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Preliminary communication

A COMPARISON OF FACE-CAPPING VERSUS FRAGMENTATION REACTIONS OF $[Rh_4(CO)_{12}]$ WITH triphos, $(MeC(CH_2PPh_2)_3)$ AND TRIPOD, $(HC(PPh_2)_3)$; CRYSTAL STRUCTURE OF $[(\text{triphos})Rh(\mu\text{-}CO)_2Rh(\text{triphos})]$

CLAUDIO ALLEVI, MARTIN GOLDING, BRIAN T. HEATON*,
Department of I.P.I. Chemistry, P.O. Box 147, The University, Liverpool L69 3BX (Great Britain)

CARLO A. GHILARDI, STEFANO MIDOLLINI and ANNABELLA ORLANDINI
C.N.R. Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, Via J. Nardi 39, 50132 Firenze (Italy)

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Summary

The initial reaction of $[Rh_4(CO)_{12}]$ with triphos results in either face-capping or fragmentation reactions which occur at different temperatures whereas only face-capping occurs with tripod; the fragmentation products further react with triphos, but not with tripod, to give $[(\text{triphos})Rh(\mu\text{-}CO)_2Rh(\text{triphos})]$ which has been structurally characterised by X-ray crystallography.

The sites of ligand substitution in homo- and hetero-metallic carbonyl clusters are still poorly understood. Trends are emerging for monodentate ligand substitutions in small homo-metallic clusters [1] but there are many fewer data available for bi- and tri-dentate ligands and even fewer data available for hetero-metallic clusters. We now report on the reactions of triphos $(MeC(CH_2PPh_2)_3)$, with $[Rh_4(CO)_{12}]$ and contrast the differing coordinative abilities of triphos with tripod, $(HC(PPh_2)_3)$.

At −60 °C, triphos reacts with $[Rh_4(CO)_{12}]$ in CH_2Cl_2 solution, under N_2, to give $[Rh_4(CO)_9(\text{triphos})]$ (**1**), which has been shown by multinuclear NMR studies * to exist as isomer A, (Fig. 1), and to be quite stable under a nitrogen atmosphere at room temperature. An analogous cluster has been prepared previously by treating tripod with $[Rh_4(CO)_{12}]$ [2]. However, whereas $[Rh_4(CO)_9(\text{tripod})]$ is more stable than $[Rh_4(CO)_{12}]$, showing no appreciable reaction with CO even at 30 bar and 100 °C in toluene, **1** undergoes further reaction with CO, at room temperature and

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* See footnote * next page.

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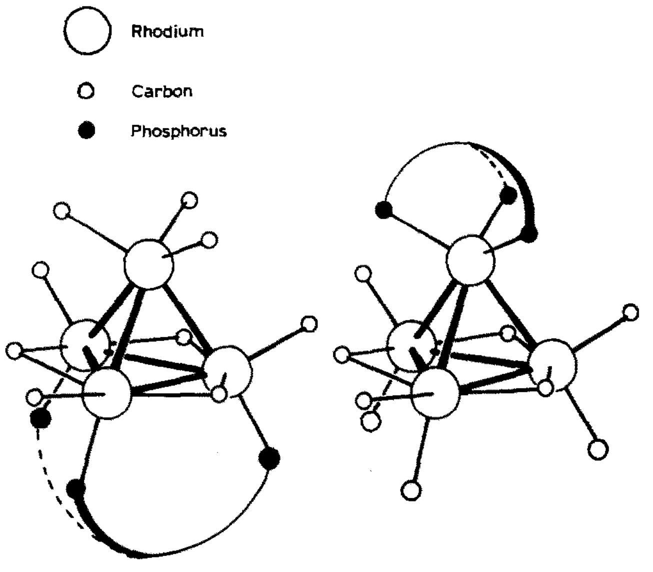

isomer A isomer B

Fig. 1. Possible isomers of $[Rh_4(CO)_9(\overline{PPP})]$ ($\overline{PPP}$ = triphos ($CMe(CH_2PPh_2)_3$, or tripod ($HC(PPh_2)_3$).

atmospheric pressure to give derivatives such as $[Rh(triphos)(CO)_2]^+$ **, $[Rh_6(CO)_{15}]^{2-}$, $[Rh_6(CO)_{16}]$ and $[Rh_5(CO)_{15}]^-$, the first being the only species containing triphos. All these products were identified by IR and ^{13}C and ^{31}P NMR measurements. Similar products were obtained on carrying out the reaction of $[Rh_4(CO)_{12}]$ with triphos at room temperature; this latter reaction occurs cleanly if carried out under an atmosphere of CO. It is difficult to be sure of the exact mechanism of these fragmentation/agglomeration reactions but, in view of the propensity of compounds containing triphos chelated to a single metal atom, the involvement of isomer **B** (Fig. 1) followed by disproportionation (eq. 1) seems attractive since the formation of all the products observed in these reactions can

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* NMR data on $[Rh_4(CO)_9(triphos)]$, isomer A, measured in CD_2Cl_2 at 25 °C. (Chemical shifts are in ppm and values to high frequency are positive; coupling constants are in Hz. Standards for different chemical shifts are $SiMe_4$ for ^{13}C, 85% H_3PO_4 in D_2O for ^{31}P and 3.16 MHz at such a magnetic field that the ^1H's in $SiMe_4$ resonate at exactly 100 MHz for ^{103}Rh).

	δ(CO)	^1J(Rh–CO)	^3J(P–CO)
apical	186.4(dq)	65.8	19.5
radial	187.9(d)	75.9	
bridge	244.1(t)	34.5	

δ(P)	δ(Rh)	^1J(Rh–P)
8.0(d)	−290 s (apical)	
	−390 d (basal)	128.7

** NMR data on $[Rh(CO)_2(triphos)]^+$ measured in CD_2Cl_2 at 25 °C; δ(P) 8.6 (d), ^1J(Rh–P) 99.6; δ(CO) 195.9 (dq), ^1J(Rh–C), 58.0; ^2J(P–CO), 22.4.

readily be accounted for by $[\mathrm{Rh_3(CO)_{10}}]^-$ undergoing either dimerisation (eq. 2) or further reaction with unreacted $[\mathrm{Rh_4(CO)_{12}}]$ (eq. 3) followed by formation of $[\mathrm{Rh_5(CO)_{15}}]^-$ from the well-known reaction of $[\mathrm{Rh_{12}(CO)_{30}}]^{2-}$ (eq. 4) with CO [3].

$$\underset{\text{(isomer }\mathbf{B})}{[\mathrm{Rh_4(CO)_9(triphos)}]} \xrightarrow{\mathrm{CO}} [\mathrm{Rh(triphos)(CO)_2}]^+[\mathrm{Rh_3(CO)_{10}}]^- \tag{1}$$

$$2[\mathrm{Rh_3(CO)_{10}}]^- \xrightarrow{\mathrm{N_2}} [\mathrm{Rh_6(CO)_{15}}]^{2-} + 5\mathrm{CO} \tag{2}$$

$$8[\mathrm{Rh_3(CO)_{10}}]^- + 9[\mathrm{Rh_4(CO)_{12}}] \xrightarrow{\mathrm{N_2}} 4[\mathrm{Rh_{12}(CO)_{30}}]^{2-} + 2[\mathrm{Rh_6(CO)_{16}}] + 36\mathrm{CO} \tag{3}$$

$$3[\mathrm{Rh_{12}(CO)_{30}}]^{2-} \xrightarrow{\mathrm{CO}} 6[\mathrm{Rh_5(CO)_{15}}]^- + [\mathrm{Rh_6(CO)_{16}}] \tag{4}$$

Although disproportionation reactions of uncharged cobalt carbonyls to give ionic species are well known [4], eq. 1 provides the first example of an analogous reaction for rhodium carbonyls and is induced by the flexibility of triphos which allows it to chelate to just one metal atom resulting in the preferential stabilisation of the rhodium(I) oxidation state, $[\mathrm{Rh(CO)_2(triphos)}]^+$. When the rigidity of the ligand skeleton hinders chelation to just one metal atom (L = tripod), or the carbonyls in the cluster are not fluxional ($\leqslant -60\,^\circ$C), the reaction proceeds with formation of isomer **A** and, in the absence of CO, stops there.

Further reaction of the fragmentation products (eq. 1–4) with triphos, under a flow of nitrogen, occurs to give $[\mathrm{(triphos)Rh(\mu\text{-}CO)_2Rh(triphos)}]$ (**2**) in high yield *. Complex **2**, which has been isolated previously in low yield from the reaction of $[\mathrm{Rh(CO)(CONH_2)(triphos)}]$ with liquid ammonia for 3 days [5], has now been structurally characterised by X-ray diffraction (Fig. 2) **. Since we have now shown that **2** can also be prepared in good yield as shown in eq. 5, we suggest that this is the most likely route for the formation of **2**. Indeed, it is already known from

$$[\mathrm{Rh(CO)_2(triphos)}]^+ + [\mathrm{Rh(CO)_4}]^- \xrightarrow{\mathrm{triphos}} \mathbf{2} \tag{5}$$

other studies that $[\mathrm{Rh(CO)_4}]^-$ can result from all the above anionic rhodium clusters. However, because of the formation of **2** in such high yield, it is possible

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* A solution of triphos (0.4 mmol) in 30 ml of acetone was added dropwise, at room temperature, under a current of nitrogen, with continuous stirring to a solution of $[\mathrm{Rh_4(CO)_{12}}]$ (0.1 mmol) in 15 ml of acetone. There was a rapid evolution of CO and from the resulting solution red-orange crystals of $[\mathrm{(triphos)Rh(\mu\text{-}CO)_2Rh(triphos)}]$. acetone precipitated (yield 85%).

** Crystal data for **2**: $\mathrm{C_{87}H_{84}O_3P_6Rh_2}$, a 28.698(12), b 18.520(8), c 14.145(6) Å, β 92.00(6)°, U 7513.3 Å^3, monoclinic space group $P2_1/a$, $Z = 4$, $M = 1569.3$, $D_c = 1.387$ g cm^{-3}, monochromatic Mo-K_α radiation, λ 0.7107 Å, μ 6.06 cm^{-1}.

The crystal was coated in paraffin and the intensity data were collected, within $2\theta < 40\,^\circ$, on a Phillips PW 1100 diffractometer using the $\omega - 2\theta$ scan technique at 295 K. The structure was solved by the heavy atom method and refined by full-matrix least-squares procedure. The phenyl rings were treated as rigid bodies and the hydrogen atoms were included in their calculated positions, but not refined. Refinements converged at both the R and R_w factor values of 0.058 for 3091 absorption corrected reflections ($(I) > 3\sigma(I)$). Atomic coordinates have been deposited at the Cambridge Crystallographic Data Centre.

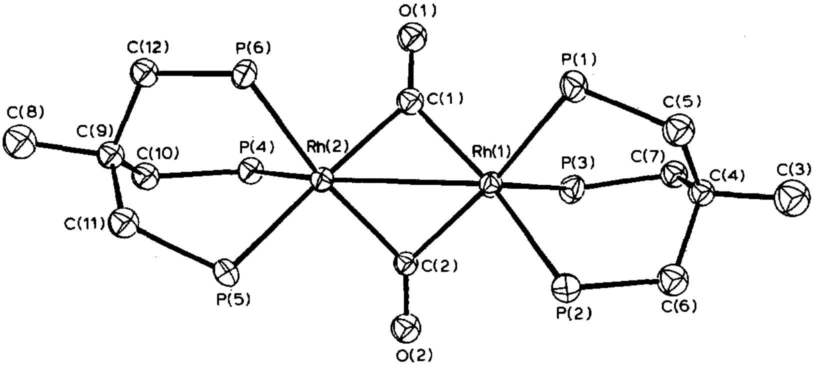

Fig. 2. X-ray structure of [(triphos)Rh(μ-CO)$_2$Rh(triphos)] together with selected bond distances and angles: Rh(1)–Rh(2), 2.822(2); Rh–P, 2.342(5) to 2.383(5); Rh–C, 2.022(17) to 2.054(15) Å; dihedral angle between the planes Rh(1)C(1)Rh(2) and Rh(1)C(2)Rh(2), 138.1°. (Phenyl rings have been omitted for clarity).

that the direct reaction of triphos with the other clusters shown in eq. 2–4 could be involved since we have shown that [$Rh_6(CO)_{16}$] reacts directly with triphos to give (**2**).

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