Inorganica Chimica Acta, 42 (1980) 33–36
©Elsevier Sequoia S.A., Lausanne – Printed in Switzerland

Tetrakis(triphenylphosphine)trihydridoruthenium(II) Cation, $(P\phi_3)_4RuH_3^+$, its Formation, Spectroscopic Characterization and Chemical Reactivity

J. M. TOWARNICKY[†] and E. P. SCHRAM*

Evans Chemical Laboratory, The Ohio State University, Columbus, Ohio 43210, U.S.A.

Received February 12, 1980

Treatment of $(\phi_3P)_4RuH_2$ *with* 1,4-$Cl_2Si_4\phi_8$, *under specific reaction conditions, affords* $[(\phi_3P)_3RuHCl]_2$, H_2 *and* 1,8-$Cl_2Si_8\phi_{16}$, *whereas slightly different conditions (varying the amount of* NEt_3 *present in the system) affords a solution which is stable towards* H_2 *evolution.* ^{31}P *and* ^1H *NMR data have been obtained on the latter solution and are interpreted to indicate the presence of* $(\phi_3P)_4RuH_3^+$ *and* $[(\phi_3P)_3RuHCl]_2$. *A possible reaction sequence is discussed which is consistent with the necessity for the presence of* NEt_3 *in the reaction system, and also explains the formation and subsequent decomposition of several reaction intermediates.*

Introduction

We have previously reported the preparation and reactivity of the dimeric complex, $[(\phi_3P)_3RuHCl]_2$, (I), by treatment of $(\phi_3P)_4RuH_2$, (II), with 1,4-dichlorooctaphenyltetrasilane, $Cl_2Si_4\phi_8$, (III), in the presence of triethylamine [1]. This reaction is accompanied by rapid evolution of one half of the hydrido hydrogen, originally present as $(\phi_3P)_4RuH_2$, and formation of 1,8-dichlorohexadecaphenyloctasilane, $Cl_2Si_8\phi_{16}$, in high yield [2]. Under slightly different reaction conditions (decreased NEt_3/Ru) we have found possible to prevent initial H_2 evolution and thereby have been able to investigate the nature of ruthenium species in solution by ^1H and ^{31}P NMR spectroscopy.

Results and Discussion

Treatment of a benzene solution of $(\phi_3P)_4RuH_2$, (II), with a benzene solution of $Cl_2Si_4\phi_8$, (III), in the presence of NEt_3 (NEt_3/Ru ~ 2.5) affords a clear red solution without H_2 evolution. Freeze drying of this solution at 0 °C results in quantitative recovery of NEt_3. When the resulting reaction residue is dissolved in either benzene of THF, 100% of the hydrido hydrogen originally associated with (II) is evolved as H_2. This result is in contrast to the behavior of the reaction residue when toluene is employed as the solvent. In the latter case 50% of the original hydrido hydrogen is evolved as H_2 and (I) is recovered in near quantitative yield. It has previously been demonstrated that in solution (I) will evolve 100% of its hydrido hydrogen as H_2 and that (I) is stable (insoluble) in the presence of toluene [1]. These results indicated the species responsible for H_2 evolution in toluene is not (I), therefore NMR spectroscopic data was obtained on the original reaction solution in the presence of NEt_3, *i.e.*, the condition under which no H_2 is evolved.

^1H NMR Spectroscopy

The ^1H NMR spectrum on the initial clear red reaction solution is reproduced in Fig. 1 and consists of two high field absorptions, a broad singlet at 17.9 τ and a quartet centered at 27 τ, J_{PH} 26 Hz, in the ratio 3:1 respectively. (In addition low field signals, due to ϕ and NEt_3, are observed). The absence, in solution, of unreacted (II) is assured based on the fact that (II) has been demonstrated to exhibit a quartet centered at 19.7 τ [3], J_{PH} 40 Hz, also, it is unlikely that NEt_3 has entered into the coordination sphere of Ru. For example, the ^1H NMR spectrum of $Py(P\phi_3P)_3RuH_2$ has been shown to exhibit two high field multiplets centered at 8.7 and 16.8 τ [3]. The absence of similar multiplets in the ^1H NMR spectrum under discussion is therefore consistent with the absence of a stable NEt_3-ruthenium complex. The presence of $[(\phi_3P)_3RuHCl]_2$, (I), in solution is indicated by the quartet centered at 27 τ [1] as well as the ^{31}P NMR data to be subsequently discussed.

Concerning the assignment of the broad singlet at 17.9 τ, this species must contain three times as many hydrido hydrogen as (I), or be the result of more than one species with coincidental chemical shifts. The simplicity of the ^{31}P NMR spectrum is consistent with the presence of a single ruthenium

---

*Author to whom correspondence should be addressed.

[†] In partial fulfillment of the Ph.D. degree, The Ohio State University, 1979.

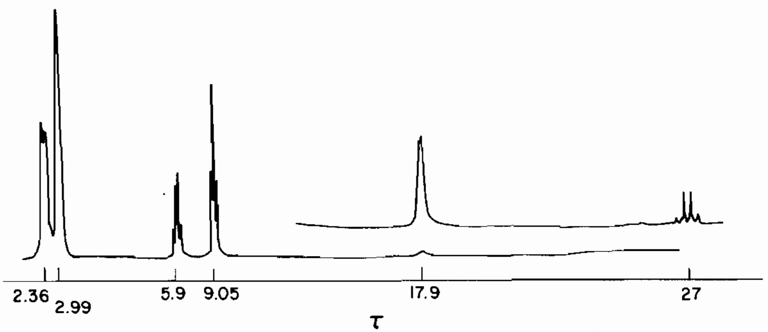

Fig. 1. ^1H NMR spectrum of $[(P\phi_3)_3RuHCl]_2$ and $(P\phi_3)_4RuH_3^+$ in the presence of $P\phi_3$, $ClSi_4\phi_8^-$ and $P\phi_3$.

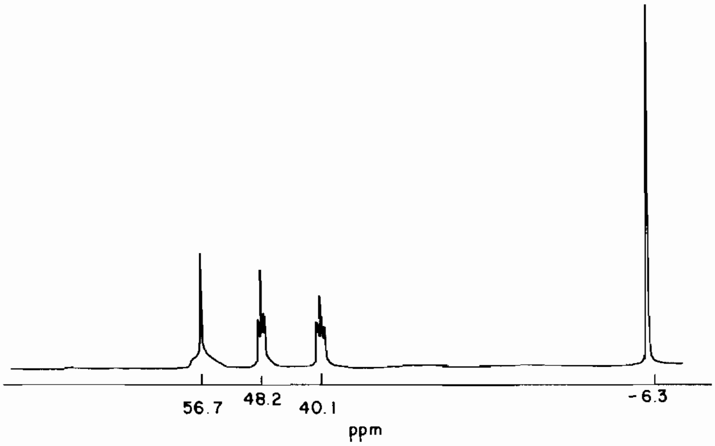

Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of $P\phi_3$, $[(P\phi_3)_3RuHCl]_2$ and $(P\phi_3)_4RuH_3^+$.

complex with three hydrido ligands. With regard to the nature of this latter species, multi hydrido complexes such as $(\phi_3P)_3RuH_4$, 17.1 τ [4], and $(\phi_3P)_3RuH_3SiEtMe_2$ [5–7], 19.4 τ, exhibit unresolved broad ^1H absorptions at the indicated chemical shifts. Furthermore, Wilkinson has described the preparation of what he believes to be $(P\phi_3)_3RuH_3^+$, and observed its decomposition in covalent solvents affording H_2 [8]. However, no NMR data were reported for this cation most likely because of rapid H_2 evolution.

^{31}P NMR Spectroscopy

The $^{31}P\{^1H\}$ NMR spectrum of the initial reaction solution is reproduced in Fig. 2. The high field absorption at –6.3 ppm is assigned to free $P\phi_3$ while the absorption at 56.3 ppm is assigned to $[(\phi_3P)_3RuHCl]_2$ [1]. The A_2X_2 pattern centered at 48.2 and 40.1 ppm, $J_{PP} = 13$ Hz, is similar to that observed for $(\phi_3P)_4RuH_2$, (II), at 48.8 and 40.5 ppm, $J_{PP} = 15$ Hz [3]. However, the absence of (II) is assured based on the absence of the ^1H quartet associated with (II) centered at –9.7 τ, $J_{PH} = 40$ Hz [4]. The observed ^{31}P A_2X_2 pattern is consistent with the presence of two magnetically equivalent pairs of $P\phi_3$ ligands while the integrated ^1H NMR data indicate three hydrido ligands, *i.e.*, consistent with the suggested stoichiometry $[(P\phi_3)_4RuH_3]^+$. This trihydrido cation differs from that reported by Wilkinson in that the latter involves three $P\phi_3$ ligands, a 16 electron complex, while $(P\phi_3)_4RuH_3^+$ is an 18 electron species.

Suggested Mechanism for the Reaction of $(P\phi_3)_4RuH_2$ with $Cl_2Si_4\phi_8$

Treatment of $(P\phi_3)_4RuH_2$ with $Cl_2Si_4\phi_8$ results in either 50% hydrido H_2 evolution (NEt_3/Ru ~ 12, system A) or no H_2 evolution (NEt_3/Ru ~ 2.5, system B). With regard to system A, $[(P\phi_3)_3RuHCl]_2$ may be recovered in near quantitative yield and subsequent solution in ϕH or THF affords the other 50% hydrido hydrogen as H_2 [1]. With regard to system B, treatment with toluene, ($[(P\phi_3)_3RuHCl]_2$ is insoluble in toluene) results in the evolution of 50% of the hydrido hydrogen as H_2, while solution in benzene or THF afford 100% yield of hydrido H_2 and isolation of $P\phi_3$, $Cl_2Si_8\phi_{16}$, and $[(P\phi_3)_3RuCl]_x$. These chemical facts are consistent with the chemical reactions represented by eqns. 1–8.

$$(P\phi_3)_4RuH_2 + NEt_3 \xrightarrow{\text{benzene}} (P\phi_3)_3RuH_2\cdots NEt_3 + P\phi_3 \tag{1}$$

$$P(\phi_3)_3RuH_2\cdots NEt_3 + Cl_2Si_4\phi_8 \longrightarrow (P\phi_3)_3RuHCl\cdots NEt_3 + HSi_4\phi_8Cl \tag{2}$$

$$(P\phi_3)_3RuHCl\cdots NEt_3 \longrightarrow \tfrac{1}{2}[P\phi_3RuHCl]_2 + NEt_3 \tag{3}$$

$$(P\phi_3)_4RuH_2 + HSi_4\phi_8Cl \longrightarrow (P\phi_3)_4RuH_3^+Si_4\phi_8Cl^- \tag{4}$$

$$Si_4\phi_8Cl^- + Cl_2Si_4\phi_8 \longrightarrow Cl^- + Cl_2Si_8\phi_{16} \tag{5}$$

$$(P\phi_3)_4RuH_3^+ + Cl^- \xrightarrow{NEt_3} P\phi_3 + H_2 + (P\phi_3)_3RuHCl\cdots NEt_3 \tag{6}$$

$$(P\phi_3)_3HCl\cdots NEt_3 \longrightarrow \tfrac{1}{2}[(P\phi_3)_3RuHCl]_2 + NEt_3 \tag{7}$$

$$[(P\phi_3)_3RuHCl]_2 \longrightarrow [(P\phi_3)_3RuCl]_x + H_2 \tag{8}$$

Equation 1 represents the amine assisted $P\phi_3$ dissociation followed by eqn. 2 which involves $RuH\cdots ClSi$ exchange perhaps facilitated by increased hydrido character as the results of a weak N–Ru interaction; there is no NMR evidence for a stable Ru–N complex. The hydrido silane product, eqn. 2, is invisioned to 'protonate' $(P\phi_3)_4RuH_2$, eqn. 4, affording a trihydro complex, *i.e.* similar to that suggested by Wilkinson, to produce $(P\phi_3)_3RuH_3^+$ [8], while eqn. 3, represents dimerization of $(P\phi_3)_3RuHCl$ in the presence of $NEt_3\cdots$conditions similar to those reported for the formation of the dimer, $[(P\phi_3)_2RuCl_2]_2$ [9]. The formation of $Cl_2Si_8\phi_{16}$ is suggested to involve anionic nucleophilic attack on $Cl_2Si_4\phi_8$ with Cl^- displacement, eqn. 5, and subsequent decomposition of the bulky cation, $(P\phi_3)_4RuH_3^+$, as the result of loss of the large stabilizing anion, $ClSi_4\phi_8^-$, eqn. 6. This latter decomposition affords $P\phi_3$, H_2 and is accompanied by dimerization of $(P\phi_3)_3RuHCl$, eqn. 7, or decomposition affording additional H_2, eqn. 8, – the reaction observed, with regard to these latter two paths, depends on the solvent employed.

Specific reactions associated with the suggested mechanism are now under investigation and the results will be reported in the near future.

Experimental

The procedures followed and the preparations of starting materials have been previously outlined [1].

Reaction of $(P\phi_3)_4RuH_2$ with $Cl_2Si_4\phi_8$

A typical reaction consists of treating a stirred suspension of 2.47 g of $(Ph_3P)_4RuH_2$ (2.14 mmol), in 100 mL benzene, and 5.2 mmol Et_3N (manometrically measured), with a solution of 1.83 g of $Cl_2Si_4Ph_8$ (2.29 mmol) in 60 mL of benzene. The reaction takes *ca.* 2h to complete as evidenced by the total solution of the reactants to give a clear deep red solution. After 36 h of stirring at 25 °C the clear solution was filtered to leave only a trace of heterogeneous white and black solid on the first (0.025 g). All reported NMR data were obtained on solutions prepared in this manner. For this described reaction mixture, NEt_3 was subsequently recovered quantitatively by freeze drying, and treating the volatile materials, benzene and NEt_3, with HCl to afford $Et_3NH^+Cl^-$, 0.71 g (5.2 mmol).

The above reaction residue was demonstrated to be 'homogenious' with regard to providing subsequent solid aliquots for investigation, by analytical analysis. Calcd., based on quantities of initial reagents, and found ( ): C, 73.78 (73.66); H, 5.24 (5.23); Cl, 3.78 (3.79); P, 6.17 (6.34); Si, 5.99 (6.03); Ru by difference, 5.03 (4.95).

Decomposition of $(P\phi_3)_4RuH_3^+$ and $[(P\phi_3)_3RuHCl]$

In benzene – A 0.3 g [0.15 mmol initial $[(P\phi_3)_4RuH_2]$ sample of the reaction mixture prepared above was dissolved in benzene to afford 0.15 mmol H_2 at 25 °C over a period of several days. After a period of several weeks no additional H_2 was obtained. *In toluene* – A 0.58 g [0.29 mmol initial $(P\phi_3)_4RuH_2]$ sample of the reaction mixture was treated with 35 mL toluene at 27 °C for 12 hrs to afford 0.14 mmol H_2 and $[(P\phi_3)_3RuHCl]_2$, 0.258 g (0.28 mmol monomer), 96% yield. An extended contact time of 48 hr produced no additional H_2.

Acknowledgement

Support of this work by The Ohio State University is appreciated.

References

1 J. M. Towarnicky and E. P. Schram, *Inorganica Chimica Acta, 41,* 55 (1980).

2 J. M. Towarnicky and E. P. Schram, *Inorganica Chimica Acta, 44,* L305 (1980).
3 S. Komiga and A. Yamamoto, *J. Molecular Catalysis, 5,* 279 (1979).
4 R. O. Harris, N. K. Hota, L. Sadavoy, and J. M. Yuen, *J. Organomet. Chem., 54,* 259 (1973).
5 H. Kono and Y. Nagai, *Chem. Lett. Jap.,* 931 (1974).
6 H. Kono, N. Wakao and K. Ito, *J. Organomet. Chem., 132,* 53 (1977).
7 H. Matsumoto, T. Nakano, Y. Nagai, and H. Kono, *Bull. Chem. Soc. Jap., 51,* 2445 (1978).
8 R. J. Young and G. Wilkinson, *J. Chem. Soc., Dalton,* 719 (1976).
9 R. C. J. Vriends, G. Van Koten and W. Vrieze, *Inorg. Chim. Acta, 26,* L29 (1978).