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Preliminary communication

CATALYTIC ACTIVITY OF $RhH(CO)(PPh_3)_3$ IN THE PRESENCE OF THIOL: A NEW WAY OF OBTAINING A VERY ACTIVE SPECIES

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Summary

Addition of the thiol t-BuSH to $RhH(CO)(PPh_3)_3$ either under nitrogen under ambient conditions or under CO/H_2 pressure under hydroformylation conditions generates the much more active dinuclear species $Rh_2(\mu\text{-S-t-Bu})_2(CO)_2(PPh_3)_2$.

The $RhH(CO)(PPh_3)_3$ complex, 1 has been extensively studied as a hydroformylation catalyst precursor; the full catalytic cycle involves mononuclear species [1—3]. We recently observed the higher and unusual activity of the dinuclear rhodium(I) complex $Rh_2(\mu\text{-S-t-Bu})_2(CO)_2\{P(OMe)_3\}_2$ (2) under very mild conditions (80°C, 5 bar) [4].

Complex 2 was found to be unchanged after catalysis, even in the presence of a slight excess of phosphite ligand [4], and whereas complex 1 gives small amounts of hexane and hex-2-ene starting from hex-1-ene, complex 2 gave a 100% yield of aldehydes. However, when $Rh_2(\mu\text{-S-t-Bu})_2(CO)_2L_2$ complexes with more basic ligands such as triaryl- or trialkyl-phosphines are used, although there is total selectivity towards formation of aldehydes, rapid deactivation occurs giving the inactive species $Rh_2(\mu\text{-S-t-Bu})_2(CO)_4$, (3).

We have concluded from infrared and ^{31}P NMR spectroscopic studies that the addition of an excess of triphenylphosphine to the complex $Rh_2(\mu\text{-S-t-Bu})_2(CO)_2(PPh_3)_2$ (4) does not cleave the thiolato bridges, whereas Knox et al. reported that the mononuclear $Rh(SR)(CO)(PPh_3)_2$ complex was formed [5]. In the presence of some of the free ligand (P/Rh = 2 to 10) complex 4 is a good catalytic precursor which does not undergo deactivation and is recovered unchanged after the catalysis. Since in the absence of added free ligand complex 1 gives the inactive tetranuclear cluster $Rh_4(\mu\text{-}PPh_2)_4(PPh_3)(CO)_5$ [6], complex 4 evidently do not generate any species, which is present in the catalytic cycle for complex 1; for instance, a hydride species without any thiol ligand. The two systems behave quite differently. We thus tried to find whether relationship could exist between complexes 1 and 4, for example, by adding thiol to 1 which is known to be very sensitive to sulfur poisons. Figure 1 shows the kinetic curves for complex 1 alone together with those for 1 plus one mole of t-BuSH. During the first 25 min the reactivities are quite similar, the presence of the mercaptan lowering the rate to a slight extent. Subsequently the system 1 + t-BuSH becomes more reactive, the rate being comparable with that for complex 4; in addition, the selectivity of the reaction and the spectroscopic data after catalysis are consistent with the presence of 4. Moreover, in a Schlenck tube, under nitrogen the 1 + t-BuSH system, generates complex 4, as shown by the infrared and ^{31}P NMR data. Finally a NMR tube was charged

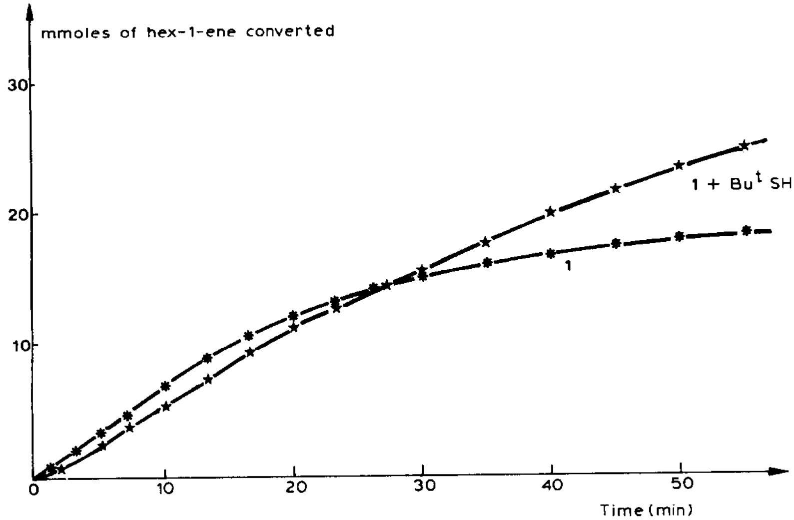

Fig. 1. Conversion of hex-1-ene using (a) complex 1 lower line and (b) complex 1 plus one mol of t-BuSH (upper line). P 5 bar; T 80°C; 40 mmol of hex-1-ene in 30 ml of dimethylformamide; 10^{-4} g-atom of rhodium.

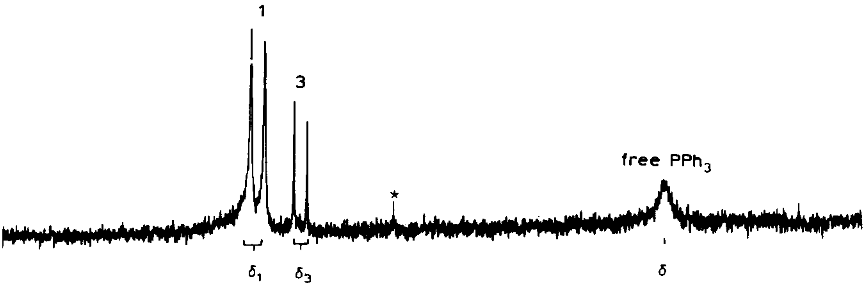

Fig. 2. ^{31}P NMR spectrum of $RhH(CO)(PPh_3)_3$ plus t-BuSH under catalytic conditions (Rh: 10^{-4} g-atom; t-BuSH: 10^{-4} mol; hex-1-ene: 10^{-4} mol; T 25°C; CO/H_2 1/1; P 2.5 bar). δ_1 41.2 ppm $J(Rh\text{—}P)$ 151.8 Hz; δ_3 36.3 ppm $J(Rh\text{—}P)$ 151.5 Hz; $\delta(PPh_3)$ −4.35 ppm; *small amounts of $OPPh_3$ δ 25.9 ppm.

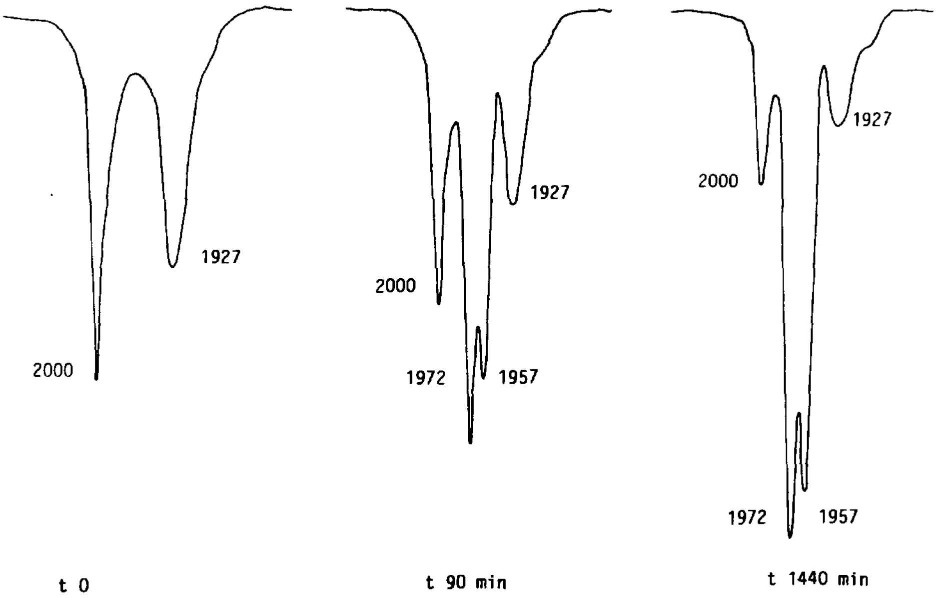

Fig. 3. Variation of time of the infrared spectrum of $RhH(CO)(PPh_3)_3$ plus t-BuSH under catalytic conditions, showing the formation of one mol of $[RhH(CO)(PPh_3)_3]$ in the presence of one mol of t-BuSH.

with 1 + t-BuSH + hex-1-ene in C_6D_6 and pressurized with a CO/H_2 gas mixture in order to monitor the reaction under the conditions used for catalysis. Figure 2 shows an ^{31}P NMR spectrum recorded before completion of the reaction.

The doublet at 41.2 ppm ($^1J(Rh{-}P)$ 152 Hz) belongs to the $RhH(CO)(PPh_3)_3$ complex, the free phosphine ligand shows up at 4.35 ppm, and the doublet at 36.3 ppm ($^1J(Rh{-}P)$ 151.5 Hz) is characteristic of complex 4. Similarly the infrared spectra of this system under N_2 or CO/H_2 reveal the consumption of complex 1, since the $\nu(CO)$ band at 1920 cm^{-1} and the $\nu(Rh{-}H)$ at 2000 cm^{-1} fall while at the same time the two $\nu(CO)$ bands at 1972 and 1957 cm^{-1} of complex 4 grow (see Fig. 3). The following equation of reaction takes account of all our observations.

$$2\ RhH(CO)(PPh_3)_3 + 2\ t\text{-}BuSH \rightarrow Rh_2(\mu\text{-}S\text{-}t\text{-}Bu)_2(CO)_2(PPh_3)_2 + 4\ PPh_3 + 2H_2$$

In the presence of a thiol the mononuclear complex 1 irreversibly gives the dinuclear complex 4. In our opinion catalyses by the two complexes involve quite independent pathways. In particular the high turnover exhibited by complex 4, the total selectivity induced by 4, and the absence of formation of $Rh_4(\mu\text{-}PPh_2)_4(PPh_3)(CO)_5$ from 4 confirm that complex 1 or the active species generated by it are not formed during the catalytic cycle for 4. Thus the thiolato ligands remain attached to the rhodium atoms during the whole catalytic cycle. This cycle is under investigation.

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