

Hydrido-Ditertiary Phosphine, -Arsine, and -Chiral Phosphine Complexes of Ruthenium(II)

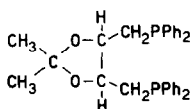
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Introduction

We reported recently on the synthesis of ruthenium(II) chiral phosphine complexes, and their use as hydrogenation catalysts.¹ Of interest, the diop ligand gave a dimeric species $\text{Ru}_2\text{Cl}_4(\text{diop})_3$ containing five-coordinate Ru(II) with a bridging diop ligand, instead of the expected $\text{RuCl}_2(\text{diop})_2$ complex.



Bressan and Rigo² simultaneously reported on the synthesis of a corresponding compound $\text{Ru}_2\text{Cl}_4(\text{dpb})_3$ where $\text{dpb} = \text{Ph}_2\text{P}(\text{CH}_2)_4\text{PPh}_2$. Presumably diop and dpb with four carbon atoms between the P donors cannot give rise to the usual d^6 octahedral $\text{RuX}_2(\text{diphosphine})_2$ because of steric problems. Extension of our work to synthesis of hydrido derivatives has led to isolation of five-coordinate $[\text{HRu}(\text{diop})_2]^+\text{Cl}^-$, and a range of new *trans*- $\text{HRuCl}(\text{diphosphine})_2$ complexes and some arsine analogues.

Chatt and Hayter³ prepared *trans*- $\text{HRuCl}(\text{dpm})_2$, $\text{dpm} = \text{Ph}_2\text{PCH}_2\text{PPh}_2$, by reaction of *cis*- $\text{RuCl}_2(\text{dpm})_2$ with LiAlH_4 , although *trans*- $\text{RuCl}_2(\text{dpe})_2$ did not react to give a hydride. Our method involves a ligand exchange reaction with $\text{HRuCl}(\text{PPh}_3)_3$,⁴ and is similar to the method used^{1,2,5,6} to prepare various dichloro-ruthenium(II) phosphine complexes [such as $\text{RuCl}_2(\text{diphosphine})_2$, where diphosphine = dpm, dpe, dpp] from $\text{RuCl}_2(\text{PPh}_3)_3$.

The hydride complexes have been characterized by elemental analysis, i.e., and ^1H and ^{31}P n.m.r. The recent report of another group⁶ which duplicated some of our published¹ and unpublished work prompts us to report our synthetic studies, while our work^{1,7} on the catalytic properties of the hydrides continues.

Experimental and Discussion

The $\text{HRuCl}(\text{chelate})_2$ complexes were made by refluxing a hexane suspension of the N,N-dimethyl-

acetamide solvate,⁴ $\text{HRuCl}(\text{PPh}_3)_3 \cdot \text{DMA}$, with the chelating ligands under nitrogen. The *trans*- $\text{HRuCl}[\text{Ph}_2\text{P}(\text{CH}_2)_n\text{PPh}_2]_2$ complexes, $n = 2, 3, 4$, were obtained as pure yellow compounds with typical Ru–H stretching frequencies (see Table). The metal–hydride ^1H n.m.r. spectra consist of a high-field 1:4:6:4:1 quintet pattern, consistent with coupling to four equivalent phosphorus atoms in *trans*-complexes, and the single peak in the proton-decoupled ^{31}P n.m.r. spectra is similarly consistent with four equivalent, non-exchanging phosphorus nuclei. The significant differences in the phosphorus chemical shifts of the dpp and dpe complexes have been noted previously, for example, with the *trans*- $\text{RuCl}_2(\text{dpp})_2$ and $-\text{RuCl}_2(\text{dpe})_2$ complexes.⁶ The $\text{HRuCl}(\text{dpb})_2$ complex, which rapidly decomposes in CDCl_3 to form $\text{Ru}_2\text{Cl}_4(\text{dpb})_3$, is clearly a *trans*-octahedral species and the steric restrictions of the dpb ligand cannot be as severe as in the dichloro complex. The hydrido-acetate complexes $\text{HRu}(\text{O}_2\text{CCH}_3)(\text{dpe})_2$ and $\text{HRu}(\text{O}_2\text{CCH}_3)(\text{dpp})_2$ were recently mentioned,⁶ but their low solubility precluded n.m.r. studies.

Our most interesting finding comes from n.m.r. data on the yellow hydrido-diop complex which, although analyzing for $\text{HRuCl}(\text{diop})_2$, is an ionic species containing five-coordinate Ru(II) with an associated chloride anion. The high-field ^1H n.m.r. shows seven equally-spaced bands with intensities roughly in the ratios 1:2:3:4:3:2:1, and is consistent with a trigonal-bipyramid cation in which the proton couples to two equivalent equatorial phosphorus nuclei ($J_{\text{PH}} = 28.8$ Hz) and to two equivalent axial phosphorus atoms ($J_{\text{PH}} = 14.2$ Hz). Such an assignment is supported by the proton-decoupled ^{31}P n.m.r. spectrum which shows the expected symmetrical A_2B_2 pattern [$J_{\text{PP}} = 40$ Hz]. Further support for unsaturated character comes from the reaction of the hydride, in the solid state or solution, with carbon monoxide ($\text{Ru}:\text{CO} = 1:1$) to give $[\text{HRu}(\text{CO})(\text{diop})_2]^+\text{Cl}^-$. The corresponding complex containing the ligand, $\text{Et}_2\text{PCH}_2\text{CH}_2\text{PEt}_2$, has been reported by Mays and coworkers.⁸ The ionic hydrides were found to be conducting in nitromethane.

The yellow ditertiary arsine complex $\text{HRuCl}[\text{Ph}_2\text{As}(\text{CH}_2)_2\text{AsPh}_2]_2$ is likely to have a *trans*-configuration. Of interest, the $\text{Ph}_2\text{AsCH}_2\text{AsPh}_2$ ligand, and ethylenediamine, replace only one triphenylphosphine from the $\text{HRuCl}(\text{PPh}_3)_3$ complex, and the ^1H n.m.r. triplets [$J_{\text{PH}} \sim 25$ Hz] indicate *cis*-phosphines in *trans*- $\text{HRuCl}(\text{PPh}_3)_2(\text{chelate})$ complexes.⁹ Wilkinson's group⁹ have similarly synthesized a *trans*- $\text{HRuCl}(\text{PPh}_3)_2(\text{bipyridine})$ complex.

Of all the hydrides studied, only the $[\text{HRu}(\text{diop})_2]^+\text{Cl}^-$ complex is effective in solution for

TABLE. N.M.R. and I.R. Data for the Ruthenium(II) Hydride Complexes.^a

Complex	I.R., cm^{-1} $\nu(\text{Ru}-\text{H})$	¹ H N.M.R. ^b		³¹ P N.M.R. ^f (ppm)
		$\tau(\text{Ru}-\text{H})$	$J_{\text{PH}}(\text{cis})$	
HRuCl(dpb) ₂	2030	28.8 (quintet) ^c	21.2 Hz ^c	—
HRuCl(dpp) ₂	2000	27.95 (quintet)	19.5 Hz	15.59 (singlet)
HRuCl(dpe) ₂	2060	29.24 (quintet)	20.0 Hz	60.8 (singlet)
[HRu(diop) ₂] ⁺ Cl ⁻	2010	28.7 (septet)	28.8 Hz ^d 14.2 Hz ^e	1.0, 19.54 (triplets) ($J_{\text{PP}} = 40$ Hz)
HRuCl[Ph ₂ As(CH ₂) ₂ AsPh ₂]	1960	31.32 (singlet)	—	—
HRuCl(PPh ₃) ₂ (Ph ₂ AsCH ₂ AsPh ₂)	1960	26.00 (triplet)	23.0 Hz	—
HRuCl(PPh ₃) ₂ (NH ₂ CH ₂ CH ₂ NH ₂)	1985	28.22 (triplet)	26.0 Hz	—

^a All the complexes gave microanalytical data in excellent agreement with theory.^c In C₆D₆ at 30 °C.^d Coupling to equatorial P.^e Coupling to axial P.^b In CDCl₃ at 30 °C unless stated otherwise.^f In CDCl₃, relative to 85% aq. H₃PO₄.

catalytic hydrogenation of olefins under mild conditions, likely because the complex is coordinatively unsaturated. The hydride is probably the active catalyst in the previously reported asymmetric hydrogenations using the Ru₂Cl₄(diop)₃ complex,¹ and similar high optical purities have been obtained using the hydride under corresponding conditions.

Acknowledgements

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