Cluster Chemistry. Reactions between Metal Carbonyl Clusters and Lewis Bases Initiated by Radical Ions: Improved Syntheses of Substituted Derivatives of M$_3$ and M$_4$ Clusters (M = Fe, Ru, Os, or Co)

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Addition of catalytic amounts of Ph$_2$CO$^{\cdot-}$ to a mixture of the appropriate cluster with stoicheiometric amounts of Lewis base in tetrahydrofuran gave the substituted derivatives [Fe$_3$(CO)$_{11}$(L)], [Ru$_3$(CO)$_{12-n}$(L)$_n$], [Os$_3$(CO)$_{11}$(L)], and [H$_4$Ru$_4$(CO)$_{12-n}$(L)$_n$] [n = 1—3; L = Bu^{t}NC, PR$_3$, P(OR)$_3$] in greatly improved yields.

A continuing hindrance to the study of metal carbonyl clusters, including their reactions with simple donor molecules, is the severe reaction conditions required to bring about substitution. These often result in further transformations of first-formed reaction products, often with concomitant bond cleavage in the reactant molecules, in further substitution of an activated monosubstituted product, as found in reactions between [Ru$_3$(CO)$_{12}$] and many tertiary phosphines or arsines, or in the formation of all possible substitution products, as with [H$_4$Ru$_4$(CO)$_{12}$] and tertiary phosphines or phosphites, which require extensive chromatography to isolate low yields of products. We describe below a novel method of introducing a variety of 2e donor ligands into metal cluster complexes in specific, stepwise reactions which generally proceed rapidly and in high yields.

Recent studies have shown that electrochemically or chemically generated [Co$_2$(CO)$_6$(μ-C$_2$R$_2$)]$^{\cdot-}$ or [Co$_3$(μ_3-CR)(CO)$_9$]$^{\cdot-}$ radical anions react extremely rapidly with tertiary phosphines or phosphites to give substituted complexes.[1] We have now found that this reaction can be extended to a wide range of polynuclear metal carbonyl clusters that are not normally labile towards substitution.

Typically, a mixture of the cluster carbonyl and the stoich-

eiometrically required amount of ligand are dissolved in tetrahydrofuran (THF), and the mixture is treated dropwise with a solution of sodium diphenylketyl in THF (ca. 0.025 M) until reaction is complete (i.r. confirmation). For the more reactive systems (see below), 2—4 drops of catalyst solution (<0.1 mol %) were sufficient, the reactions being completed within five minutes at ambient temperature. Since the reactions are essentially specific and quantitative, work-up involves only a simple extraction–crystallisation sequence, thus avoiding tedious chromatographic separations. Table 1 summarises some typical reactions and products, and can be amplified by the following comments concerning particular cluster systems:

(i) [Fe$_3$(CO)$_{12}$] required somewhat more catalyst than indicated above, and some fragmentation of the Fe$_3$ cluster was observed, with concomitant lowering of yields of the substituted cluster. Nevertheless, yields were significantly higher than those obtained by a much more laborious thermal route.[2]

(ii) [Ru$_3$(CO)$_{12}$] has been the most studied cluster, and reacts quickly to give excellent yields of mono-, di-, tri-, or tetra- (in one case) substituted products. The thermal route often gives only the trisubstituted complex, [Ru$_3$(CO)$_9$(L)$_3$].[3]

(iii) [H$_4$Ru$_4$(CO)$_{12}$] also reacts readily to give the appropri-

Table 1. Products obtained from radical ion-initiated reactions between metal carbonyl clusters and Lewis bases.

Cluster	Ligand	Molar ratio	Product	ν(CN)	ν(CO) (hexane)/cm^{-1}	Yield /%	Reference
$[Fe_3(CO)_{12}]$	CNBu^t	1:1	$[Fe_3(CO)_{11}(CNBu^t)]$	2174m	2082m, 2039s, 2031s, 2012s, 1996m	52	a
	PPh$_3$	1:1	$[Fe_3(CO)_{11}(PPh_3)]$		2083m, 2031s, 2009s, 1979w, 1825w	26	b
	P(Otol)$_3$	1:1	$[Fe_3(CO)_{11}\{P(Otol)_3\}]$		2089w, 2065w(sh), 2049s, 2038s, 2018s, 1996w, 1959m	25	b
$[Ru_3(CO)_{12}]$	CNBu^t	1:1	$[Ru_3(CO)_{11}(CNBu^t)]$	2170w	2093w, 2047s, 2040s, 2016m, 1998m, 1995m	78	c
		1:2	$[Ru_3(CO)_{10}(CNBu^t)_2]$	2155m	2065m, 2020vs, 2007(sh), 1996m, 1990s, 1986s	61	c
	PPh$_3$	1:1	$[Ru_3(CO)_{11}(PPh_3)]$		2097m, 2047s, 2031m(sh), 2026m(sh), 2017s, 2001w, 1989w	81	d
		1:2	$[Ru_3(CO)_{10}(PPh_3)_2]$		2072w, 2047w, 2019s, 1996vs (in CH$_2$Cl$_2$)	96	d
		1:3	$[Ru_3(CO)_9(PPh_3)_3]$		2044m, 1978(sh), 1967s	65	d
	P(OMe)$_3$	1:1	$[Ru_3(CO)_{11}\{P(OMe)_3\}]$		2104vw, 2074vw, 2051s, 2038s, 2019vs, 2001s, 1995s, 1984m, 1974m, 1962w	72	a
	PPh(OMe)$_2$	1:3	$[Ru_3(CO)_9\{PPh(OMe)_2\}_3]$		2054w, 2034vw, 1999s, 1988vs, 1968m, 1959(sh)	44	d
		1:4	$[Ru_3(CO)_8\{PPh(OMe)_2\}_4]$		2061m, 2020(sh), 2000(sh), 1986vs, 1976(sh), 1964(sh), 1920(sh)	91	d
	PMe$_3$	1:3	$[Ru_3(CO)_9(PMe_3)_3]$		2072m, 2018m, 1990m, 1976s, 1951vs, 1897vs, 1863vw	76	a
	dppe	1:0.5	$[Ru_3(CO)_{11}]_2(\mu$-dppe)		2098m, 2048s, 2030s, 2028(sh), 2017vs	43	a
		1:2	$[Ru_3(CO)_8(dppe)_2]$		2055m, 1981s, 1952vs, 1920w(sh) (in CH$_2$Cl$_2$)	53	a
	AsPh$_3$	1:1	$[Ru_3(CO)_{11}(AsPh_3)]$		2100w, 2048m, 2038(sh), 2018vs, 2000m, 1990w, 1975w, 1965w	66	a
	dpam	1:1	$[Ru_3(CO)_{10}(dpam)]$		2083m, 2067m, 2024m, 2009vs, 1990(sh), 1964m, 1944w	53	a
	SbPh$_3$	1:1	$[Ru_3(CO)_{11}(SbPh_3)]$		2100w, 2050s, 2032m, 2019vs, 2000w, 1988w, 1976w 1964w	44	a
$[H_4Ru_4(CO)_{12}]$	CNBu^t	1:2	$[H_4Ru_4(CO)_{10}(CNBu^t)_2]$	2168s	2092m, 2084w, 2060s, 2034vs, 2020s, 2000s, 1982s	34	c
	PPh$_3$	1:1	$[H_4Ru_4(CO)_{11}(PPh_3)]$		2095m, 2082m, 2068vs, 2059s, 2028vs, 2015m, 2009s, 1969w	55	e
	P(OPh)$_3$	1:1	$[H_4Ru_4(CO)_{11}\{P(OPh)_3\}]$		2096w, 2071s, 2058vs, 2034s, 2013s, 2000w(sh)	76	f
	P(OMe)$_3$	1:4	$[H_4Ru_4(CO)_9\{P(OMe)_3\}_3]$		2068m, 2036s, 2014m, 1998s, 1985m, 1978m, 1963w	47	f
$[Os_3(CO)_{12}]$	CNBu^t	1:1	$[Os_3(CO)_{11}(CNBu^t)]$		2100m, 2054s, 2039s, 2019vs, 2006s, 1988s, 1984(sh)	17	g
	PPh$_3$	1:2	$[Os_3(CO)_{11}(PPh_3)]$		2108w, 2058m, 2038s, 2005m, 1998m, 1988m, 1979m	24	h
			$[Os_3(CO)_{10}(PPh_3)_2]$		2088w, 2072vw, 2056w, 2033s, 2012m, 2002vs, 1997(sh), 1970m, 1955w	21	h
			$[Os_3(CO)_9(PPh_3)_3]$		2070(sh), 2056vw, 2040(sh), 2030w, 1994s, 1969vs, 1950m	17	h
$[Co_3(CCl)(CO)_9]$	CNBu^t	1:5	$[Co_3(CCl)(CO)_6(CNBu^t)_3]$	2180w, 2140s	2042s, 2032w(sh), 2008s, 1993s, 1979s	62	i
	dppe	1:1	$[Co_3(CCl)(CO)_7(dppe)]$		2066s, 2020s, 2013s, 2000w, 1976w	51	a
$[Rh_6(CO)_{16}]$	CNBu^t	1:4	$[Rh_6(CO)_{12}(CNBu^t)_4]$	2161vs	2070(sh), 2051m, 2032vs, 2008vs, 1990w, 1985(sh), 1956w, 1778vs(br)	30	a

a All new compounds have satisfactory elemental microanalyses, i.r., and ^{1}H n.m.r. spectra; dppe $=$ Ph$_2$PCH$_2$CH$_2$PPh$_2$, dpam $=$ CH$_2$(AsPh$_2$)$_2$. b Reference 2; Otol $\equiv$ OC$_6$H$_4$Me-p. c M. I. Bruce, D. Schultz, R. C. Wallis, and A. D. Redhouse, *J. Organomet. Chem.*, 1979, **169**, C15. d Reference 3. e F. Piacenti, M. Bianchi, P. Frediani, and E. Benedetti, *Inorg. Chem.*, 1971, **10**, 2759. f S.A.R. Knox and H. D. Kaesz, *J. Am. Chem. Soc.*, 1971, **93**, 4594. g M. Mays and P. D. Gavens, *J. Chem. Soc., Dalton Trans.*, 1980, 911. h C. W. Bradford, W. van Bronswijk, R. J. H. Clark, and R. S. Nyholm, *J. Chem. Soc. A*, 1970, 2889. i J. Newman and A. R. Manning, *J. Chem. Soc., Dalton Trans.*, 1974, 2549.

ate stoicheiometric product, in contrast with the thermal reactions which often give all possible derivatives [H$_4$Ru$_4$(CO)$_{12-n}$(L)$_n$] ($n = 0$—4).

(iv) [Os$_3$(CO)$_{12}$] and [H$_4$Os$_4$(CO)$_{12}$] are significantly less reactive than the analogous ruthenium complexes, and tend to give mixtures of products; however, the lower temperature required gives improved yields of primary substitution products, and little or no decomposition is found.

(v) [Co$_3$(μ_3-CCl)(CO)$_9$] reacts quickly and cleanly[1] to give the stoicheiometric product, with up to three ligands being incorporated per cluster.

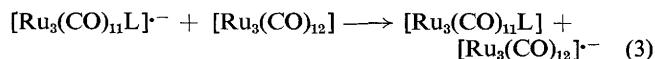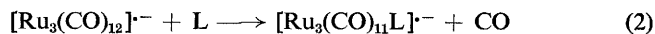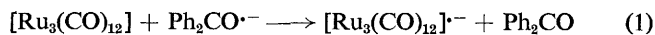(vi) [M$_4$(CO)$_{12}$] (M = Co, Rh, or Ir) readily undergoes substitution by tertiary phosphines or phosphites, and the present method offers no advantage.

(vii) [H$_3$M$_3$(CO)$_{12}$] (M = Mn or Re) does not give substituted clusters; the manganese complex readily forms [Mn$_2$(CO)$_{10}$] and [Mn$_2$(CO)$_8$(L)$_2$] under the reaction conditions, while the rhenium complex undergoes a slow, nonspecific reaction.

This radical-catalysed reaction described above appears to be general for systems which satisfy the following requirements: (i) the cluster carbonyl can be reduced to an anion which has a significant lifetime without fragmentation occurring; (ii) the incoming ligand is less π-acidic than CO (to facilitate electron transfer from the substituted to the unsubstituted cluster radical anion); (iii) the ligand is not reduced by Ph$_2$CO$^{\cdot-}$.

The mechanism proposed for these reactions is essentially that discussed earlier,[1] and is related to the electron-transfer chain-catalysed reactions found in organic systems;[4] as an example, equations (1), (2), and (3) give the chain reaction for [Ru$_3$(CO)$_{12}$]. The reactive species is the radical anion

$$[Ru_3(CO)_{12}] + Ph_2CO^{\cdot -} \longrightarrow [Ru_3(CO)_{12}]^{\cdot -} + Ph_2CO \qquad (1)$$

$$[Ru_3(CO)_{12}]^{\cdot -} + L \longrightarrow [Ru_3(CO)_{11}L]^{\cdot -} + CO \qquad (2)$$

$$[Ru_3(CO)_{11}L]^{\cdot -} + [Ru_3(CO)_{12}] \longrightarrow [Ru_3(CO)_{11}L] + [Ru_3(CO)_{12}]^{\cdot -} \qquad (3)$$

$[Ru_3(CO)_{12}]^{\cdot -}$ where the excess electron is in an Ru–Ru (σ^*) antibonding orbital, which leads to a weakened bond. Cleavage of an Ru–Ru bond gives a 17e Ru centre which readily undergoes attack by L and elimination of CO (equation 2). Reformation of the Ru–Ru bond gives $[Ru_3(CO)_{11}L]^{\cdot -}$ which rapidly transfers an electron to $[Ru_3(CO)_{12}]$ to continue the catalytic cycle (equation 3).

As can be seen from Table 1, this method affords many complexes which cannot be obtained from the analogous thermal reactions. For systems where the reaction is favourable, the short reaction times, mild conditions, and easy product isolation will all facilitate further study of the initial reactions occurring between ligands and metal carbonyl clusters.

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