*Journal of Organometallic Chemistry*, 117 (1976) C113—C115

**Preliminary communication**

# CATIONIC HYDRIDO-OLEFIN COMPLEXES OF RUTHENIUM(II). THE CRYSTAL STRUCTURE OF HYDRIDO(1,3-BUTADIENE)TRIS-(DIMETHYLPHENYLPHOSPHINE)RUTHENIUM(II) HEXAFLUOROPHOSPHATE

T.V. ASHWORTH, ERIC SINGLETON*
*National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria, 0001 (Republic of South Africa)*
and M. LAING*
*Chemistry Department, University of Natal, Durban 4001 (Republic of South Africa)*
(Received June 24th, 1976)

## Summary

A route to the stable hydrido-diene salts [(diene)$RuHL_3$]$PF_6$, (diene = cycloocta-1,5-diene, hexa-1,3-diene and buta-1,3-diene, L = $PMe_2Ph$; diene = cycloocta-1,5-diene, L = $P(OMe)_3$, $P(OCH_2)_3CMe$ $P(OMe)Ph_2$ and $PMePh_2$) has been found and the structure of [$RuH(C_4H_6)(PMe_2Ph)_3$]$PF_6$ has been determined by X-ray diffraction.

Though hydrido-olefin complexes are known to be intermediates in hydrogenation [1] and isomerisation [2] reactions very few have been characterized and only one [3] has been elucidated structurally. Attempts to react hydridoruthenium(II) phosphine complexes with dienes has given only unstable products [4] and, as yet, no hydrido-olefin compounds containing tertiary phosphine ligands have been fully characterized. During our studies on cationic ruthenium(II) systems [5] we have synthesized hydrido-dieneruthenium(II) salts containing tertiary phosphorus groups by methods, which, from our initial investigations, may provide general routes to a range of characterizable complexes.

We have recently prepared the hexafluorophosphate salt [$CODRuH(NH_2$-$NMe_2)_3$]$PF_6$ (I) from [$CODRuCl_2$]$_x$, ($x > 2$, COD = cycloocta-1,5-diene) and $NH_2NMe_2$ in methanol/water mixtures containing $NH_4PF_6$ and found that I reacts with three molar equivalents of L [L = $P(OMe)_3$, $P(OCH_2)_3CMe$, $P(OMe)Ph_2$, $PMe_2Ph$ and $PMePh_2$] in degassed methanol to give the complexes [$CODRuHL_3$]$PF_6$ (II) in high yield. The diene ligand in II, (L = $PMe_2Ph$), is readily replaced and this lability has been used to extend the

---

*To whom correspondence should be addressed.

range of hydrido-diene complexes. Thus treatment of II, (L = $PMe_2Ph$) with an excess of conjugated diolefin in warm methanol produced the salts $[(diene)RuH(PMe_2Ph)_3]PF_6$ (III), (diene = hexa-1,3-diene and buta-1,3-diene).

The complexes are crystalline and stable in degassed solvents and were characterized by IR, microanalytical and $^1H$ NMR measurements. The doublet of triplets observed for the hydride resonances in the $^1H$ NMR spectra of II [L = $P(OMe)_3$ and $P(OCH_2)_3CMe$] is consistent with a facial arrangement of phosphite ligands. The labile nature in solution of III and the other compounds II produced broad unresolved resonances with no $^1H$—$^{31}P$ or $^{31}P$—$^{31}P$ coupling and no stereochemical assignments were possible. The presence of a hydride ligand in III, (diene = buta-1,3-diene) could not be detected from either IR or $^1H$ NMR evidence. It was thus decided to determine the X-ray crystal structure of this particular complex with the aims of discovering (i) its precise formulation and (ii) the arrangement of the phosphine ligands to see if the lability in solution is a consequence of interligand contacts.

$[RuH(C_4H_6)(PMe_2Ph)_3]PF_6$ forms well shaped yellow monoclinic crystals, space group $P2_1/n$, $a = 17.85$, $b = 18.96$, $c = 10.31$ Å, $\beta = 106.1°$, $Z = 4$. Intensity data were collected on a Phillips four-circle diffractometer with graphite-monochromated Mo$K_\alpha$ radiation ($\lambda = 0.7107$ Å). The $RuP_3$ moiety was located from a Patterson map, and all remaining atoms were found in the subsequent Fourier maps. The structure was refined [6] by the block diagonal least squares method to $R = 0.070$ for the 2429 observed data. The crystals contained approximately half a molecule of $CH_2Cl_2$ solvent per asymmetric unit.

The ruthenium atom has a distorted octahedral coordination geometry with the six sites occupied by the three P atoms of the phosphine ligands, Ru—P = 2.28, 2.32 and 2.34 Å, the two "double bonds" of the butadiene molecule and a vacant site which must contain the hydride ligand (Fig. 1). The phosphine ligands have a facial configuration and the four Ru—C lengths for the butadiene group lie between 2.14 and 2.38 Å. The trend of long-short-long C—C bonds, (1.48, 1.34 and 1.43 Å), the systematic alteration of the C atoms above and below their mean plane and the reduction of the C—C—C angles

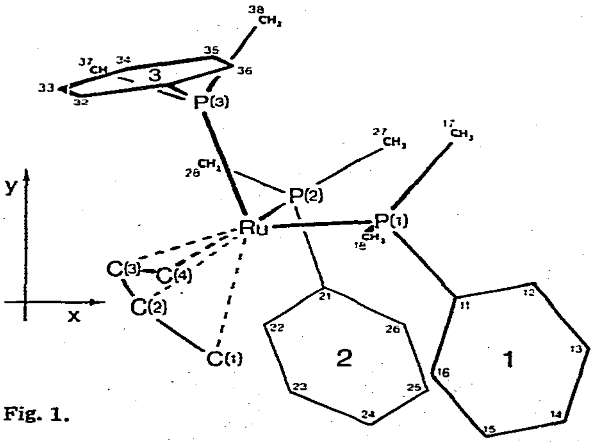

Fig. 1.

to 118 and 119° within the butadiene ligand has been observed in other butadiene metal complexes [3,7].

It is evident from this structure that the *fac* isomer is only favoured because of the excessive strain that would result from contacts between atoms of the butadiene group and the two *trans* phosphine ligands in the *mer* isomer. In fact a *fac* configuration of phosphites was obtained even with the smallest ligand $P(OCH_2)_3CMe$ and hence we assign this stereochemistry to all the other diene-hydrides prepared here. It is interesting to note that for larger ligands the interligand repulsions would prevent formation of even the *fac* isomer and this probably accounts for the inability to characterize hydridodieneruthenium(II) complexes with such ligands as $PPh_3$ [4].

It has also become apparent from the short interligand contacts in several ruthenium(II) complexes containing three [8], four [9] and five [10] $PMe_2Ph$ ligands that four or five of these phosphines in the coordination sphere causes excessive intramolecular strain. This may explain our failure to date to isolate π-allyl species from $[RuH(PMe_2Ph)_4(MeOH)]^+$ [11] as the diene-hydride structure containing three $PMe_2Ph$ groups is sterically favoured over a π-allyl complex containing four $PMe_2Ph$ ligands.

## References

1 R.E. Hanson, S.K. Gupta and D.J. Brown, Chem. Rev., 73 (1973) 21.
2 R.F. Heck, Organotransition Metal Chemistry, Academic Press, New York and London, (1974) 76.
3 G. Del Piero, G. Perego and M. Cesari, Gazz. Chim. Ital., 105 (1975) 529.
4 J.R. Sanders, J. Chem. Soc. Dalton, (1973) 743; P.S. Hallman, B.R. McGarvey and G. Wilkinson, J. Chem. Soc. A, (1968) 3143.
5 T.V. Ashworth and E. Singleton, J. Organometal. Chem., 77 (1974) C31.
6 M. Laing, Acta Crystallogr., B28 (1972) 986.
7 G. Huttner, D. Neugebauer and A. Razavi, Angew. Chem. Int. Edit. Engl., 14 (1975) 352.
8 M. Laing and L. Pope, Acta Crystallogr., B32 (1976) in press.
9 T.V. Ashworth, M.J. Nolte and E. Singleton, J. Chem. Soc. Dalton, (1976) accepted for publication.
10 T.V. Ashworth, M. Laing, M.J. Nolte and E. Singleton, in preparation.
11 T.V. Ashworth and E. Singleton, J. Chem. Soc. Chem. Commun., submitted for publication.