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Preliminary communication

INTERMOLECULAR LIGAND EXCHANGE IN TETRANUCLEAR METAL CARBONYL COMPLEXES

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Summary

A ready intermolecular ligand exchange process occurs when solutions of $Co_2Rh_2(CO)_{12}$ and $Co_2Rh_2(CO)_8(PF_3)_4$ are mixed at room temperature.

It is well-known that in certain tetranuclear metal carbonyl complexes the carbonyl groups can undergo rapid site exchange [1-3]. The bridge-terminal carbonyl exchange in $Rh_4(CO)_{12}$ has been shown to occur by a single process [1,2] while more recently studies on the mixed metal carbonyl $RhCo_3(CO)_{12}$ have established two distinct and independent ligand exchange processes. In both the above systems the exchange processes are intramolecular and we now present evidence which shows that intermolecular ligand exchange is also possible in these types of polynuclear metal carbonyl complexes.

When a pentane solution of $Rh_2Co_2(CO)_{12}$ [4] (I) is mixed at room temperature with an equimolar amount of the new complex $Rh_2Co_2(CO)_8$-$(PF_3)_4$ (II) (made by the reaction of either $TlCo(CO)_4$ [5] or $Co_2(CO)_8$ with $[RhCl(PF_3)_2]_2$ [6-8], eqns. 1 and 2) an immediate intermolecular ligand exchange of CO and PF_3 molecules occurs and $Rh_2Co_2(CO)_{10}(PF_3)_2$ (III) is readily identified in the reaction mixture.

$$[RhCl(PF_3)_2]_2 + 2TlCo(CO)_4 \xrightarrow{-2TlCl} Rh_2Co_2(CO)_8(PF_3)_4 \qquad (1)$$

$$2[RhCl(PF_3)_2]_2 + 3Co_2(CO)_8 \xrightarrow[\text{hexane}/RT]{-8CO} 2Rh_2Co_2(CO)_8(PF_3)_4 + 2CoCl_2 \qquad (2)$$

The identity of III was confirmed by its synthesis via an alternative route via the reaction of $[RhCl(CO)(PF_3)]_2$ [6] with $TlCo(CO)_4$. The proposed structures for II and III are based on elemental analyses, IR, NMR,

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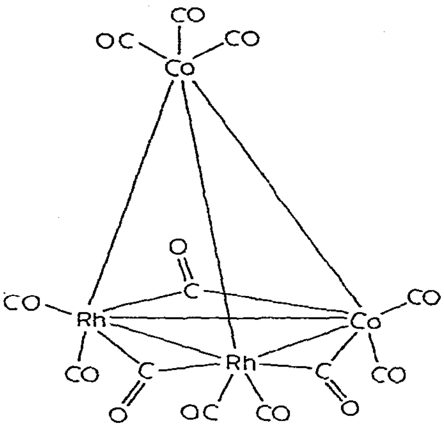
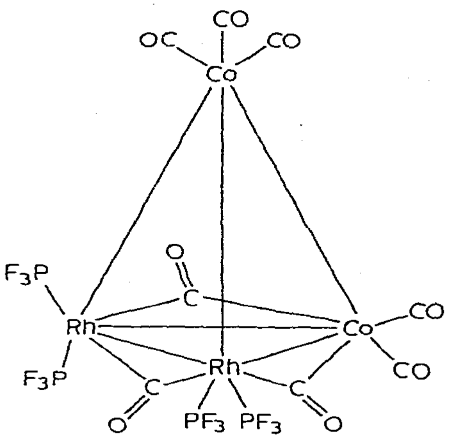
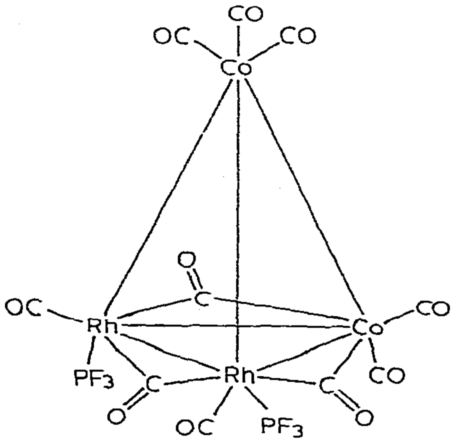


(I)



(II)



(III)

and mass spectral data. The ^{19}F NMR spectrum of II shows two distinct equatorial and axial PF_3 environments [$\varphi(F_1) = 8.8$ ppm, $^1J(PF_1) \approx 1410$ Hz; $\varphi(F_2) = 12.3$ ppm $J(PF_2) \approx 1465$ Hz], while only one type of PF_3 is observed in III [$\varphi(F) = 10.8$ ppm, $J(PF) \approx 1450$ Hz] indicating that the two PF_3 groups are either both axial or both equatorial. The resonances are somewhat broadened at room temperature. On cooling the solutions of II and III to —30 °C, further fine structure can be observed.

In a previous papper [6] we described the rapid intermolecular ligand exchange that occurs between the binuclear complexes $[RhCl(CO)_2]_2$ and $[RhCl(PF_3)_2]_2$, while very recently Masters and Visser [9] reported the biheterometallic system $PtPdCl_4L_2$ ($L = PBu_3$), formed in mixtures of $[PtCl_2L]_2$ and $[PdCl_2L]_2$, but this is the first report of an intermolecular ligand exchange between two compounds containing tetranuclear clusters of metal atoms. We are currently studying both inter- and intra-molecular exchange processes in these and other mixed trifluorophosphine-carbonyl polynuclear systems.

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