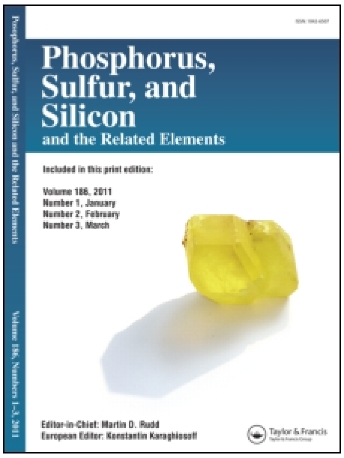


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE REACTION OF THIOLS WITH [RhH(PPh$_3$)$_4$]: RHODIUM THIOLATE COMPLEXES AND HYDROGENATION CATALYSTS

Laurence Carlton[a]
[a] Department of Chemistry, University of the Witwatersrand, Johannesburg, Republic of South Africa

To cite this Article Carlton, Laurence(1991) 'THE REACTION OF THIOLS WITH [RhH(PPh$_3$)$_4$]: RHODIUM THIOLATE COMPLEXES AND HYDROGENATION CATALYSTS', Phosphorus, Sulfur, and Silicon and the Related Elements, 59: 1, 231 — 234

To link to this Article: DOI: 10.1080/10426509108045730
URL: http://dx.doi.org/10.1080/10426509108045730

Phosphorus, Sulfur, and Silicon, 1991, Vol. 59, pp. 231–234
Reprints available directly from the publisher
Photocopying permitted by license only

THE REACTION OF THIOLS WITH $[RhH(PPh_3)_4]$: RHODIUM THIOLATE COMPLEXES AND HYDROGENATION CATALYSTS

LAURENCE CARLTON
Department of Chemistry, University of the Witwatersrand, Johannesburg, Republic of South Africa.

Abstract The unstable complexes $[RhH_2(SR)(PPh_3)_3]$ (R = Pr^i, $CH_3(CH_2)_{11}$, C_6F_5) formed by the reaction of RSH with $[RhH(PPh_3)_4]$ are catalysts for the homogeneous hydrogenation of cyclohexene at ambient temperature and pressure. Their catalytic activity is significantly higher than that of the corresponding thiolate–bridged complexes $[Rh_2(\mu\text{-}SR)_2(PPh_3)_4]$ into which they are steadily converted during the course of the reaction.

INTRODUCTION

Dinuclear rhodium thiolate complexes $[Rh_2(\mu\text{-}SR)_2L_4]$ (R = Bu^t, L = $P(OMe)_3$, PPh_3) catalyse the hydrogenation of alkenes under mild conditions[1], the phosphine complexes being moderately effective. The triphenylphosphine complexes can be prepared by the reaction of thiols with $[RhH(PPh_3)_4]$. A low temperature NMR study[2] of this reaction shows that the initial product is $[RhH_2(SR)(PPh_3)_3]$ (R = Pr^i, Ph, CH_2Ph); this unstable complex loses H_2 via the five–coordinate species $[RhH_2(SR)(PPh_3)_2]$ which then rapidly dimerises forming $[Rh_2(\mu\text{-}SR)_2(PPh_3)_4]$. In this communication the activity as catalysts for the homogeneous hydrogenation of cyclohexene of species generated in mixtures of $[RhH(PPh_3)_4]$ and RSH is examined by low temperature ^1H and ^{31}P NMR spectroscopy, H_2 uptake and gas chromatography.

RESULTS AND DISCUSSION

The reaction of $[RhH(PPh_3)_4]$ with $CH_3(CH_2)_{11}SH$ or C_6F_5SH in toluene at temperatures $\leq -25^0C$ gives the unstable complex $[RhH_2(SR)(PPh_3)_3]$. With

R = $CH_3(CH_2)_{11}$ this compound decays at 20°C in a manner similar to that of the isopropyl analogue[2]. However with R = C_6F_5 two new types of complex are formed on warming to 20°C: $[RhH_2(SC_6F_5)(HSC_6F_5)(PPh_3)_2]$ (hydrogens mutually *cis*, phosphines axial) and $[RhH_2(PPh_3)_2(\mu\text{–}SC_6F_5)_2RhH_2(PPh_3)_2]$. The addition of a large excess of PPh_3 reconverts both to $[RhH_2(SC_6F_5)(PPh_3)_3]$, but on standing at 20°C for 24 hours $[Rh_2(\mu\text{–}SC_6F_5)_2(PPh_3)_4]$ is found to be the major product.

Under H_2 (1 atmosphere) the decay of $[RhH_2(SR)(PPh_3)_3]$ is slowed; with R = Pr^i approximately 25% is lost on standing for 10 minutes at 20°C. Under a nitrogen atmosphere the loss after 10 minutes is approximately 90%.

Upon adding cyclohexene (to give ~ 20% solution) to toluene solutions at < –40°C containing $[RhH_2(SR)(PPh_3)_3]$ (R = Pr^i, $CH_3(CH_2)_{11}$, C_6F_5) under H_2 there is no evidence of a reaction with the dihydro complex, but, when the solution is warmed to 20°C for 1 minute, the concentration of $[RhH_2(SR)(PPh_3)_3]$ is reduced and $[Rh(SR)(PPh_3)_3]$ and $[Rh_2(\mu\text{–}SR)_2(PPh_3)_4]$ are formed, indicating coordination (in place of the labile phosphine *trans* to hydrogen) and hydrogenation of cyclohexene.

At 20°C mixtures of $RhH(PPh_3)_4]$ and excess RSH (R = Pr^i, $CH_3(CH_2)_{11}$, C_6F_5) in cyclohexene/toluene (20%) catalyse the hydrogenation of the alkene at rates of up to 20 mol per hour per mol of rhodium (Figure 1). The alkene conversion profiles (monitored by uptake of H_2 with final reaction solutions analysed by gas chromatography) show an initial phase of rapid activity (up to 20 minutes for R = Pr^i, $CH_3(CH_2)_{11}$, up to ~ 60 minutes for R = C_6F_5) after which the rate slows to a much lower value.

When a mixture of $[Rh_2(\mu\text{–}SPr^i)_2(PPh_3)_4]$ and PPh_3 (two equivalents per Rh) is used to catalyse the hydrogenation the alkene conversion rate is somewhat lower than that observed with a mixture of $[RhH(PPh_3)_4]$ and Pr^iSH (Figure 1, B and D) after the initial burst of activity has ceased.

These findings are consistent with a reaction pathway (Scheme 1) in which a monomeric species $[RhH_2(SR)(PPh_3)_3]$ is responsible for the initial phase of rapid activity. Conversion of this complex to the thiolate–bridged dimer $[Rh_2(\mu\text{–}SR)_2(PPh_3)_4]$ leads to the slower phase in which the dimer participates.

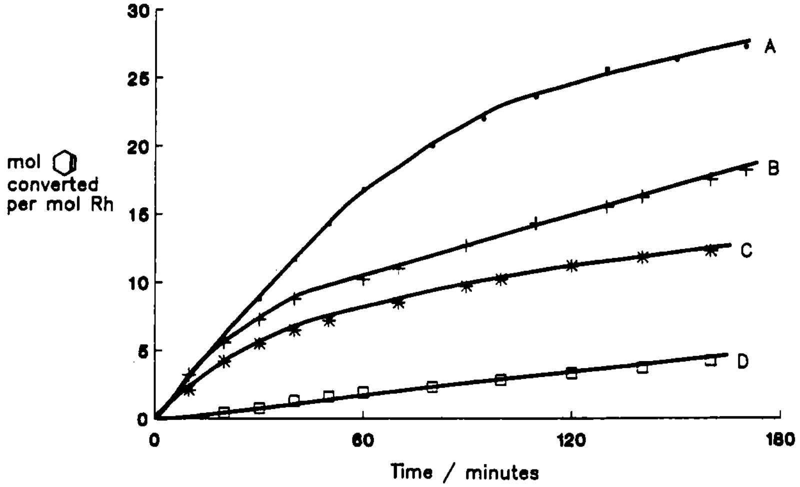
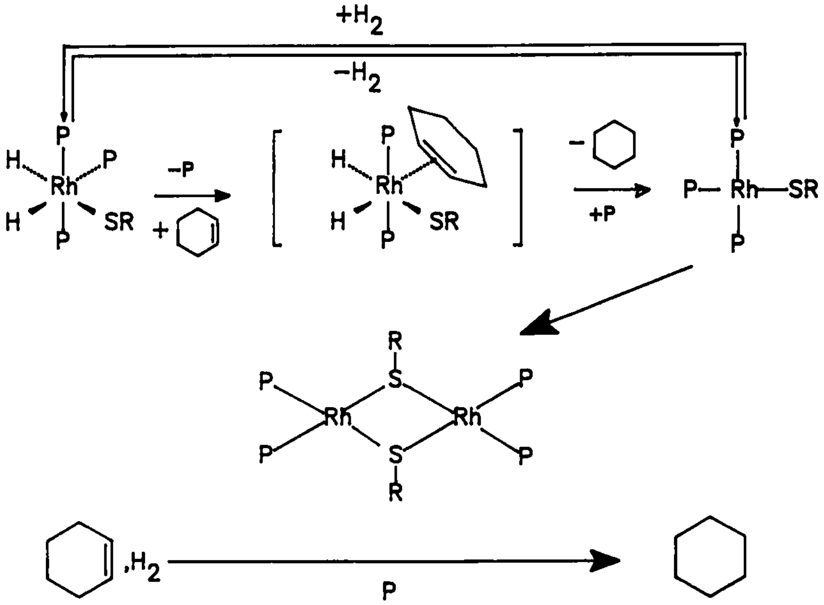


Figure 1. Cyclohexene hydrogenation (20% solution in toluene, 20°C, 1 atm.H$_2$) catalysed by a mixture of [RhH(PPh$_3$)$_4$] (0.01 M) and (A) C$_6$F$_5$SH, (B) Pr^{i}SH, (C) CH$_3$(CH$_2$)$_{11}$SH, (0.03 to 0.05 M each) and by a mixture of [Rh$_2$(μ–SPr^i)$_2$(PPh$_3$)$_4$] (0.005 M) and PPh$_3$ (0.02 M), (D).



Scheme 1

ACKNOWLEDGEMENTS

I thank Ms R.Weber and Mr.J.Wollbrandt for gas chromatographic analyses and the University of the Witwatersrand for financial support.

REFERENCES

1. P. Kalck, R. Poilblanc, R.P. Martin, A. Rovera and A. Gaset, *J. Organomet. Chem.*, **195**, C9 (1980).
2. L. Carlton and Z. Bulbulia, *J. Organomet. Chem.*, **389**, 139 (1990).