059w, 2045s, 2001s, 1989s, 1979m, 1941w	42
$P(CH_2CH_2CN)_3$	2	91	2076w, 2056w, 2022m, 2000s, 1988vs, 1950m, 1937m	42
	3	72	2087m, 2025vs, 1991vs, 1920w	42
$PPh(OMe)_2$	1	74	2103m, 2051s, 2035s, 2020s, 2002ms, 1997ms, 1990(sh), 1978(sh), 1967(sh)	42
	2	63 (14)	2081w, 2058w, 2005s, 1986s, 1971(sh)	42
	3	44 (7)	2054w, 2034w, 1999s, 1988vs, 1968m, 1959(sh)	41,42
	4	91 (57)	2061w, 2030mw, 2000(sh), 1986vs, 1967vs, 1920m	41,42
$P(OMe)_3$	1	81 (43)	2104m, 2064w, 2051vs, 2038s, 2019vs, 2001s, 1997s, 1984m	41,40,42,52
	2	81(35)	2088w, 2050w, 2034s, 2008vs, 1991m, 1980(sh)	42,52
	3	70 (15)	2062w, 2032m, 2005vs, 1993vs, 1964(sh)	42,52
$P(OCH_2)_3CEt$	1	50	2106w, 2051s, 2043m, 2023s, 2002m, 1990w	42
	2	57	2092w, 2053(sh), 2038s, 2022(sh), 2010vs, 1988(sh)br	42
	3	92	2058m, 2012(sh), 1997vs(br), 1975(sh)	42
$P(OPh)_3$	1	80		42
$P(OC_6H_4Me\text{-}4)_3$	1	64	2104m, 2088w, 2050s, 2038s, 2020vs, 2003s, 1990m	42
	2	26	2088w, 2036m, 2010s, 1993m, 1980(sh)	42
	3	66	2062m, 2010s, 1998vs, 1976(sh)	42
dppm	1	90 (28)	2083m, 2023w, 2013s, 2003s, 1987w, 1966m, 1964(sh), 1961m	41,40,53
	2	26 (12)	2056w, 2046w, 2023m, 2012(sh), 1998(sh), 1981vs, 1970s, 1945m	42
	0.5	98	2094m, 2054(sh), 2046m, 2012(sh), 1998(sh), 1978s, 1969s, 1946(sh), 1912vw	42
dppe	1	52	2080m, 2014vs, 1999s, 1981w, 1965w, 1935w	43
	0.5	43 $\mu(Ru_3)_2$	2098m, 2048s, 2030s, 2028(sh), 2017vs	41,43
	2	53	2055m, 1981s, 1952vs, 1920w(sh)	41,43
	0.5	n.g. $(CO)_{11}$	2097m, 2047s, 2026(sh), 2018s, 2000w, 1990w	43

TABLE 1 (Continued)

Substituted cluster carbonyls prepared by $Na^+[Ph_2CO]^-$ catalysed reactions

Ligand	*n*	Yield (%) [a]	ν(CO) (cm^{-1})	Refs.
$(PPh_2)_2C_2$	1	71	2102m, 2068(sh), 2052vs, 2034s, 2021vs, 2005(sh), 1997w, 1987(sh), 1970w	54
$AsPh_3$	1	66	2100w, 2048m, 2038(sh), 2018vs, 2000m, 1990(sh)	41,42
	2	48 (1.5)	2080m, 2050w, 2026s, 1997vs(br), 1980(sh)	54
dpam	1	53 (75)	2083m, 2067m, 2024m, 2009vs, 1990(sh), 1964m, 1944w	41,42
	2	8 (21)	2054m, 2041s, 2026m, 2011vs, 2006(sh), 1963vs	42
dpae	1	78 (60)	2082m, 2066w, 2048m, 2022(sh), 2013vs, 2002vs, 1986s, 1964s, 1950(sh)	42
$SbPh_3$	1	44	2101m, 2050s, 2032m, 2019vs, 2000w, 1989w, 1976m, 1965m	41,42
From $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$				
$CNBu^t$	1		2044s, 1980vs(br)	55
PPh_3	1		2092m, 2064s, 2017vs, 2005vs, 1996s, 1953m, 1948(sh)	55
From $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$				
PPh_3	1	52	2075s, 2045vs, 2026vs, 2009vs, 1991m, 1981vs, 1973vs	56
$P(OMe)_3$	1	37	2078s, 2056(sh), 2046vs, 2037(sh), 2032vs, 2009vs, 1993(sh), 1980vs, 1973vs, 1942w	56
dppm	1	80	2057(sh), 2053vs, 2022s, 2003s, 1994m, 1970m, 1950w	56
From $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$				
dppm	1	76	2068vs, 2045vs, 2010vs, 1999vs, 1996(sh), 1986m, 1961m, 1955m	56
ebdp	1	70	2069vs, 2047vs, 2012vs, 1999vs, 1985m, 1963m, 1954w	56
dpam	1	56	2071vs, 2046vs, 2009vs, 1999vs, 1988(sh), 1965w, 1953m(br)	56
From $Ru_4H_4(CO)_{12}$				
PPh_3	1	55	2095m, 2082m, 2068vs, 2059s, 2028vs, 2015m, 2009s, 1969w	41,42
	2	53	2079m, 2062s, 2052m, 2036m, 2022vs, 2013s, 2003w, 1977w, 1960w	41
$P(OMe)_3$	1	90	2097w, 2069vs, 2060vs, 2031vs, 2018m, 2009m, 1976w	41,57
	3	47	2068m, 2036s, 2014m, 1998s, 1985m, 1978s, 1963w	41,42
$P(OPh)_3$	1	76	2098m, 2072vs, 2061s, 2036s, 2013s	41,42
$P(OC_6H_4Me\text{-}4)_3$	1	65	2098m, 2071s, 2061s, 2036s, 2028w, 2016s, 2000(sh), 1983w	41
$CNBu^t$	1	63	2104w, 2078s, 2070s, 2042s, 2022s, 2012m, 1998w, 1984w	41,42
	2	34	2092m, 2084w, 2060s, 2034vs, 2020s, 2000s, 1982s	41,42

$PPh_2\{CH_2CH_2Si-(OEt)_3\}$	1	n.g.		29
From $RuCo_3(\mu-H)(CO)_{12}$				
PPh_3	2	25	2083s, 2049s, 2038s, 2012s, 1960w, 1897w, 1868m, 1850m	58
From $RuRh_3(\mu-H)(CO)_{12}$				
PPh_3	2		2079m, 2066s, 2037s, 2020s, 1982m, 1900m, 1870m, 1845m	58
From $Os_3(CO)_{12}$				
$CNBu^t$	1	17	2100m, 2054s, 2039s, 2019vs, 2006s, 1988s, 1984(sh)	41
PPh_3 [d]	1	24	2108w, 2058m, 2038s, 2005m, 1998m, 1988m, 1979m	41
	2	21	2088w, 2072vw, 2056w, 2033s, 2012m, 2002vs, 1997(sh), 1970m, 1955w	
	3	17	2070(sh), 2056vw, 2040(sh), 2030w, 1994s, 1969vs, 1950m	
$P(OMe)_3$	1	90	2111m, 2055s, 2039m, 2021s, 2002w, 1992m, 1981w, 1967vw	40
NCMe	1	70	2103w, 2052s, 2040s, 2020m, 2000vs, 1984(sh), 1981m, 1969vw, 1960vw	40
From $Co_3(\mu_3-CPh)(CO)_9$				
PPh_3	1	90		40
dppm	1	[e]		40
From $Co_3(\mu-CCl)(CO)_9$				
$CNBu^t$	3	62	2042s, 2032w(sh), 2008s, 1993s, 1987m(sh), 1980m	55
$P(OC_6H_4Me-4)_3$	1	78		57
dppe	1	51	2066s, 2020s, 2013s, 2000w, 1976w	41
From $Rh_6(CO)_{16}$				
$CNBu^t$	5	30	2070(sh), 2051m, 2032vs, 2008vs, 1990w, 1985(sh), 1956w, 1778vs(br)	41
From $Ir_4(CO)_{12}$				
PPh_3	1	90		40

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[a] n.g., Not given; thermal yield in parentheses. [b] Accompanied by 5% disubstituted complex. [c] Pyrolysis product $Ru_3(\mu-H)(\mu-PPhR)(CO)_{10}$ obtained in 62% overall yield. [d] Reaction affords mixture of all three complexes, separated by TLC. [e] 50–90% of η^1- and η^2-dppm complexes according to conditions.

We and other groups have studied the application of the reaction to other cluster complexes. We have found that sodium diphenylketyl is an efficient catalyst for the substitution of CO in $Co_3(\mu_3\text{-CR})(CO)_9$ (R = Cl, Me) or $Rh_6(CO)_{16}$ (with 5 molar equivalents of $CNBu^t$, $Rh_6(CO)_{11}(CNBu^t)_5$ was obtained essentially pure but in low yield) [47]. These and other results are summarised in Table 1.

A most interesting extension of these reactions is to the exchange of ML_n moieties in cluster complexes. Thus the reaction between $Co_3(\mu_3\text{-CPh})(CO)_9$ and $\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2$ affords $Co_2Mo(\mu_3\text{-CPh})(CO)_8(\mu\text{-}C_5H_5)$ in > 50% yield; the $Na[Ph_2CO]$ generates the anion from the corresponding Group 6 dimer, or from $Hg\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2$ in related reactions [40,59]. Redox-catalysed metal exchange has also been employed in the syntheses of $CoFeM(\mu_3\text{-E})(CO)_8(\eta\text{-}C_5H_5)$ (M = Mo, W and E = S, Se; M = Mo and E = $PNEt_2$) from $Co_2Fe(\mu_3\text{-E})(CO)_9$ and $Na[M(CO)_3(\eta\text{-}C_5H_5)]$ in the presence of sodium diphenylketyl [60].

Other methods of activating $Ru_3(CO)_{12}$ towards specific CO substitution have been described recently. These include the use of catalytic amounts of [ppn][OAc] or [ppn][CN], which promote substitution by tertiary phosphines (such as PPh_3, dppm or dppe) but not by trialkyl phosphites or $AsPh_3$ [61]. It is of interest in this regard that the reaction between $Ru_3(CO)_{12}$ and a molar amount of [ppn]Cl affords $[ppn][Ru_3(\mu\text{-Cl})(CO)_{10}]$ quantitatively, while with $Ru_4(\mu\text{-H})_4(CO)_{12}$, deprotonation ensues with formation of $[ppn][Ru_4(\mu\text{-H})_3(CO)_{12}]$ in 92% yield. Other $[ppn]^+$ salts show varying degrees of activity; rates of ligand substitution in $Ru_3(CO)_{12}$ were enhanced by addition of methoxide ion, which formed the labile methoxycarbonyl complex $[Ru_3(CO_2Me)(CO)_{11}]^-$ [62,63]. Specific site activation by bridging acyl groups also facilitates substitution of CO by tertiary phosphines or tertiary phosphites. Thus, the complex $Ru(\mu\text{-H})(\mu\text{-O=CMe})(CO)_{10}$ reacts with PPh_3 in 4 h to give $Ru_3(\mu\text{-H})(\mu\text{-O=CMe})(CO)_9(PPh_3)$ in 48% yield. Progressively faster reactions are found with $Ru_3(\mu\text{-H})(\mu\text{-X})(CO)_{10}$ and $Ru_3(\mu\text{-X})(\mu\text{-O=CEt})(CO)_{10}$ (X = Cl, Br or I); quantitative yields of the monosubstituted PPh_3 derivatives are obtained in one minute from the latter complexes [64].

The ETC substitution reactions are related to the now well-established ET-promoted reactions first recognised in organic chemistry [65], for which there exist several good reviews [66–69]. Extensive studies of reagent- and catalyst-induced substitution reactions of metal carbonyl complexes, which may be oxidatively promoted, e.g. by Me_3NO, have also been reviewed previously in this journal [70]. In addition, photo-induced radical catalyses have been described by several authors [71–88]; in the present context, efficient ETC syntheses of $M_3(CO)_{11}(PMe_2Ph)$ have been achieved by irradiating solutions of the reactants containing $\{Fe(CO)_2(\eta\text{-}C_5H_5)\}_2$ (M =

Ru or Os) or $\{Mo(CO)_3(\eta\text{-}C_5H_5)\}_2$ (M = Ru) [75,76]. A considerable amount of work has been done on electrochemically-catalysed substitution reactions, some of which have been emulated chemically [77–80]. Most of these resulted from electrochemical and ESR studies on bi- and polynuclear systems [81–83].

This account is specifically concerned with metal cluster complexes, but as indicated above, this type of reaction can also be applied to mono- or binuclear systems. Indeed, the first example of reactions of metal carbonyls catalysed by anionic species was the specific formation of $Fe(CO)_4(L)$ (L = PPh_3, $P(OMe)_3$ or $P(OPh)_3$) from $Fe(CO)_5$ and L, which was achieved by first treating $Fe(CO)_5$ with sodium diphenylketyl to form $Na_2[Fe_2(CO)_8]$ [84]. The regioselective substitution of $Co_2(\mu\text{-}RC_2R')(CO)_6$ complexes has been mentioned above; the latest example involves the electrochemically catalysed sequential coordination of the three arsenic atoms of AsMe $\{C_6H_4(AsMe_2)\text{-}2\}_2$ (ttas) to one cobalt atom in $Co_2\{\mu\text{-}C_2(CF_3)_2\}(CO)_6$ [85].

C. MECHANISM OF THE SUBSTITUTION REACTION

Electrochemical studies have shown that the additional electron on radical anions such as $[Co_3(\mu\text{-}CY)(CO)_9]^{\cdot}$ occupies a metal–metal antibonding orbital [81–83,86,87]. Addition of sodium diphenylketyl to a solution of $Ru_3(CO)_{12}$ results in electron transfer from the ketyl radical anion to the cluster. It is likely that Ru–Ru bond cleavage occurs to generate a labile 17e metal centre; related mononuclear 17e carbonyls are very readily substituted [88,89]. The substituted cluster radical anion is less stable than that formed from the carbonyl and rapid electron transfer to unreacted cluster carbonyl establishes a cycle that is followed until either carbonyl or ligand is used up.

$$Ru_3(CO)_{12} + e \rightleftharpoons [Ru_3(CO)_{12}]^{\cdot}$$

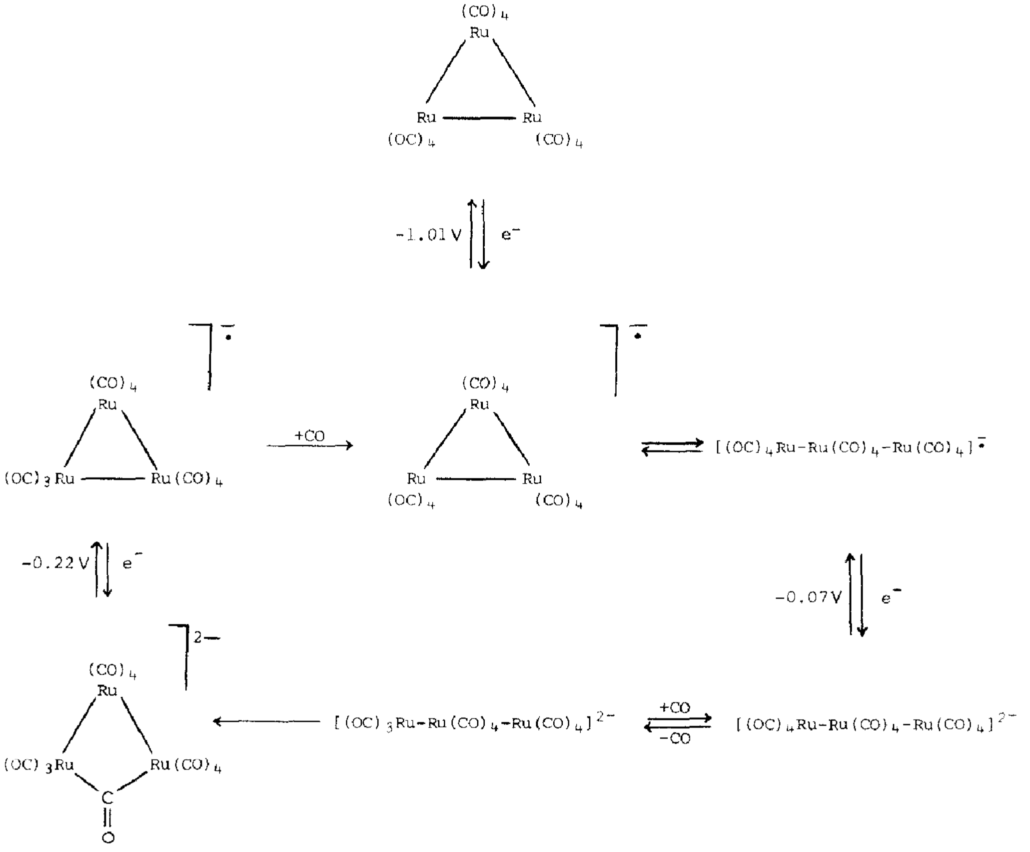
$$[Ru_3(CO)_{12}]^{\cdot} + L \rightarrow [Ru_3(CO)_{11}(L)]^{\cdot} + CO$$

$$[Ru_3(CO)_{11}(L)]^{\cdot} + Ru_3(CO)_{12} \rightarrow [Ru_3(CO)_{12}]^{\cdot} + Ru_3(CO)_{11}(L)$$

That the substituted cluster carbonyl radical anion is less stable has been demonstrated electrochemically, but formation of a reduced species was found to be chemically and electrochemically irreversible, apparently precluding its intermediacy in the substitution reactions [90]. An explanation involving fragmentation of the cluster, followed by substitution and reassembly of the fragments [40] does not accord with the high degree of specificity and excellent yields which are characteristic of these reactions.

These problems have been resolved by detailed studies of the electrochemical reduction of $Ru_3(CO)_{12}$, which have been interpreted in terms of initial formation of a short-lived radical anion, $[Ru_3(CO)_{12}]^{\cdot-}$, which may either lose CO to form $[Ru_3(CO)_{11}]^{\cdot-}$ or ring-open to form an isomeric linear $[Ru_3(CO)_{12}]^{\cdot-}$ which can be further reduced to $[Ru_3(CO)_{12}]^{2-}$. Irreversible loss of CO from this dianion forms linear $[Ru_3(CO)_{11}]^{2-}$, which then readily forms the triangular isomer [91]. These results (Scheme 3) rationalise an unusual feature of the chemically catalysed reactions, namely that substitution by the entering ligand is faster than reduction to $[Ru_3(CO)_{12}]^{2-}$, which does not form under the usual reaction conditions. In the absence of Lewis bases, $Ru_3(CO)_{12}$ reacts with sodium diphenylketyl to give anionic Ru_4 and Ru_6 cluster carbonyls; $[Ru_6(CO)_{18}]^{2-}$ is apparently formed by condensation by $Ru_3(CO)_{12}$ with $[Ru_3(CO)_{11}]^{2-}$ [92].

An important paper describes successive reductions of $Fe_3(\mu_3\text{-}PPh)_2(CO)_9$ to the radical anion and dianion; the former undergoes facile replacement of CO by Group 15 ligands. ESR studies showed that opening of the Fe_3P_2 cluster by formation of intermediate $[Fe_3(\mu_3\text{-}PPh)(\mu\text{-}PPh)(CO)_9]^{\cdot-}$ species facilitates the ligand substitution reaction [93]. Such a mechanism can also



Scheme 3. Reduction of $Ru_3(CO)_{12}$ (adapted from ref. 98). Some of these intermediates, e.g. $[Ru_3(CO)_{12}]^{\cdot-}$, may also have μ-CO ligands.

account for the ready substitution of $Ru_3(\mu_3\text{-}NPh)_2(CO)_9$ by Group 14 and 15 ligands [94].

D. NATURE AND STRUCTURE OF SUBSTITUTION PRODUCTS

Our own studies have concentrated on two areas in particular: a systematic determination of the structures of the substituted products and the further reactions of selected complexes, which in many cases we have found to take place under unusually mild conditions. Table 1 summarises the products that have been obtained by us and by other workers by the sodium diphenylketyl-catalysed substitution reactions of various cluster carbonyl complexes. It can be seen that the complexes obtained from $Ru_3(CO)_{12}$ are formed in high yield and under essentially stoichiometric conditions; seldom are mixtures obtained from stoichiometric amounts of reactants.

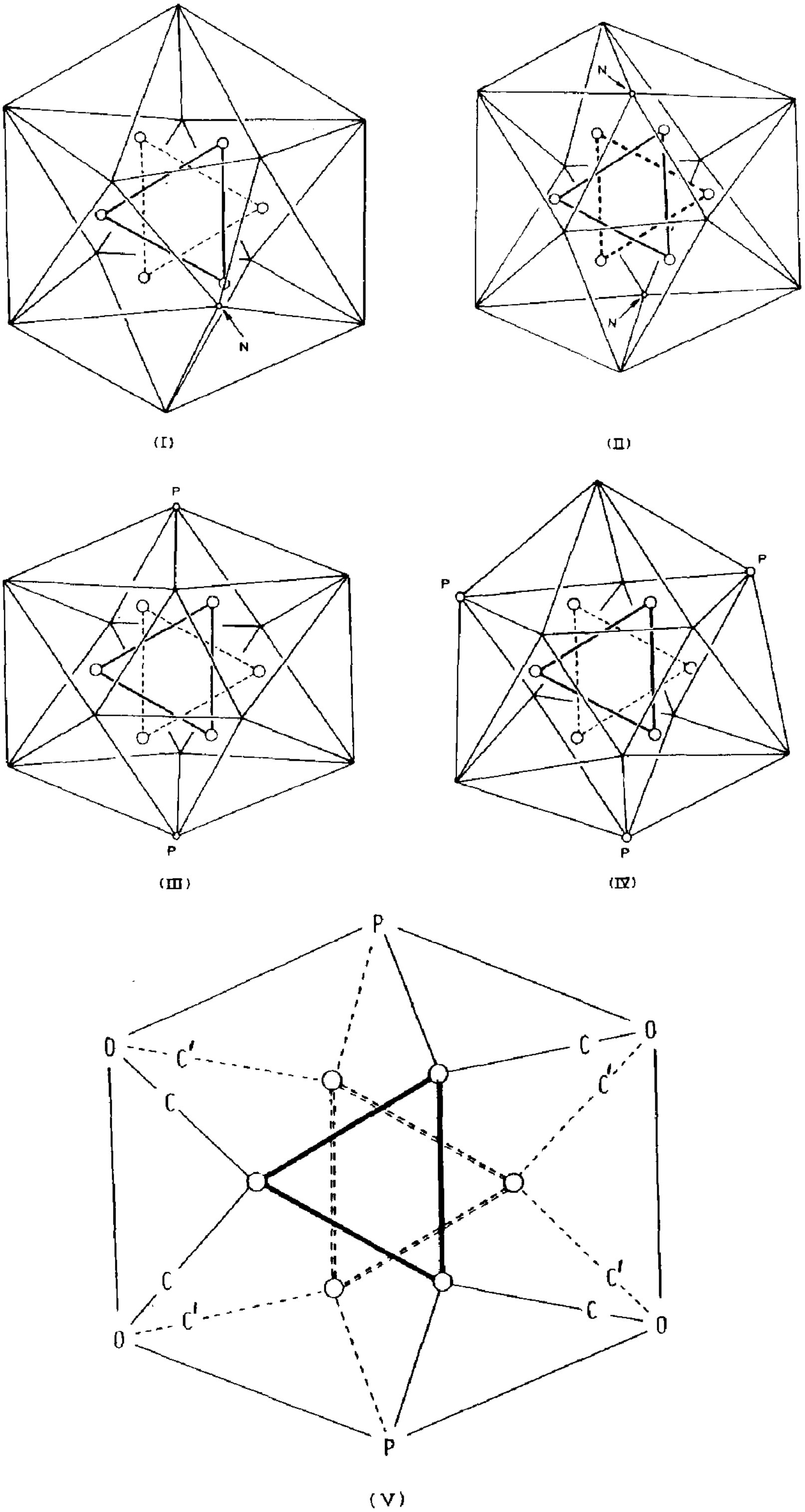
Most of our work has involved the reactions of $Ru_3(CO)_{12}$. We have found that as the degree of substitution increases, so the amount of catalyst required increases. Thus, mono- and disubstituted complexes can be obtained readily by the addition of only a few drops of the catalyst solution, whereas the trisubstituted complexes require addition of rather more (ca. 0.5 ml). This is probably because the lifetime of the cluster radical anion decreases with increasing degree of substitution, and can be related to the increasing reactivity of the 17e centre resulting from the presence of the more strongly σ-donating ligands. The net result is a tendency for formation of mononuclear complexes by degradation of the cluster. Complexes containing more than three Group 15 ligands can be obtained in a few cases, such as those with PMe_3, $P(OMe)_3$ and $PPh(OMe)_2$; however, considerable excesses of the ligands have to be used, and reactions have to be carried out at elevated temperatures. The use of suitably designed ligands which are resistant to further intramolecular reaction could undoubtedly expand the range of these complexes. The recent report [95] of complexes $Os_3(CO)_{12-n}\{P(OMe)_3\}_n$ ($n = 4$–6), obtained by extensive thermal and photolytic reactions of the phosphite with $Os_3(CO)_{12}$, lends some support to this suggestion.

Competing with substitution are fragmentation and other reactions, particularly when there are other functional groups on the cluster. Thus, with $Fe_3(CO)_{12}$, the formation of mononuclear products is prevented by working at lower temperatures (−30 °C) [40]. Polysubstitution of $Ru_4(\mu\text{-}H)_4(CO)_{12}$ proceeds as far as the trisubstituted complex under normal conditions, but after this point, deprotonation of the cluster hydride competes with radical anion formation and the tetrasubstituted complexes are not formed. Similar substitution reactions have been found with other cluster hydrides of ruthenium, such as $Ru_3(\mu\text{-}H)(\mu_3\text{-}C_2Bu^t)(CO)_9$ or $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}S)(CO)_9$ [96].

In collaboration with Professor Allan White (University of Western Australia), we have carried out a systematic study of the crystal and molecular structures of several of the substituted ruthenium cluster complexes. Table 2 summarises the available structural studies of trinuclear cluster carbonyls of Fe, Ru and Os substituted with simple 2e-donor ligands. Previous attempts had been thwarted by disorder problems: an early (photographic) study of $Ru_3(CO)_{10}(AsPh_3)_2$, for example, gave only the heavy atom positions, allowing the determination of equatorial substitution but giving no further details [128]. We have determined that the disorder problem characteristic of these complexes is one which can be resolved by using a model in which the outer atoms of the ligands (O of CO, N of RNC, P of PR_3) form a polyhedron which remains unaltered while the metal core may take up two positions related by a 60° rotation within this polyhedron (Fig. 1) [129]. A similar model has been used to describe the structures of several trinuclear carbonyl clusters containing a two-fold disorder of the metal core, which often appears as a "star of David" pattern of heavy atoms. Some examples are $Fe_3(CO)_{12}$ [130,131], $Fe_3(\mu_3\text{-}E)_2(CO)_9$ (E = As [132], Bi [133]), $Fe_3(\mu_3\text{-}CF)_2(CO)_9$ [134] and $Os_3(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_{10}$ [135].

In the examples we have chosen, the extent of the disorder ranges from zero to 1 : 1. The "peripheral atom polyhedron" (p.a.p.) has been found to refine with no indication of occupation of other sites for the atoms O (of CO), N (of CNR), or P (of PR_3) [129]. That the disorder is a dynamic phenomenon appears to be indicated by the results of a variable temperature X-ray study of $Ru_3(CO)_{11}(CNBu^t)$ [114]. At room temperature, the extent of the disorder was determined to be 14 : 86, whereas at 133 K, the ratio was 6 : 94; on warming to room temperature again, the same 14 : 86 disorder was found. In contrast, the molecular structure of $Os_3(CO)_{11}(CNBu^t)$ is not disordered, as a result of the greater Os–C bond strength in this cluster. Interestingly, solution studies of the NMR spectra of these complexes showed that the ruthenium complex was fluxional at the lowest temperature that could be attained (−100°C) [136], but that the osmium derivative gave a well-resolved spectrum at −60°C, showing the presence of a mixture of the axial and equatorial isomers [137]. Consequently we feel that this is another manifestation of the long-known fluxionality of CO groups around metal cores, now extended to other ligands. Unfortunately, we cannot determine the rate of the fluxional process by the X-ray method, so cannot relate our results to the plethora of NMR studies of these molecules. Only in two cases have solid-state NMR studies of cluster carbonyls been reported: the CO groups in $Fe_3(CO)_{12}$ exchange rapidly in the solid state at 100 K [138], while those in $Co_4(CO)_{12}$ are static below 297 K [139].

There are four main structural types which have been found for these



(I) (II) (III) (IV) (V)

Fig. 1. Polyhedra constructed using peripheral atoms (O of CO, N of CNR, P of PR_3) of ligands in several complexes $Ru_3(CO)_{12-n}(L)_n$, showing location of disordered M_3 clusters. The projection chosen has the plane of the Ru_3 triangle in the plane of the paper: (I) $Ru_3(CO)_{11}(CNBu^t)$ (populations 0.14, 0.86; 295 K); (II) $Ru_3(CO)_{10}(CNBu^t)_2$ (0.5, 0.5); (III) $Ru_3(CO)_{10}\{P(OMe)_3\}_2$ (0.5, 0.5); (IV) $Ru_3(CO)_9(PMe_3)_3$ (0.06, 0.94); (V) plot of Ru_3 core and equatorial ligands in $Ru_3(CO)_{10}\{P(OMe)_3\}_2$, showing how the two orientations of the Ru_3 core are accommdated by an appropriate oscillation of the metal-to-ligand bonds about the peripheral atoms (from ref. 129).

TABLE 2

Structural studies of $M_3(CO)_{12-n}(L)_n$ complexes

L	n	Type [a]	M–M bond lengths (Å)				P.a.p. volume (Å^3)	Refs.
			a	b	c	Average		
(i) $Fe_3(CO)_{12}$ derivatives								
CO		A	2.558(1)	2.677(2)	2.683(1)	2.639	126.8	97,98
CNBu^t	1	C [b]	2.563(1)	2.687(1)	2.691(1)	2.647		50
			2.536(2)	2.684(3)	2.692(3)	2.637		
	2	HA	2.553(1)	2.696(2)	2.702(2)	2.650		123
$CNCF_3$	1	F	2.526(2)	2.685(3)	2.693(3)	2.635		99
PMe_2Ph	3	P	2.540(7)	2.688(7)	2.689(7)	2.639	107.7	100
PPh_3 (molecule A)	1	D	2.558(9)	2.711(9)	2.703(9)	2.657	117.9	101
(molecule B)	1	E	2.568(8)	2.666(8)	2.703(9)	2.646	115.3	
diars	(2)	N	2.597(1)	2.602(1)	2.662(1)	2.620		102
(ii) $Fe_2Ru(CO)_{12}$ derivatives								
PPh_3	1	D	2.575(1)	2.771(1)	2.796(1)	2.714	125.3	52
$P(OMe)_3$	1	D	2.581(3)	2.766(2)	2.757(1)	2.701	125.0	52
(iii) $FeRu_2(CO)_{12}$ derivatives								
PPh_3	1	H	2.788(1)	2.827(1)	2.772(1)	2.796	133.4	52
	2	M	2.664(2)	2.664(2)	2.854(2)	2.727	123.3	52
(iv) $Ru_3(CO)_{12}$ derivatives								
CO		B	2.851(1)	2.852(1)	2.860(1)	2.854	140.4	103
CNBu^t	1	G	2.858(1)	2.848(1)	2.867(1)	2.858		37
	2	I	2.849(2)	2.837(4)	2.837(3)	2.841		37
bipy	(2)	HB [d]	2.757(1)	2.836(1)	2.855(1)	2.816		136,137
$N_2C_4H_4$	(2)	O	2.744(1)	2.861(1)	2.859(1)	2.821		104
PMe_3	3	Q	2.860(1)	2.862(2)	2.854(1)	2.859	127.2	105
PCy_3	1	H [b]	2.902(2)	2.878(2)	2.859(2)	3.880	136.5	105
			2.920(2)	2.875(2)	2.874(2)	2.890		

$PPh_2(C_6H_4CH{=}CH_2\text{-}2)$	(2)	L	2.855(2)	2.834(2)	2.871(2)	2.853		47
PPh_3	1	H	2.907(3)	2.876(3)	2.875(3)	2.886	136.9	106
	2	J	2.846(3)	2.838(4)	2.842(4)	2.842		107
$PPh(OMe)_2$	1	H	2.872(1)	2.846(1)	2.858(1)	2.859		107
	2	J	2.860(1)	2.865(1)	2.868(1)	2.864		107
	3	Q [c]	2.900(1)	2.870(1)	2.887(2)	2.886		107
			2.884(1)	2.882(1)	2.876(2)	2.881		
			2.887(1)	2.894(1)	2.876(2)	2.896		
			2.885(1)	2.882(2)	2.874(2)	2.880		
	4	S	2.797(1)	2.879(1)	2.879(1)	2.852	118.1	108
$P(OMe)_3$	2	J	2.845(1)	2.859(1)	2.845(1)	2.850	131.0	105
	4	T	2.848(2)	2.857(1)	2.865(2)	2.857		107
dppm	(2)	L	2.834(1)	2.841(1)	2.860(1)	2.845		109
	(4)	U	2.826(2)	2.833(2)	2.858(2)	2.839		126
dppe [d]	(2)	L	2.856(1)	2.855(1)	2.847(1)	2.853		43
			2.856(1)	2.855(1)	2.845(1)	2.852		127
ffars	(2)	L	2.858(6)	2.831(3)	2.831(3)	2.840		110
	(4)	T	2.853(3)	2.853(3)	2.785(4)	2.830		111
$(PBu_2)_3SiMe$	(3)	R	2.915(1)	2.918(1)	2.917(1)	2.917		112
$AsPh_3$	1	H	2.895(1)	2.850(1)	2.859(1)	2.868		107
$AsMe_2Ph$	3	Q [b]	2.851(1)	2.838(1)	2.846(1)	2.845		107
			2.846(1)	2.838(1)	2.848(1)	2.844		
(v) $Os_3(CO)_{12}$ derivatives								
CO		B	2.882(1)	2.875(1)	2.874(1)	2.877		113
$CNBu^t$	1	G	2.875(1)	2.867(1)	2.885(1)	2.876		114
NCMe	1	G	2.856(2)	2.861(2)	2.894(2)	2.870		115
	2	I	2.842(2)	2.875(2)	2.879(2)	2.865		115
$NHC(CH_2)_5$	1	G	2.860(2)	2.890(2)	2.887(2)	2.879		116
PPh_3	1	H	2.918(1)	2.891(1)	2.886(1)	2.898		117
	3	Q	2.904(4)	2.907(4)	2.919(4)	2.910		117
$PPh(OMe)_2$	1	H	2.886(1)	2.882(1)	2.882(1)	2.883		117
	2	J	2.880(1)	2.891(1)	2.893(1)	2.888		117

TABLE 2 (Continued)

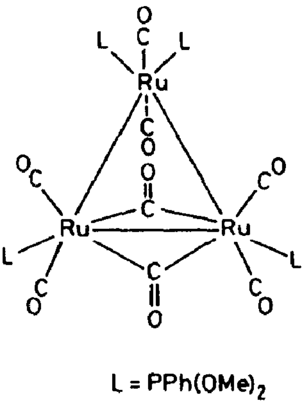
Structural studies of $M_3(CO)_{12-n}(L)_n$ complexes

L	*n*	Type [a]	M–M bond lengths (Å)				P.a.p. volume (Å^3)	Refs.
			a	*b*	*c*	Average		
$P(OMe)_3$	1	H	2.908(4)	2.890(4)	2.892(4)	2.897		118
	2	J [b]	2.869(1)	2.890(2)	2.888(2)	2.882		117
			2.881(2)	2.891(2)	2.888(2)	2.887		
$PBu^t_2(NH_2)$	1	H [b]	2.953(1)	2.900(1)	2.881(1)	2.911		119
			2.925(1)	2.892(1)	2.889(1)	2.902		
cis-$C_2H_2(CF_3)_2$	1	H	2.906(1)	2.760(2)	3.045(2)	2.904		120
cis-$C_2H_2(CF_3)_2$, PEt_3	(2)	J	2.951(2)	2.874(2)	2.911(2)	2.912		121
cis-C_4H_6	(2)	K	2.884(3)	2.863(3)	2.861(3)	2.869		122
trans-C_4H_6	(2)	L	2.932(3)	2.856(3)	2.858(3)	2.882		122

[a] See Fig. 2. [b] Values for two independent molecules given. [c] Values for four independent molecules given. [d] Two independent determinations.

complexes. The simplest, of which the parent carbonyls $Ru_3(CO)_{12}$ and $Os_3(CO)_{12}$ are the prototypes, consists of the three metal atoms arranged in a triangular cluster, each hearing four terminal ligands. In the second, exemplified by $Fe_3(CO)_{12}$, one edge of the triangle is bridged by two CO groups, more or less asymmetrically. In $Fe_3(CO)_{10}$(diars) and $FeRu_2(CO)_{10}(PPh_3)_2$, two edges are each bridged asymmetrically by a CO ligand. Finally, complexes containing CO groups bridging all three Ru–Ru edges are known in the cases of $Ru_3(\mu\text{-}C_4H_4N_2\text{-}1,2)(\mu\text{-}CO)_3(CO)_7$ and $Ru_3\{\mu_3\text{-}(PBu_2)_3SiMe\}(\mu\text{-}CO)_3(CO)_6$. Each of these structure types may have several variants, according to the position of substitution by the ligand(s) (Fig. 2).

The presence of bridging rather than terminal CO groups results in a contraction of the ligand polyhedron, and the structures of cluster carbonyls have been extensively discussed in terms of packing of the M_n cluster within the close-packed CO ligand assembly [140,141]. We have found the first ruthenium complex to have the $Fe_3(CO)_{12}$-structure with two CO ligands bridging one of the three Ru–Ru bonds, namely $Ru_3(CO)_8\{PPh(OMe)_2\}_4$, which has structure (**12**) [108]. A survey of known structures of this type suggests that when the p.a.p. has a volume of less that 127 Å^3, this structure type may be found. The third variant, in which two CO ligands semi-bridge two metal–metal bonds, has a p.a.p. volume of ca. 123 Å^3.

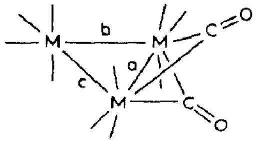


L = PPh(OMe)$_2$

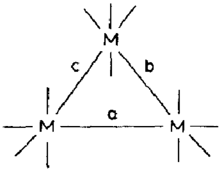
(12)

We have obtained the first set of molecular structures of the complexes $Ru_3(CO)_{12-n}(L)_n$ ($n = 0$–4), which have been determined for L = PPh(OMe)$_2$ [108,142]. An interesting feature is the progressive increase in average Ru–Ru separation from 2.854 Å ($n = 0$) to 2.88 Å ($n = 3$), followed by a sharp decrease to 2.852 Å ($n = 4$) which accompanies the change from the $Ru_3(CO)_{12}$ structure type (for $n = 3$) to the $Fe_3(CO)_{12}$-type (for $n = 4$). The wide range of structures now available have allowed the following general trends to be established:

(a) Carbonyls (L = CO)

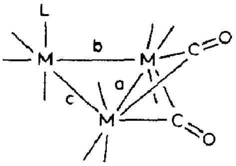


(A)

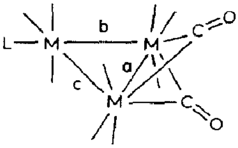


(B)

(b) Monosubstituted complexes



(C)



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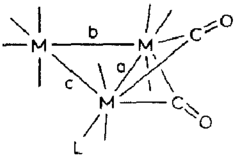
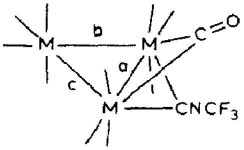


(E)



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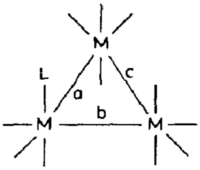

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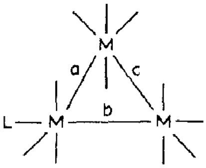
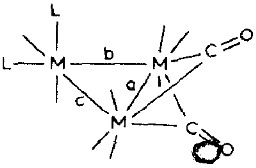
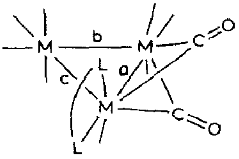


(H)

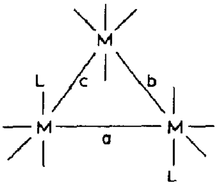
(c) Disubstituted complexes



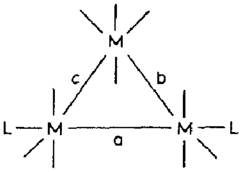
(HA)



(HB)



(I)



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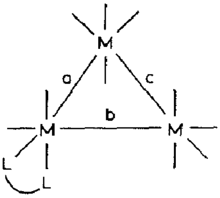

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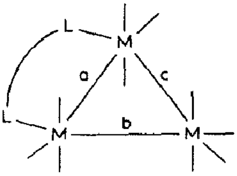
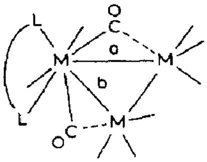
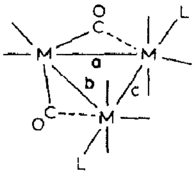


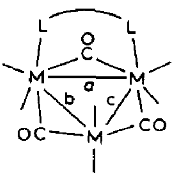
(L)



(M)

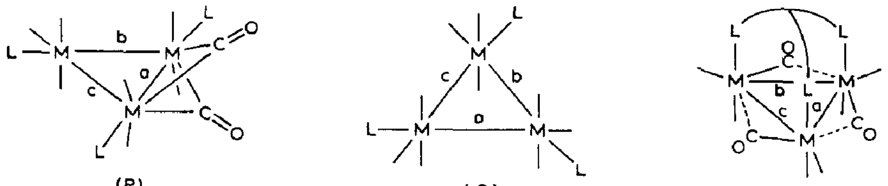


(N)



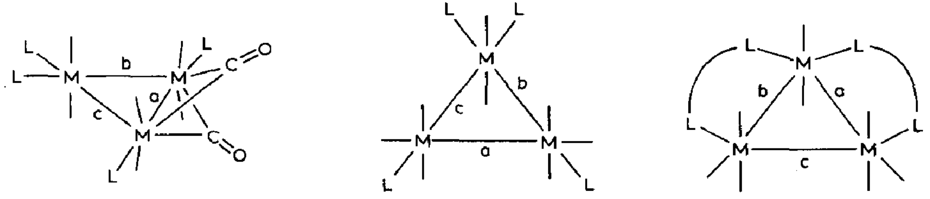
(O)

(d) Trisubstituted complexes



(P) (Q) (R)

(e) Tetrasubstituted complexes



(S) (T) (U)

Fig. 2. Continued.

(i) the average M–M distances increase with degree of substitution in a common structure type;

(ii) the M–M bond *cis* to the P- or As-ligand is the longest of the three M–M separations, but when a strong π-acceptor ligand (such as an olefin) is present, this bond is the shortest one;

(iii) the P- and As-ligands coordinate in equatorial sites, and in polysubstituted complexes, adopt a configuration minimising steric interactions between them;

(iv) for a given M, the M–P bond lengths increase in order of decreasing π-acidicity of the P-ligand;

(v) bonds from axial CO groups to M are generally longer than those from equatorial CO groups, except when the latter are *cis* to a P-ligand.

In some previous studies, the increase in M–M distance found on replacement of one CO by an N- or P-donor-ligand has been ascribed to an increase in electron density within the cluster as a result of the reduced back-bonding ability of the entering ligand when compared with CO. However, these observations can also be rationalised in terms of an expansion of the M_3 cluster (relative to that of the parent carbonyl) as ligands which are more bulky than CO are introduced; the degree of lengthening also parallels the increase in basicity (at least, for P-ligands). The most likely explanation is that the observed structural features result from both steric and electronic effects, the final geometry also depending on solid-state effects which are generally not taken into consideration in routine X-ray structural studies.

E. SOME COMPLEXES AND THEIR REACTIONS

Reactions of $Fe_3(CO)_{12}$ with $CNBu^t$ under ETC conditions afforded $Fe_3(CO)_{11}(CNBu^t)$ (**13**; Scheme 4) which has the $Fe_3(CO)_{12}$-structure, with the isocyanide ligand occupying an axial position on the unique iron atom. Gentle heating of (**13**) gave the decarbonylated complex $Fe_3(\mu_3\text{-}\eta^2\text{-}CNBu^t)(CO)_9$ (**14**) in which the isocyanide now acts as a triply-bridging six-electron donor ligand to the cluster [47]. Addition of hydride ion to (**14**) gave $[Fe_3(\mu_3\text{-}2\eta^1,\eta^2\text{-}HC{=}NBu^t)(CO)_9]^-$ which can be protonated to form $Fe_3(\mu\text{-}H)(\mu_3\text{-}HC{=}NBu^t)(CO)_9$; addition of $AuCl(PPh_3)$ to the anion afforded the $AuFe_3$ cluster (**15**) in the crystal of which the two independent molecules have significantly different dihedral angles for the butterfly cluster, leading to the suggestion that energy differences between the two conformations are small and that the wings of the butterfly may flap in solution! [143].

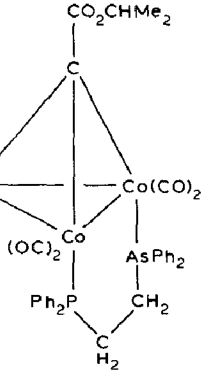
With the exception of the mixed isocyanide-Group 15 ligand complexes mentioned above, and the complexes $Ru_3(CO)_9(PEt_3)_n(PBu_3)_{3-n}$ ($n = 0$–3) briefly described 20 years ago [144], no simple mixed ligand derivatives of $Ru_3(CO)_{12}$ had been described, as there was no rational synthetic method that could be employed for their preparation. The ETC route provides an excellent method for the synthesis of such complexes, several examples of which are listed in Table 3 [57]. An attempt to resolve complexes of the type $Ru_4(\mu\text{-}H)_4(CO)_9(L)(L')(L'')$, which would contain a different ligand on each metal atom and hence be chiral, was frustrated by the rapid fluxionality of the example selected, $Ru_4(\mu\text{-}H)_4(CO)_9(PMe_2Ph)\{P(OCH_2)_3CEt\}\{P(OC_6H_4Me\text{-}4)_3\}$ (**16**), which was made by the sequence of the reactions [146]

$$Ru_4(\mu\text{-}H)_4(CO)_{12} + P(OC_6H_4Me\text{-}4)_3$$
$$\rightarrow \underset{(90\%)}{Ru_4(\mu\text{-}H)_4(CO)_{11}\{P(OC_6H_4Me\text{-}4)_3\}} + CO$$

$$Ru_4(\mu\text{-}H)_4(CO)_{11}\{P(OC_6H_4Me\text{-}4)_3\} + P(OCH_2)_3CEt$$
$$\rightarrow \underset{(70\%)}{Ru_4(\mu\text{-}H)_4(CO)_{10}\{P(OCH_2)_3CEt\}\{P(OC_6H_4Me\text{-}4)_3\}} + CO$$

$$\mathrm{Ru_4(\mu\text{-}H)_4(CO)_{10}\{P(OCH_2)_3CEt\}\{P(OC_6H_4Me\text{-}4)_3\} + PMe_2Ph}$$
$$\rightarrow \mathrm{Ru_4(\mu\text{-}H)_4(CO)_9(PMe_2Ph)\{P(OCH_2)_3CEt\}\{P(OC_6H_4Me\text{-}4)_3\} + CO}$$
$$(60\%)$$

A similar result was reported in the case of $\mathrm{Co_3\{\mu_3\text{-}C(CO_2CHMe_2)\}(\mu\text{-}PPh_2CH_2CH_2AsPh_2)(CO)_7}$ (**17**) [147]. More recently, analytical reverse-phase HPLC techniques were used to separate the diastereoisomers of the complex $\mathrm{Co_3(\mu\text{-}CMe)(\mu\text{-}PMe_2CH_2PPh_2)(CO)_6(L)}$ (L = (*R*)-(+)-PMeCy ($\mathrm{C_6H_4OMe}$-2)), in which the ligand L is attached to the same cobalt atom as the $\mathrm{PPh_2}$ group of the bidentate ligand [148]. Displacement of L by CO resulted in racemisation of the cluster framework.



(17)

The first isolated η^2-olefin complex of $\mathrm{Ru_3(CO)_{12}}$, (**18**; Scheme 5) was prepared as mentioned above from the olefinic tertiary phosphine, $\mathrm{PPh_2(C_6H_4CH{=}CH_2\text{-}2)}$ (sp). This complex is rapidly converted to the hydrido-alkyne cluster (**19**) at temperatures as low as 40°C [47], whilst at higher temperatures, condensation to the $\mathrm{Ru_4C_2}$ cluster (**20**) occurs [149]. The closely related olefin styrene was reported to form the analogous complex (**21**) on heating with $\mathrm{Ru_3(CO)_{12}}$ at 81°C [150]. The final dehydrogenation of (**19**) occurs with elimination of "$\mathrm{HRu(CO)_3}$" which is isolated as $\mathrm{Ru_4(\mu\text{-}H)_4(CO)_{12}}$; higher yields of (**20**) are obtained if the reaction is carried out in the presence of $\mathrm{Ru_3(CO)_{12}}$. It is reasonable to assume that simple olefin complexes of $\mathrm{Ru_3(CO)_{12}}$ are more reactive than (**18**), and undergo conversion to the hydrido-alkyne and $\mathrm{Ru_4C_2}$ complexes even more readily, thus accounting for their non-isolation to date.

A minor product from the pyrolysis of (**18**), or of (**19**) under CO, is the binuclear η^3-benzylic complex (**22**). In this reaction, an unusual rearrangement of the vinyl group to ethylidene has occurred, with concomitant attachment of the $\mathrm{C_6H_4}$ group to one of the metal atoms [68]. A second

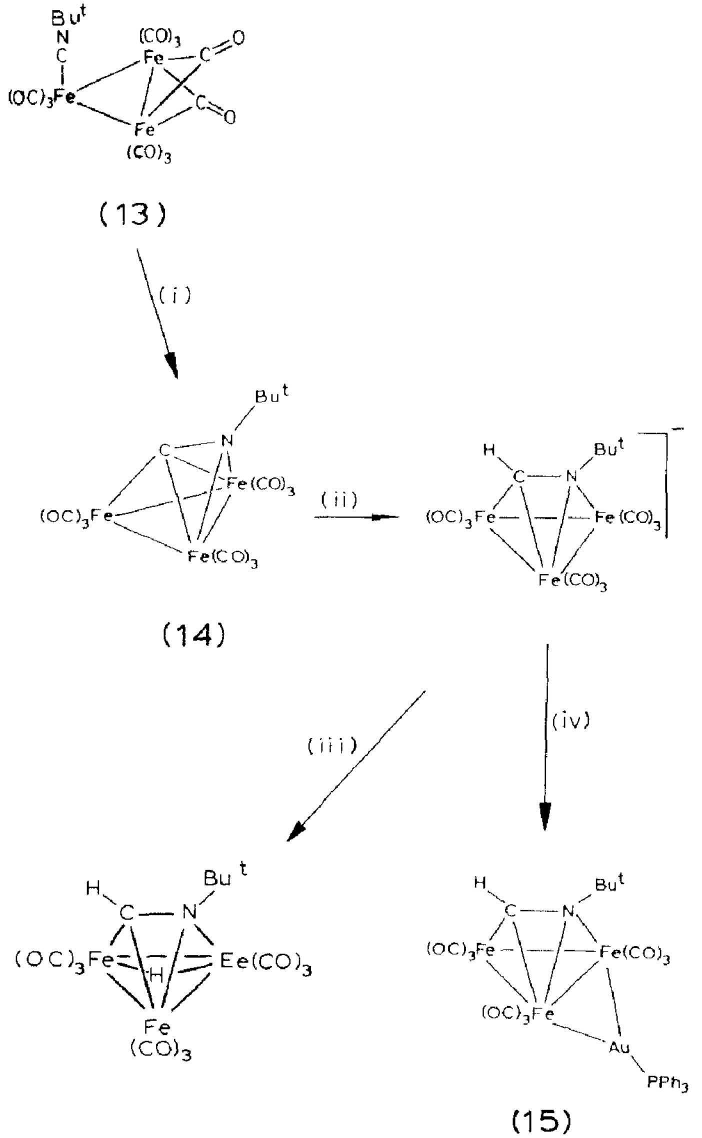
TABLE 3

Mixed ligand complexes prepared by $Na^+[Ph_2CO]^-$ catalysed reactions

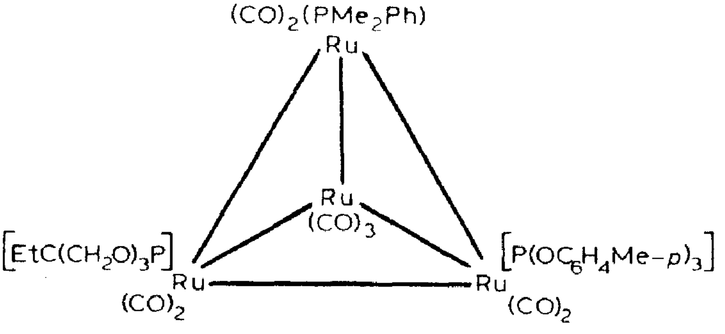
Ligands	Yield (%) [a]	$\nu(CO)$ (cm^{-1})	Refs.
From $Ru_3(CO)_{12}$			
PMe_3 $P(OMe)_3$	87	2081m, 2061w, 2047m, 2024s, 2002vs, 1966s, 1958(sh), 1935w	42
PMe_2Ph $CNBu^t$	42	2098w, 2068w, 2045m, 2029s, 2016s, 2004m, 1986w	42,57
$P(C_6H_4Me\text{-}4)_3$ $AsPh_3$	39	2077w, 2062m, 2047w, 2024s, 1998vs, 1989(sh), 1979s, 1957s, 1908m	42
$P(C_6H_4Me\text{-}4)_3$ $CNBu^t$	88	2066m, 2024s, 1996s, 1978m	42
$CNBu^t$ CNCy	85	2097w, 2065m, 2022vs, 2001m, 1995m, 1990(sh), 1985w	42
PMe_3 PPh_3 $P(OMe)_3$	41	2050m, 1980vs, 1957s, 1946(sh)	42,57
PMe_3 dppe	81	2031m, 2009ms, 1995s, 1987s, 1973vs, 1940m	42
$P(OMe)_3$ dpam	51	2027w, 2012s, 2003vs, 1988s, 1967s, 1959(sh), 1952(sh)	42,57
$AsPh_3$ $P(OCH_2)_3CEt$	34	2078w, 2057w, 2038s, 2027m, 2014vs, 1990m	42

$PPh_2(C_6H_4CH{=}CH_2)$ $CNBu^t$	18	2074(sh), 2063m, 2051w, 2037w, 2024m, 2011vs, 1999vs, 1993m, 1985m, 1970s, 1961(sh)	57
From $Ru_4H_4(CO)_{12}$			
PMe_2Ph $P(OCH_2)_3CEt$	66	2082s, 2061vs, 2043w, 2028w, 2017s, 2002m, 1992w, 1955w	42
$P(OMe)_3$ $PPh(OMe)_2$	70	2079s, 2058vs, 2032s, 2024vs, 2018(sh), 2000s, 1983w, 1974w, 1966w	59,57
PMe_2Ph $P(OMe)_3$ $PPh(OMe)_2$	75	2061s, 2031vs, 2010s, 1992s, 1984w, 1971m, 1956w, 1941w	59,57
PMe_2Ph $P(OCH_2)_3CEt$ $P(OC_6H_4Me\text{-}4)_3$	64	2065s, 2041s, 2009s, 2000m(sh), 1986(br)	42
From $Co_3(\mu_3\text{-}CCl)(CO)_9$			
$PPh(OMe)_2$ $P(OC_6H_4Me\text{-}4)_3$	64	2067s, 2026(sh), 2023(sh), 2018s, 2007m, 1983m	57
From $Co_4(CO)_9\{(PPh_2)_3CH\}$			
PMe_2Ph	n.g.		148
$PMePh_2$	n.g.		148
PPh_3	n.g.		148

[a] n.g., Not given.



Scheme 4. Some chemistry of $Fe_3(\mu\text{-}CO)_2(CO)_9(CNBu^t)$ (**13**). Reagents: (i) Heat at 120° C; (ii) $K[HBBu^s_3]$; (iii) HPF_6; (iv) $AuCl(PPh_3)$.



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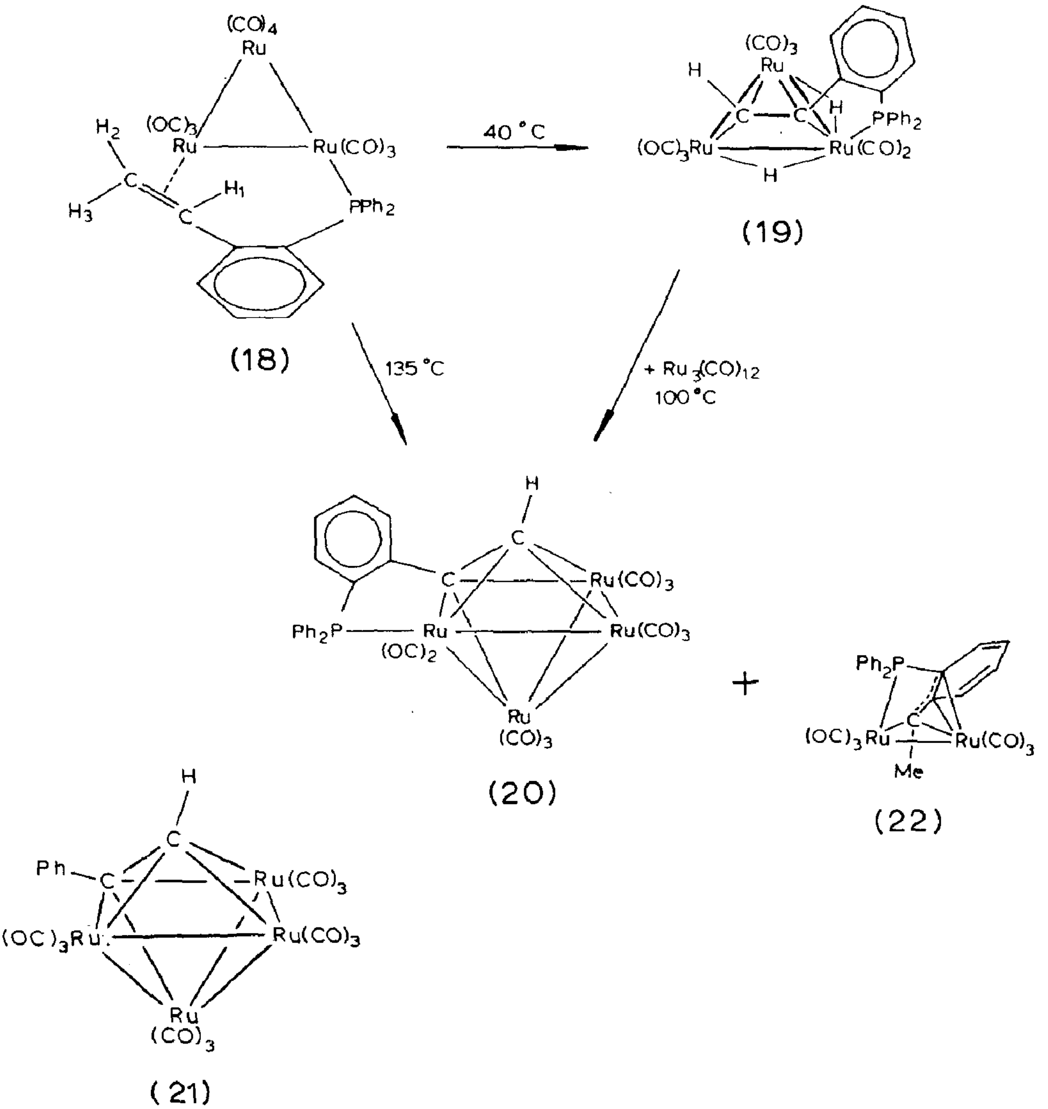
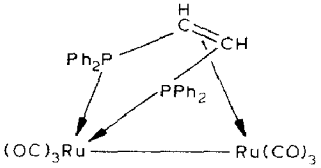


Scheme 5. Some chemistry of $Ru_3(\mu\text{-}\eta^2,P\text{-}CH_2{=}CHC_6H_4PPh_2)(CO)_{10}$ (**18**).

binuclear complex (**23**) was obtained by gently heating $Ru_3(CO)_{10}$(ebdp) (ebdp = *cis*-$CH(PPh_2){=}CH(PPh_2)$), or directly from the ligand and $Ru_3(CO)_{12}$ at 80 °C. The complex is formed by coordination of the C=C double bond and concomitant migration of one of the P atoms to chelate the second metal atom. Complex (**23**) contains a Ru → Ru donor bond, and the coordination about the two metal atoms differs: the P-bonded Ru is close to square pyramidal (if the Ru–Ru bond is ignored), while the olefin–$Ru(CO)_3$ system is nearly trigonal bipyramidal (now counting the second Ru as the fifth ligand) [152].



(23)

The ready formation of $Ru_3(CO)_{10}(\mu\text{-dppm})$ and its arsenic analogue (**11**; E = P and As) has allowed a study of some of their reactions, including those of the anions $[Ru_3(\mu_3\text{-EPhCH}_2\text{EPh}_2)(CO)_9]^-$, which are formed by the reaction of $K[HB(CHMeEt)_3]$ (K-Selectride) with (**11**) over a period of some hours [153,154]. Scheme 6 shows some of their reactions. Of note are the formation of aryldiazo complexes (**24**) in reactions with aryldiazonium salts, and their ready cyclometallation reactions which give (**25**) [154], and the edge-bridging allyl complex (**26**) obtained from allyl chloride [155]. The expected formation of the Group 11 derivatives (**27**; M = Cu, Ag and Au) has allowed the first structural comparison of the three Group 11 metal–Ru bonds [152]; in contrast with a theoretical expectation [156], it is the silver derivative which has anomalously long Ru–M bonds, although there is no difference in the overall coordination. The similarities found between the copper and gold complexes are paralleled by a recent structural comparison of the complexes $MCo_3Ru(CO)_{12}(PPh_3)$ (M = Cu and Au) which contain face-bonded $M(PPh_3)$ moieties; in this paper, Braunstein et al. [157] report extended Hückel MO calculations which also suggest that there should be no great differences between the two metal complexes.

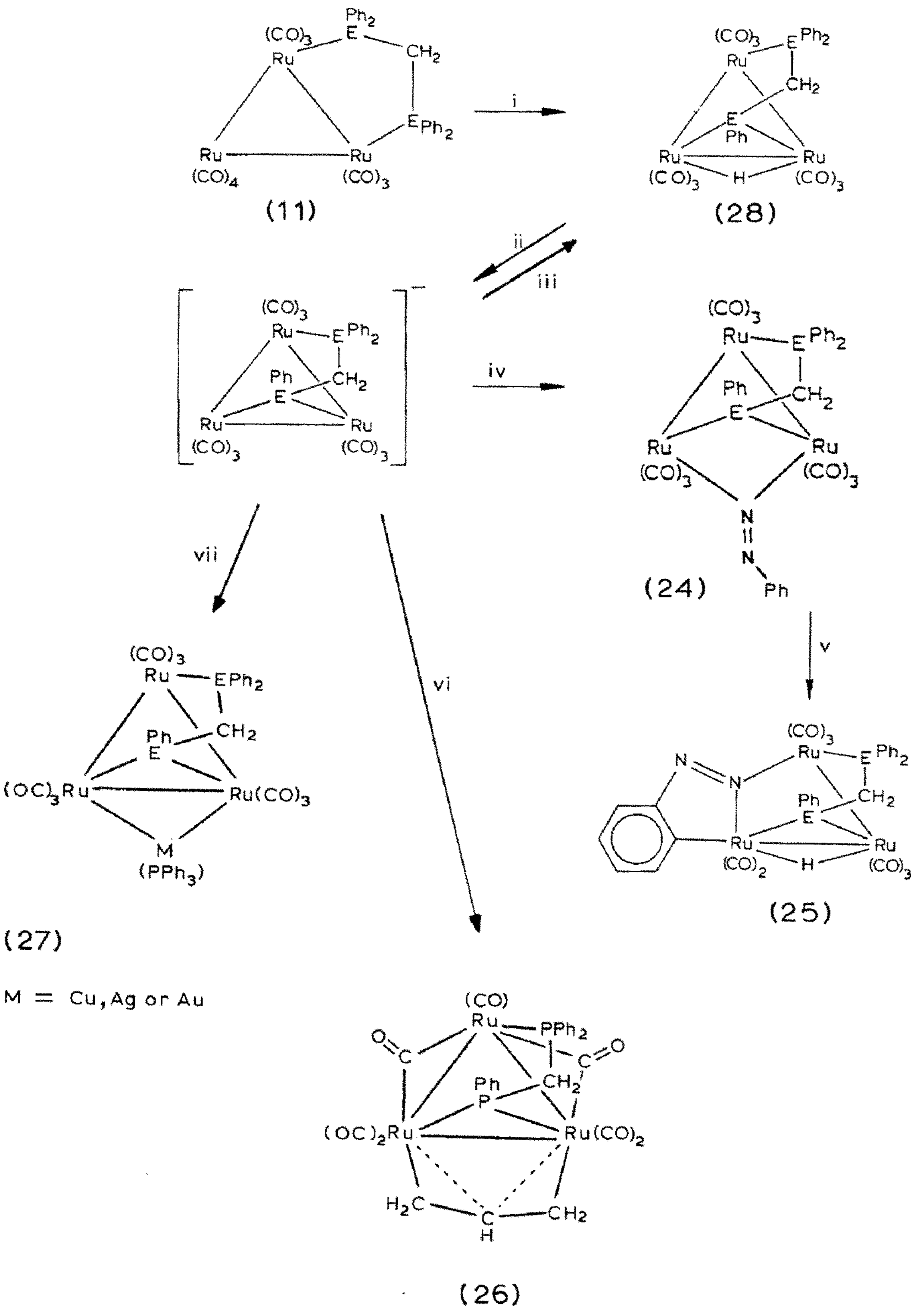
The availability of a range of substituted ruthenium carbonyl cluster complexes prompted us to examine their reactions with dihydrogen. Although these studies are not yet complete, several interesting features have emerged. It is, of course, well known that treatment of $Ru_3(CO)_{12}$ with dihydrogen in refluxing octane gives a high yield of $Ru_4(\mu\text{-H})_4(CO)_{12}$ [158]. Similar reactions of complexes containing monodentate tertiary phosphines afford a mixture of complexes $Ru_4(\mu\text{-H})_4(CO)_{12-n}(L)_n$ ($n = 0$–3). The reactions are complex, but the products obtained from variously substituted complexes can be rationalised by the occurrence of the following features [159]:

(i) facile rearrangement/redistribution reactions occurring between the complexes;

(ii) ready displacement of ligands L by CO (and perhaps H_2), and vice versa;

(iii) final product ratios being determined by steric effects of ligands L, in addition to other factors;

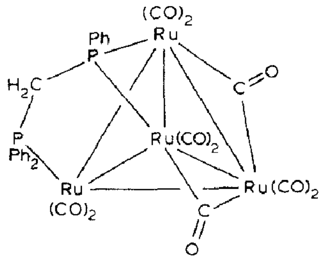
(iv) cleavage of Ru–Ru bonds by oxidative addition of hydrogen.



Scheme 6. Some chemistry of $Ru_3(\mu\text{-}H)(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9$. Reagents: (i) H_2 (20 atm, 80°C, 20 h); (ii) $K[BHBu^s_3]$; (iii) H^+; (iv) $[PhN_2][PF_6]$; (v) 80°, 1 h; (vi) $CH_2{=}CHCH_2Cl$ (E = P); (vii) $MCl(PPh_3)$ (E = P, M = Cu, Ag, Au; E = As, M = Au).

It is interesting that no complexes formed by fragmentation of the tertiary phosphine ligands were isolated from these reactions, although it is known that pyrolysis of $Ru_3(CO)_9(PPh_3)_3$, for example, gives a series of complexes formed by alteration of the PPh_3 ligand [21].

Extension of the hydrogenation reaction to complexes containing bidentate ligands results, as expected, in a predominance of products retaining the Ru_3 cluster. Indeed, hydrogenation of (**11**; E = P or As) affords quantitative yields of $Ru_3(\mu\text{-}H)(\mu_3\text{-}EPhCH_2EPh_2)(CO)_9$ (**28**; Scheme 6), deprotonation of which with K-Selectride gives the anion featured in Scheme 6 [159]. These reactions parallel those first found for the octacarbonyl clusters of both ligands by Bonnet and co-workers [160]. The P- or As-bonded phenyl group is probably lost as benzene, by combination with a cluster-bonded hydrogen atom; in support of this, heating $Ru_4(\mu\text{-}H)_4(\mu\text{-dppm})(CO)_{10}$ in cyclohexane (82°C, 1 h) results in the clean formation of $Ru_4(\mu\text{-}H)_3(\mu_3\text{-}PPhCH_2PPh_2)(CO)_{10}$ (**29**). Extended hydrogenation of (**11**) or (**28**) (85°C, 40 h, 20 atm) results in addition of hydrogen across the $Ru\text{–}P\text{–}CH_2$ systems, with formation of the substituted μ_3-phosphinidene cluster, $Ru_3(\mu\text{-}H)_2(\mu_3\text{-}PPh)(CO)_8(PMePh_2)$ (**30**) [159].



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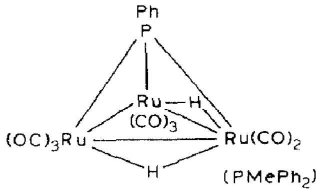

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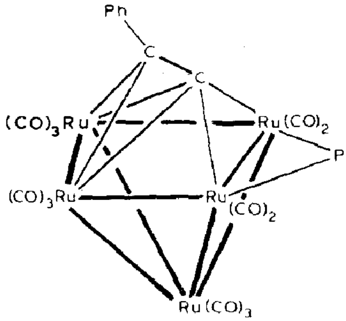
F. COMPLEXES CONTAINING MORE THAN ONE CLUSTER NUCLEUS

The mild conditions of the ETC reaction have made it possible to synthesise complexes in which two cluster carbonyl moieties are bonded to a bidentate tertiary phosphine, for example. The reaction between two equivalents of $Ru_3(CO)_{12}$ and one equivalent of dppe or the linear bis-tertiary phosphine $C_2(PPh_2)_2$ (dppa) afforded the hexanuclear complexes $\{Ru_3(CO)_{11}\}_2(\mu\text{-L-L})$ [42,54]. We considered that the latter might undergo condensation on heating with interaction of the acetylenic group with both clusters. There has been much study of similar complexes by Carty's group [161], and the possibility of cleavage of the P–C(*sp*) bonds in the phosphine was also recognised by us.

In the event, gentle heating (90°C) of the dppa complex (**31**; Scheme 7) resulted in a rapid darkening of the solution from red to black, thin-layer chromatographic (TLC) separation affording the pentanuclear "swallow" cluster (**32**) containing a μ_5-diphenylphosphinoacetylide group, in > 80% yield, together with some $Ru_3(CO)_{12}$. Addition of CO to the square pyramidal complex (**33**) to form a complex with a similar open Ru_5 cluster (**34**) has been described by Carty and co-workers [162], but ready loss of CO occurs to regenerate (**33**). In our case, the presence of the second PPh_2 group holds the Ru_5 cluster open. This feature, and the high isolated yield of this complex, prompted us to examine some of its reactions with small molecules.



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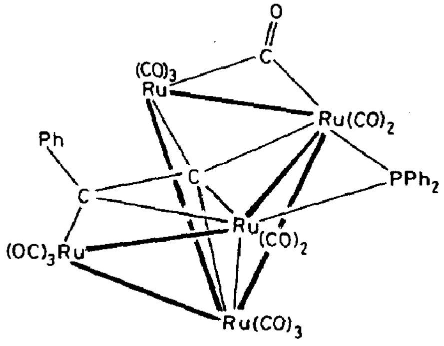
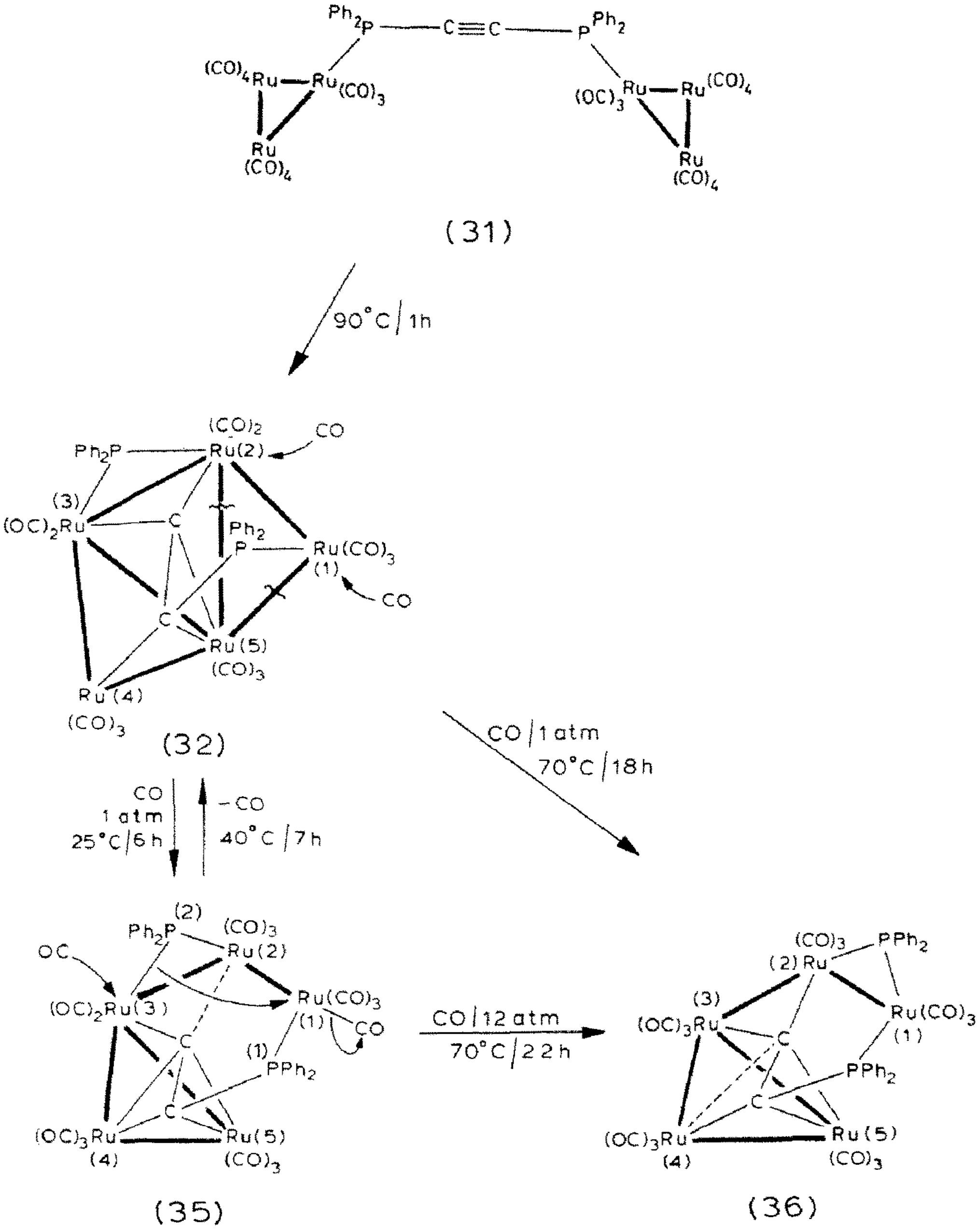


(34)

Bubbling CO into a cyclohexane solution of (**32**) at ambient temperatures resulted in the formation of the red complex (**35**) and at higher temperatures, (**36**) [163]. These were characterised crystallographically as isomers which retained the μ-η^1,η^2-C_2PPh_2 group bonded to a Ru_3 cluster, as commonly found in products from reactions between 1-alkynes and $Ru_3(CO)_{12}$. In this case, however, the other two metal atoms are bonded chain-wise to the Ru_3 triangle. Following the bird–insect analogy, this arrangement may be termed a "scorpion" cluster. The nature of the isomerism is of interest. In (**35**), Ru(1) receives the normal complement of electrons from the four CO groups and the P(1) atom, so that this isomer is another example of the growing class of complexes containing metal–metal donor bonds. The isomerisation of (**35**) to (**36**) proceeds best in the presence of CO, and we think that the reaction proceeds as depicted in Scheme 7, where an entering CO attacks at Ru(3), displacing the PPh_2 group from Ru(3) so that it swings around to bond to Ru(1), with concomitant displacement of a CO molecule from this atom. The result is to redistribute electron density over the cluster; the Ru(1)–Ru(2) bond is now formally a two-electron covalent bond.

The reaction of (**32**) with dihydrogen gave several products (Scheme 8). Under pressure (25°C, 10 atm, 18 h), two tetranuclear complexes were

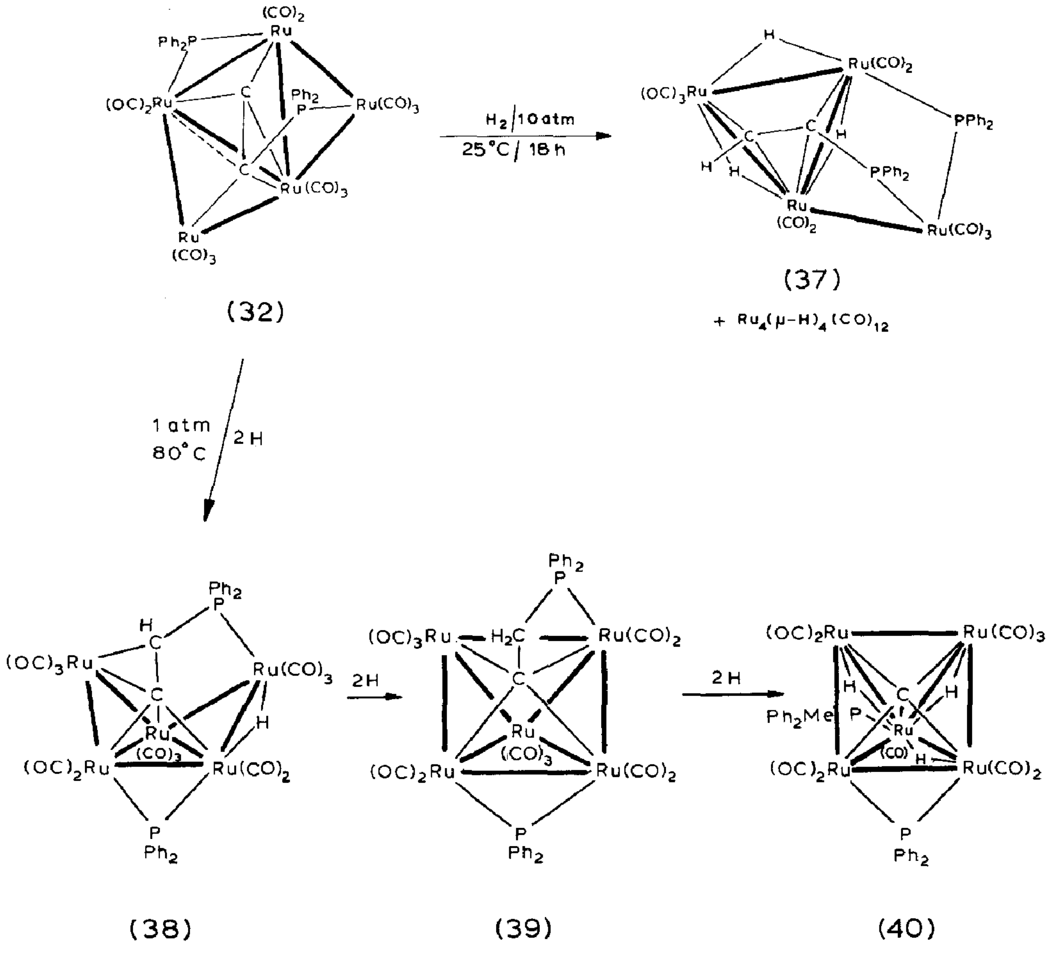


Scheme 7. Synthesis of a pentanuclear ruthenium cluster and its reactions with CO.

obtained, namely $Ru_4(\mu\text{-}H)_4(CO)_{12}$ and complex (**37**) [164]. In the latter, the acetylide ligand in (**32**) is converted to diphenylphosphinoethyne which interacts in a $2\eta^1,\eta^2$ mode with an Ru_3 triangle, while the fourth ruthenium atom is attached to Ru(1); the Ru(2)–Ru(4) separation, which although at 3.7831(6) Å is too long to be a bond, is nevertheless bridged by a PPh_2

group. The fragmentation of the Ru_5 cluster in (**32**) generates an "$HRu(CO)_3$" fragment, which is isolated, in part, as the tetranuclear hydrido-carbonyl.

Under normal pressure, passage of hydrogen into a refluxing cyclohexane solution of (**32**) results in the successive formation of three pentanuclear complexes [164]. All of these have been characterised crystallographically, and the results show that the three compounds are formed by the successive addition of one, two and three molecules of dihydrogen to (**32**), in each case one H atom adding to the cluster and one to the acetylide ligand. Scheme 8 illustrates the structure of the three complexes. In contrast to the result obtained under pressure, the hydrogen is found to add to the β-carbon of the acetylide, to give in the first instance, the diphenylphosphinovinylidene ligand, which interacts with all five metal atoms in (**38**). The open Ru_5

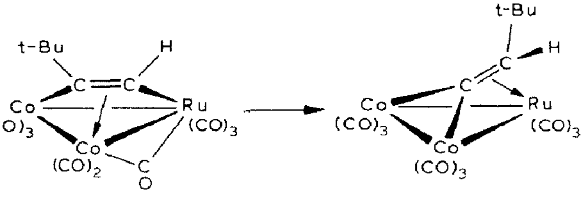


Scheme 8. Reactions of a pentanuclear ruthenium complex with H_2.

cluster geometry remains essentially unchanged apart from the additon of one hydrogen atom to the cluster. Further addition of 2H results in conversion of the vinylidene into a diphenylphosphinomethylidyne group, the α-carbon of which caps the square face of a square pyramidal Ru_5 cluster (**39**). The third complex (**40**) was found to be a derivative of the well-known $Ru_5C(CO)_{15}$ cluster, the β-carbon becoming fully hydrogenated to form the methyl group of a $PMePh_2$ ligand. The net result of the reaction has been to convert an acetylide to carbon and methyl, truly an unusual reaction.

$$C{\equiv}CPPh_2 + 3\ H \rightarrow C + MePPh_2$$

The strange course of this reaction is a direct result of the formation of the strong metal–metal bonds in the final product (**40**) and the tendency to form a *closo* cluster. In the literature to date, we note that the ready isomerisation of a 1-alkyne to the corresponding vinylidene has been observed in the conversion of $Co_2Ru(\mu_3\text{-}2\eta^1,\eta^2\text{-}HC_2Bu^t)(CO)_9$ (**41**) to the isomeric $Co_2Ru(\mu_3\text{-}2\eta^1,\eta^2\text{-}C{=}CHBu^t)(CO)_9$ (**42**), both of which were characterised crystallographically [165,166]. The ready conversion of the alkyne to the vinylidene may explain why the initial products from the hydrogenation at normal and elevated pressures differ in this respect.

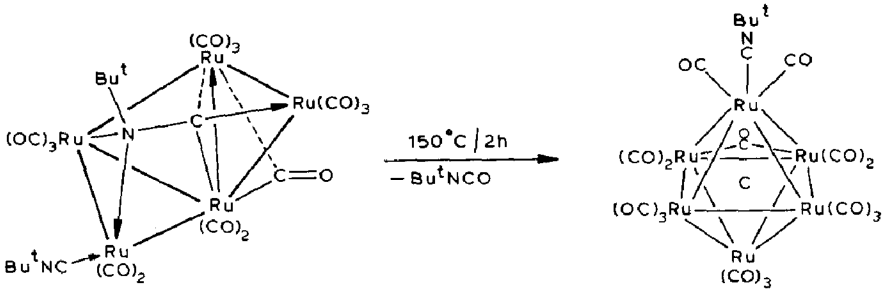


(41) (42)

When the total transformation of (**32**) to (**40**) is considered, one is reminded that two other examples of similar transformations of triply-bonded small molecules have been described. Many years ago, Lewis, Johnson and their co-workers [167,168] reported the formation of the hexanuclear carbido complex $Ru_6C(CO)_{17}$ by heating $Ru_3(CO)_{12}$ at 170°C, the net reaction being

$$2\ CO \rightarrow C + CO_2$$

The pentanuclear complex (**43**), which is formed by heating $Ru_3(CO)_{11}(CNBu^t)$ (120°C, 16 h) [169], is transformed on further heating (150°C, 2 h) to $Ru_6C(CO)_{16}(CNBu^t)$ (**44**) [170]; the nitrogen-containing fragment is probably lost as Bu^tNCO.



(43) (44)

$$CO + Bu^tNC \rightarrow C + Bu^tNCO$$

The Ru_5 complex in this case has the same geometry as that found in (**32**), and it is evident that extended interaction of these multiply-bonded small molecules with several metal atoms markedly alters their reactivity, allowing unusual transformations to occur. The ready formation of carbido complexes in these reactions brings to mind the facile generation of carbon bound to some electropositive metal surfaces by dissociative chemisorption of CO or other organic molecules on, for example, iron, ruthenium, cobalt, nickel, or palladium at elevated temperatures [171–174].

G. CONCLUSION

The development of a facile route to derivatives of cluster carbonyls substituted with Group 14 and 15 donor ligands has enabled us to study much of the fascinating chemistry of these complexes that was earlier obscured by the harsh reaction conditions that were necessary for their preparation. A wealth of cluster-mediated transformations of small molecules has been uncovered, and many of these reactions are related to those thought to occur on metal surfaces. We have been fortunate to discover an example of a complex containing one of these small molecules bonded to an open five-atom cluster, and following our assumption that this might resemble more a molecule adsorbed on such a surface than the usual three-atom clusters, we have indeed shown that unusual reactivity does attach to molecules in such situations.

In the short time since our original publication describing the ETC substitution of $Ru_3(CO)_{12}$, several other groups have used this type of reaction and their results are also summarised in Table 1. Another weapon in the armoury of the synthetic cluster chemist has been forged, and with it, the opportunity to discover more facets of the chemistry of these interesting species.

ACKNOWLEDGEMENTS

It is a pleasure to acknowledge the gifted experimental skills of my co-workers who are mentioned in the text or in the references. The initial contributions of Dr. Brian Nicholson (University of Waikato) were essential to the success of this study, and the structural contributions of Prof. Allan White (University of Western Australia) and Dr. Michael Snow (University of Adelaide) and their groups afforded us the necessary insight into molecular geometries to understand the transformations wrought by the synthetic chemists. Financial support of much of this work under the Australian Research Grants Scheme is gratefully acknowledged.

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