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Preliminary communication

CLUSTER CHEMISTRY. DIRECTED SYNTHESES OF MIXED LIGAND DERIVATIVES OF RUTHENIUM AND COBALT CLUSTER CARBONYLS

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Summary

Sequential radical-anion-initiated reactions of cluster carbonyl complexes ($Ru_3(CO)_{12}$, $H_4Ru_4(CO)_{12}$, $Co_3(\mu\text{-}CR)(CO)_9$) with isocyanides or Group V donor ligands have given a range of derivatives containing two or more different ligands attached to the cluster; these compounds can be obtained in moderate to high yields by designed syntheses under mild conditions.

Studies of the interaction of many polynuclear metal carbonyls with simple donor ligands have often been frustrated by the harsh conditions required to induce reaction. In general, these have precluded (i) identification of the initial reaction products, and hence (ii) studies of their further transformations, and (iii) designed syntheses of specifically substituted complexes. Thus, in thermal reactions of $Ru_3(CO)_{12}$ with Group V donor ligands (L), the usual products are the relatively unreactive $Ru_3(CO)_9(L)_3$, the mono- and disubstituted complexes being obtained only rarely; similar reactions with $H_4Ru_4(CO)_{12}$, on the other hand, give all possible complexes $H_4Ru_4(CO)_{12-n}(L)_n$ (n = 0—4), which are separated with difficulty.

We have recently described a simple route to substituted metal cluster carbonyls by their reactions with stoichiometric amounts of ligand, under mild conditions and initiated by radical anions such as sodium diphenylketyl [1]. We now report that application of this reaction to the sequential incorporation of various ligands allows designed syntheses of a wide range of cluster complexes containing two or more different ligands to be achieved. As found earlier, these reactions proceed at or just above room temperature, with reaction times of between a few minutes and half an hour. The progress of the reaction can be monitored conveniently by inspection of the ν(CO) region of

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TABLE 1

SELECTED SPECTROSCOPIC DATA

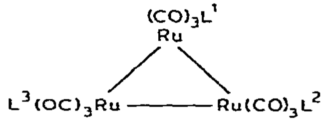
Complex	ν(CO) (cm^{-1})	^{1}H NMR (δ, ppm)
I^a	2098w, 2068w, 2045m, 2029s, 2016s, 2004m, 1986w	1.86d P—Me 1.49s CMe_3
II	2050m, 1980vs, 1957s, 1946(sh)	3.68d P—OMe 1.70d P—Me
III	2085w, 2027w, 2012s, 2003vs, 1988s, 1967m, 1959(sh), 1952(sh)	2.99d P—OMe
IV^b	2074(sh), 2063m, 2051w, 2037w, 2024m, 2011vs, 1999vs, 1993m, 1985m, 1970s, 1961(sh)	4.65m, 3.07d, 2.38d $CH{=}CH_2$ 1.43s CMe_3
VI	2061s, 2031vs, 2010s, 1992s, 1984w, 1971m, 1956w, 1941w	3.57d, 3.55d P—OMe 1.78m P—Me —17.0s(br) Ru—H
VII	2067s, 2026(sh), 2023(sh), 2018s, 2007m, 1983m	3.66d P—OMe 2.35s C_6H_4Me

$^a\nu$(CN) 2168w. $^b\nu$(CN) 2165w.

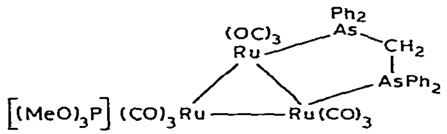
the IR spectrum of the reaction mixture. Isolation of product is a simple routine of solvent removal and crystallisation, thus avoiding tedious chromatography, which in some cases may result in alteration or loss of product.

The following are indicative of the range of complexes which we have prepared by this method; some spectroscopic data are collected in Table 1.

(a) $Ru_3(CO)_{10}(CNBu^t)(PMe_2Ph)$ (I): Addition of a solution of sodium diphenylketyl (0.15 ml of 0.01 *M* solution in tetrahydrofuran) to an equimolar mixture of $Ru_3(CO)_{11}(PMe_2Ph)$ and $CNBu^t$ (0.5 mmol) in the same solvent (10 ml) resulted in gas evolution and a deepening of colour. The reaction was complete at room temperature in five minutes, to give the product (isolated yield 42%).



(I, L^1 = CO, L^2 = $CNBu^t$, L^3 = PMe_2Ph ;
II, L^1 = PMe_3, L^2 = PPh_3, L^3 = $P(OMe)_3$)



(III)

(b) $Ru_3(CO)_9(PMe_3)(PPh_3)[P(OMe)_3]$ (II): A similar reaction between $Ru_3(CO)_{11}[P(OMe)_3]$ and PMe_3 afforded $Ru_3(CO)_{10}(PMe_3)[P(OMe)_3]$ (87%), which in turn reacted with PPh_3 to give the trisubstituted complex (41%).

(c) $Ru_3(CO)_9(dpam)[P(OMe)_3]$ (III): This complex was obtained as a benzene solvate from an analogous reaction between $Ru_3(CO)_{10}(dpam)$ and $P(OMe)_3$ (51%)*.

(d) $Ru_3(CO)_9(sp)(CNBu^t)$ (IV): In this instance, reaction of $Ru_3(CO)_{10}(sp)$ (V) with $CNBu^t$ required rather more initiator (ca 1 ml) and gave the mixed ligand complex in 18% yield**.

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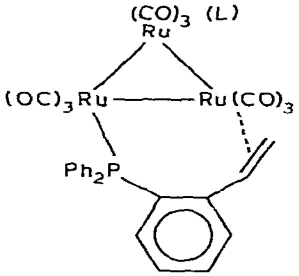
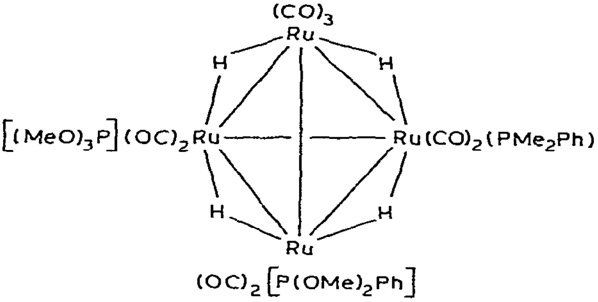
*dpam = bis(diphenylarsino)methane.

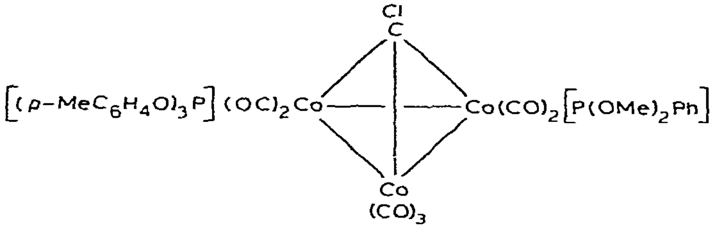
**sp = o-styryldiphenylphosphine.



(IV, L = CNBu^t;
V, L = CO)



(VI)



(VII)

(e) $H_4Ru_4(CO)_9(PMe_2Ph)[P(OMe)_2Ph][P(OMe)_3]$ (VI): This derivative was obtained from $H_4Ru_4(CO)_{12}$ in a sequence of reactions with $P(OMe)_3$ (90%), $P(OMe)_2Ph$ (70%) and finally PMe_2Ph (60%).

(f) $Co_3(\mu_3\text{-}CCl)(CO)_7[P(OMe)_2Ph][P(OC_6H_4Me\text{-}p)_3]$ (VII): In similar fashion, this complex was formed from reactions between $Co_3(\mu_3\text{-}CCl)(CO)_9$ and $P(OC_6H_4Me\text{-}p)_3$ (78%), followed by $P(OMe)_2Ph$ (64%).

The complexes mentioned above include several interesting ligand combinations, such as the first reported tertiary arsine-tertiary phosphine substituted complex (III), the first with three different phosphorus-donor ligands (II and VI), the first η^2-olefin complexes obtained from $Ru_3(CO)_{12}$ (IV and V), and the unusual olefin-isocyanide-tertiary phosphine combination in IV. We also note that complexes VI and VII are chiral, and thus provide the opportunity for resolution into a new type of optically active cluster, which derives its chirality from a combination of different ligands on a homometallic cluster. This is distinct from the previously described examples containing optically active ligands, e.g. $H_4Ru_4(CO)_8[(-)\text{-diop}]_2$ [2], or four different skeletal atoms, such as $MoFeCO(\mu_3\text{-}S)(CO_8)(\eta\text{-}C_5H_5)$ [3]*.

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*diop = 2,3-isopropylidene-2,3-dihydroxy-1,4-bis(diphenylphosphino)butane.

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