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# Preparation of Polyhydride Complexes of Ruthenium by Direct Hydrogenation of Zerovalent Olefinic Derivatives. Dinuclear Complexes of General Formula $Ru_2H_6L_4$ and $Ru_2H_4N_2L_4$. X-ray Crystal Structure of $Ru_2H_4N_2(PPh_3)_4$

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The room-temperature hydrogenation of $Ru(styrene)_2(PPh_3)_2$ in hexane produces a mixture of the mono- and dinuclear complexes $RuH_6(PPh_3)_2$ and $Ru_2H_6(PPh_3)_4$ as identified by $^1H$ and $^{31}P$ NMR spectroscopy. Recrystallization of the mixture under $N_2$ affords $Ru_2H_4N_2(PPh_3)_4$ as red crystals. The crystals are monoclinic of space group $P2_1/n$ with $a$ = 14.7968 (21) Å, $b$ = 20.8167 (20) Å, $c$ = 21.4421 (21) Å, $\beta$ = 96.5791 (13)°, $U$ = 6561.1 Å$^3$, $D_{calcd}$ = 1.30 g·cm$^{-3}$, and $Z$ = 4. The structure was refined by using 2541 reflections with $F > 6\sigma$ to a final $R$ value of 0.083. The short metal–metal distance (2.553 (5) Å) is compatible with the existence of a triple metal–metal bond. The number, position, and spectroscopic properties of the hydride ligands are discussed.

## Introduction

Polynuclear polyhydrides are presently attracting considerable interest. Thus, if the chemistry of carbonyl polynuclear compounds is well documented, much less is known on carbonyl-free polynuclear species and particularly polyhydrides. Two systems (containing Re and Rh, respectively) have been extensively studied so far. The studies on rhenium follow the characterization of the "agnohydride"[1] shown to be $Re_2H_8L_4$,[2] a remarkable symmetrical species containing four bridging hydrides and a triple metal–metal bond. Numerous papers described its reactivity toward organic halides,[3] nitriles,[4] alkyl isocyanides,[4] and phosphites[5] to give the triply hydrido-bridged unsymmetrical complex $Re_2H_4(PMe_2Ph)_4[P(OCH_2)_3CEt]_2$. Another trihydro-bridged species was obtained by photolysis of $ReH_5[P(Me_2Ph)_3]_3$.[6] $Re_2H_8L_4$ was also shown to react with $[Cu(MeCN)_4]PF_6$ to give the mixed-hydrido cluster $[Re_4Cu_2H_{16}L_6](PF_6)_2$.[7] Finally, $Re_2H_8(PPh_3)_4$ can be oxidized reversibly to the isolable salt $[Re_2H_8(PPh_3)_4]PF_6$,[8] and substitution reactions have been carried out on the paramagnetic species.[8,9]

The rhodium system has been studied in order to obtain unsaturated clusters as models for surface chemistry. This includes the preparation of $Rh_2H_2[P(O\text{-}i\text{-}Pr)_3]_4$[10] and its characterization as a dihydro-bridged species[11] as well as its reactivity toward CO[12] and its reaction with molecular hydrogen to give a complex containing one terminal and three bridging hydrides.[13]

**Table I. Fractional Coordinates and Potential Energy of the Hydrido H Atoms Located by Molecular Mechanics[a,24]**

| | $x$ | $y$ | $z$ | PE, kcal·mol$^{-1}$ |
|---|---|---|---|---|
| H(1) (terminal) | 0.6448 | 0.2943 | 0.4122 | 0.27 |
| H(2) (bridged) | 0.5402 | 0.3645 | 0.3711 | 1.38 |
| H(3) (bridged) | 0.4937 | 0.2603 | 0.3642 | 0.79 |
| H(4) (bridged) | 0.5221 | 0.3188 | 0.2661 | 1.47 |

[a] In the calculations the hydrogen atoms of the phenyl groups have been included but relocated so that the C–H distance is 1.08 Å. Potential functions: from ref 30 for Ru–H, N–H, C–H, and H–H; from ref 31 for P–H. Mean metal–hydrogen bond lengths used: Ru–H(terminal) = 1.65 Å from ref 15 and Ru–H(bridged) = 1.89 Å.

Recently, a dinuclear osmium complex containing three bridging hydrides and a metal–metal triple bond has been reported.[14] As far as ruthenium is concerned, only two polyhydrido-bridged complexes were known prior to this work, i.e., $Ru_2H_4(PMe_3)_6$,[15] containing two bridging hydrides and $[Ru_2(\mu\text{-}H)_3(PMe_3)_6]BF_4$[15] in which the two ruthenium atoms are separated by a distance of 2.540 Å.

We were interested in preparing such species, and we wanted to compare their reactivity (i) with that of rhenium hydrides and (ii) with that of the well-known carbonyl clusters of ruthenium (the preparation of clusters from these reactions was not ruled out since hydride clusters of rhodium,[16] iridium,[17] and platinum[18] had been obtained by similar ways). As we had noticed that in solution some mononuclear polyhydrides of ruthenium led to red polynuclear species,[19] we decided to prepare directly such compounds. We used a similar method for the preparation of mononuclear complexes with $Ru(styrene)_2(PPh_3)_2$[20] as the starting material. Preliminary accounts for this work have been published.[21]

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**Table II. Fractional Atomic Coordinates and Isotropic of Equivalent Temperature Factors (Å$^2$ × 100) with Esd's in Parentheses**

| atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}/U_{iso}$ | atom | $x/a$ | $y/b$ | $z/c$ | $U_{eq}/U_{iso}$ |
|---|---|---|---|---|---|---|---|---|---|
| Ru(1) | 0.6010 (2) | 0.2949 (2) | 0.3377 (2) | 3.0 (3) | C(34) | 0.980 (2) | 0.183 (1) | 0.3497 (9) | 7 (2) |
| Ru(2) | 0.4354 (2) | 0.3318 (2) | 0.3229 (2) | 2.9 (2) | C(35) | 0.926 (2) | 0.157 (1) | 0.3929 (9) | 6 (1) |
| P(1) | 0.7052 (7) | 0.3617 (5) | 0.3095 (5) | 2.9 (8) | C(36) | 0.831 (2) | 0.160 (1) | 0.3811 (9) | 4 (1) |
| P(2) | 0.6656 (7) | 0.2018 (6) | 0.3135 (5) | 3.8 (8) | C(31) | 0.790 (2) | 0.188 (1) | 0.3261 (9) | 3 (1) |
| P(3) | 0.3616 (7) | 0.3453 (5) | 0.4121 (5) | 3.2 (8) | C(38) | 0.316 (1) | 0.220 (2) | 0.425 (1) | 5 (1) |
| P(4) | 0.3204 (7) | 0.2851 (6) | 0.2556 (5) | 3.2 (8) | C(39) | 0.264 (1) | 0.167 (2) | 0.439 (1) | 8 (2) |
| N(1) | 0.412 (3) | 0.419 (2) | 0.285 (2) | 6 (3) | C(40) | 0.179 (1) | 0.176 (2) | 0.460 (1) | 8 (2) |
| N(2) | 0.409 (3) | 0.465 (2) | 0.261 (2) | 11 (4) | C(41) | 0.146 (1) | 0.239 (2) | 0.466 (1) | 5 (1) |
| C(2) | 0.639 (2) | 0.476 (1) | 0.2456 (9) | 4 (1) | C(42) | 0.198 (1) | 0.291 (2) | 0.452 (1) | 4 (1) |
| C(3) | 0.598 (2) | 0.537 (1) | 0.2438 (9) | 5 (1) | C(37) | 0.283 (1) | 0.282 (2) | 0.431 (1) | 4 (1) |
| C(4) | 0.575 (2) | 0.565 (1) | 0.2989 (9) | 4 (1) | C(44) | 0.274 (2) | 0.438 (1) | 0.485 (1) | 6 (1) |
| C(5) | 0.592 (2) | 0.532 (1) | 0.3558 (9) | 5 (1) | C(45) | 0.218 (2) | 0.491 (1) | 0.492 (1) | 5 (1) |
| C(6) | 0.633 (2) | 0.471 (1) | 0.3577 (9) | 3 (1) | C(46) | 0.180 (2) | 0.525 (1) | 0.439 (1) | 5 (1) |
| C(1) | 0.657 (2) | 0.444 (1) | 0.3026 (9) | 3 (1) | C(47) | 0.197 (2) | 0.505 (1) | 0.379 (1) | 5 (1) |
| C(8) | 0.849 (2) | 0.3379 (9) | 0.405 (1) | 4 (1) | C(48) | 0.253 (2) | 0.453 (1) | 0.372 (1) | 5 (1) |
| C(9) | 0.929 (2) | 0.3538 (9) | 0.443 (1) | 4 (1) | C(43) | 0.292 (2) | 0.419 (1) | 0.425 (1) | 3 (1) |
| C(10) | 0.972 (2) | 0.4124 (9) | 0.435 (1) | 6 (1) | C(50) | 0.502 (2) | 0.406 (1) | 0.485 (1) | 5 (1) |
| C(11) | 0.935 (2) | 0.4549 (9) | 0.389 (1) | 6 (1) | C(51) | 0.569 (2) | 0.414 (1) | 0.536 (1) | 6 (1) |
| C(12) | 0.855 (2) | 0.4389 (9) | 0.351 (1) | 4 (1) | C(52) | 0.579 (2) | 0.369 (1) | 0.584 (1) | 8 (2) |
| C(7) | 0.813 (2) | 0.3804 (9) | 0.359 (1) | 3 (1) | C(53) | 0.522 (2) | 0.315 (1) | 0.582 (1) | 8 (2) |
| C(14) | 0.675 (1) | 0.330 (1) | 0.184 (1) | 6 (1) | C(54) | 0.456 (2) | 0.307 (1) | 0.531 (1) | 8 (2) |
| C(15) | 0.700 (1) | 0.315 (1) | 0.125 (1) | 9 (2) | C(49) | 0.445 (2) | 0.352 (1) | 0.483 (1) | 4 (1) |
| C(16) | 0.790 (1) | 0.321 (1) | 0.114 (1) | 6 (1) | C(56) | 0.153 (2) | 0.318 (1) | 0.2948 (9) | 3 (1) |
| C(17) | 0.856 (1) | 0.342 (1) | 0.161 (1) | 6 (1) | C(57) | 0.077 (2) | 0.358 (1) | 0.2937 (9) | 5 (1) |
| C(18) | 0.831 (1) | 0.357 (1) | 0.220 (1) | 4 (1) | C(58) | 0.061 (2) | 0.404 (1) | 0.2469 (9) | 5 (1) |
| C(13) | 0.741 (1) | 0.351 (1) | 0.232 (1) | 3 (1) | C(59) | 0.120 (2) | 0.411 (1) | 0.2011 (9) | 7 (2) |
| C(20) | 0.640 (2) | 0.067 (2) | 0.338 (1) | 10 (2) | C(60) | 0.196 (2) | 0.370 (1) | 0.2022 (9) | 6 (1) |
| C(21) | 0.612 (2) | 0.016 (2) | 0.374 (1) | 14 (3) | C(55) | 0.212 (2) | 0.324 (1) | 0.2490 (9) | 3 (1) |
| C(22) | 0.573 (2) | 0.029 (2) | 0.429 (1) | 13 (2) | C(62) | 0.406 (2) | 0.319 (1) | 0.148 (1) | 7 (2) |
| C(23) | 0.562 (2) | 0.092 (2) | 0.448 (1) | 15 (3) | C(63) | 0.415 (2) | 0.317 (1) | 0.084 (1) | 7 (2) |
| C(24) | 0.590 (2) | 0.143 (2) | 0.412 (1) | 12 (2) | C(64) | 0.359 (2) | 0.278 (1) | 0.044 (1) | 7 (2) |
| C(19) | 0.629 (2) | 0.130 (2) | 0.357 (1) | 6 (2) | C(65) | 0.293 (2) | 0.240 (1) | 0.067 (1) | 6 (2) |
| C(26) | 0.555 (2) | 0.192 (1) | 0.200 (1) | 6 (1) | C(66) | 0.284 (2) | 0.241 (1) | 0.131 (1) | 6 (2) |
| C(27) | 0.530 (2) | 0.172 (1) | 0.139 (1) | 6 (1) | C(61) | 0.340 (2) | 0.281 (1) | 0.172 (1) | 5 (1) |
| C(28) | 0.589 (2) | 0.134 (1) | 0.108 (1) | 8 (2) | C(68) | 0.362 (1) | 0.165 (1) | 0.286 (1) | 7 (2) |
| C(29) | 0.672 (2) | 0.115 (1) | 0.140 (1) | 7 (2) | C(69) | 0.347 (1) | 0.100 (1) | 0.295 (1) | 6 (2) |
| C(30) | 0.696 (2) | 0.134 (1) | 0.202 (1) | 4 (1) | C(70) | 0.258 (1) | 0.075 (1) | 0.285 (1) | 6 (1) |
| C(25) | 0.638 (2) | 0.172 (1) | 0.232 (1) | 3 (1) | C(71) | 0.185 (1) | 0.116 (1) | 0.266 (1) | 6 (2) |
| C(32) | 0.844 (2) | 0.214 (1) | 0.2829 (9) | 6 (1) | C(72) | 0.200 (1) | 0.181 (1) | 0.257 (1) | 5 (1) |
| C(33) | 0.939 (2) | 0.211 (1) | 0.2947 (9) | 8 (2) | C(67) | 0.289 (1) | 0.206 (1) | 0.267 (1) | 4 (1) |

## Results and Discussion

**Hydrogenation of $Ru(C_8H_8)_2(PPh_3)_2$ and Isolation of $Ru_2H_4N_2(PPh_3)_4$.** $Ru(C_8H_8)_2(PPh_3)_2$ has been shown to be an extremely reactive species able to react with a variety of substrates,[20] $H_2O$, CO, olefins, and even $PPh_3$ to give $PPh_2PC_6H_4C_6H_4PPh_2$ and seems a valuable starting material for hydrogenation reactions. Thus, when hydrogen is passed through a suspension of $Ru(C_8H_8)_2(PPh_3)_2$ in hexane for 1 h, a pink precipitate is formed. An infrared spectrum reveals the presence of terminal as well as bridging hydrides [1945 (m, br), 1600 cm$^{-1}$ (v br)]. Attempts to recrystallize this powder from toluene/hexane under argon were unsuccessful: brown solutions and eventually brown oils showing no NMR evidence for the presence of hydrides were obtained.[22] Nevertheless under dinitrogen, bright red crystals of another complex, analyzing for $Ru_2H_4N_2(PPh_3)_4$ (1), deposited. From infrared spectroscopy, it can be proposed to contain terminal [1940 cm$^{-1}$ (m)] and bridging hydrides [1650 (m), 1560 cm$^{-1}$ (m)] as well as coordinated dinitrogen [2140 cm$^{-1}$ (s)]. As the structure of this compound could not be solved by spectroscopic means only, a determination of its structure by X-ray diffraction was undertaken.

**Crystal Structure and Localization of the Hydrido Atoms by Molecular Mechanics.** Final values of the positional and thermal parameters for the non-hydrogen atoms are presented in Table II.[23] Distances and angles of interest are recorded in Table III, and the labeling scheme can be found in the perspective view of the molecule (Figure 1).

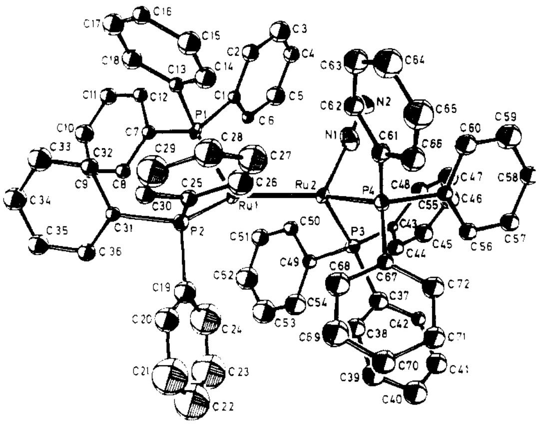

**Figure 1.** Perspective view and labeling scheme of the structure as found by X-ray crystallography for compound 1. Ellipsoids are drawn at a 35% probability level.

The most difficult problem we had to face to determine the structure of this complex was the number and the

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(22) This can be due to the formation of species containing diphenylphosphido-bridged species.

(23) Anisotropic thermal parameters for the eight first atoms of Table II as well as parameters for the phenyl groups H atoms are available as supplementary material.

**Table III. Distances (Å) and Angles (deg) of Interest for Compound 1**

| | | | |
|---|---|---|---|
| | Bond Distances | | |
| Ru(1)-Ru(2) | 2.553 (5) | P(1)-C(13) | 1.81 (3) |
| Ru(1)-P(1) | 2.21 (1) | P(2)-C(19) | 1.87 (4) |
| Ru(1)-P(2) | 2.25 (1) | P(2)-C(25) | 1.85 (3) |
| Ru(2)-P(3) | 2.33 (1) | P(2)-C(31) | 1.87 (3) |
| Ru(2)-P(4) | 2.32 (1) | P(3)-C(37) | 1.84 (3) |
| Ru(2)-N(1) | 2.01 (4) | P(3)-C(43) | 1.88 (3) |
| P(1)-C(1) | 1.85 (3) | P(3)-C(49) | 1.85 (3) |
| P(1)-C(7) | 1.85 (3) | P(4)-C(55) | 1.78 (2) |
| | | P(4)-C(61) | 1.86 (3) |
| | | P(4)-C(67) | 1.74 (3) |
| | | N(1)-N(2) | 1.08 (4) |
| H(1)-Ru(1) | 1.654[a] | H(2)-Ru(2) | 1.889 |
| H(2)-Ru(1) | 1.890 | H(3)-Ru(2) | 1.889 |
| H(3)-Ru(1) | 1.889 | H(4)-Ru(2) | 1.886 |
| H(4)-Ru(1) | 1.886 | | |
| H(1)···H(2) | 2.235 | H(2)···H(3) | 2.276 |
| H(1)···H(3) | 2.456 | H(2)···H(4) | 2.430 |
| H(1)···H(4) | 3.473 | H(3)···H(4) | 2.506 |
| | Bond Angles | | |
| C(1)-P(1)-Ru(1) | 109.1 (8) | C(7)-P(1)-C(1) | 99 (1) |
| C(7)-P(1)-Ru(1) | 123.8 (8) | C(13)-P(1)-C(1) | 101 (1) |
| C(13)-P(1)-Ru(1) | 117.4 (9) | C(13)-P(1)-C(7) | 104 (1) |
| C(19)-P(2)-Ru(1) | 115 (1) | C(25)-P(2)-C(19) | 99 (1) |
| C(25)-P(2)-Ru(1) | 116.6 (9) | C(31)-P(2)-C(19) | 98 (1) |
| C(31)-P(2)-Ru(1) | 123 (1) | C(31)-P(2)-C(25) | 101 (1) |
| C(37)-P(3)-Ru(2) | 117.7 (8) | C(43)-P(3)-C(37) | 100 (1) |
| C(43)-P(3)-Ru(2) | 122.2 (8) | C(49)-P(3)-C(37) | 105 (1) |
| C(49)-P(3)-Ru(2) | 110.4 (9) | C(49)-P(3)-C(43) | 99 (1) |
| C(55)-P(4)-Ru(2) | 116.6 (9) | C(61)-P(4)-C(55) | 101 (1) |
| C(61)-P(4)-Ru(2) | 116.0 (8) | C(67)-P(4)-C(55) | 101 (1) |
| C(67)-P(4)-Ru(2) | 120.1 (9) | C(67)-P(4)-C(61) | 100 (1) |
| N(2)-N(1)-Ru(2) | 171 (5) | | |
| P(1)-Ru(1)-Ru(2) | 117.8 (3) | P(2)-Ru(1)-P(1) | 98.7 (4) |
| P(2)-Ru(1)-Ru(2) | 131.2 (3) | | |
| P(3)-Ru(2)-Ru(1) | 118.0 (3) | N(1)-Ru(2)-Ru(1) | 116 (1) |
| P(4)-Ru(2)-Ru(1) | 125.2 (3) | N(1)-Ru(2)-P(3) | 99 (1) |
| P(4)-Ru(2)-P(3) | 100.5 (4) | N(1)-Ru(2)-P(4) | 93 (1) |
| H(1)-Ru(1)-P(1) | 93.5 | H(2)-Ru(1)-H(3) | 74 |
| H(1)-Ru(1)-P(2) | 95 | H(2)-Ru(1)-H(4) | 80 |
| H(1)-Ru(1)-H(2) | 78 | H(3)-Ru(1)-P(1) | 163 |
| H(1)-Ru(1)-H(3) | 87.5 | H(3)-Ru(1)-P(2) | 98 |
| H(1)-Ru(1)-H(4) | 156 | H(3)-Ru(1)-H(4) | 83 |
| H(2)-Ru(1)-P(1) | 90 | H(4)-Ru(1)-P(1) | 90 |
| H(2)-Ru(1)-P(2) | 169 | H(4)-Ru(1)-P(2) | 106 |
| H(2)-Ru(2)-P(3) | 86.5 | H(3)-Ru(2)-P(4) | 103 |
| H(2)-Ru(2)-P(4) | 172 | H(3)-Ru(2)-N(1) | 162 |
| H(2)-Ru(2)-N(1) | 89 | H(3)-Ru(2)-H(4) | 83 |
| H(2)-Ru(2)-H(3) | 74 | H(4)-Ru(2)-P(3) | 165 |
| H(2)-Ru(2)-H(4) | 80 | H(4)-Ru(2)-P(4) | 92.5 |
| H(3)-Ru(2)-P(3) | 87 | H(4)-Ru(2)-N(1) | 88 |

[a] Values with no standard deviation imply at least one atom located by molecular mechanics (see text).

position of the hydrides. We will thus describe a calculation by molecular mechanics that we carried out with the crystallographic data (from which we derived the positions of all non-hydrogen atoms) and then describe the whole structure.

A first study of the Fourier transform $^1$H NMR of compound 1 had shown three signals of approximately equal intensity for the hydrido atoms. It was then deduced that there were six hydrogen atoms linked to the Ru atoms (four bridged and two terminal).[21] A subsequent study of the possible location of these atoms by molecular mechanics using Orpen's program[24] in a first step did not refute clearly this statement. Concerning potential energy minima, none was found around Ru(2), two were found around Ru(1) (one of them characterized by a rather large potential energy), and three were found in the mid-plane orthogonal to the Ru(1)-Ru(2) axis. It is well-known that two H atoms may sometimes be located in the same potential energy well when rather large and flat. A PE map in the Ru(1)-Ru(2) mid-plane showed that it was the case for one of the minima (approximate fractional coordinates 0.518, 0.313, and 0.330). As a consequence, corefinement was performed for six hydrogen atoms. The results gave potential energies ranging from 3.8 to 11.6 kcal·mol$^{-1}$. Although the threshold value for site energies above which the atom can be rejected is not accurately known, comparison of our results with Orpen's statistics[24] led us to consider that it was not possible to admit the existence of two terminal hydrogen atoms on Ru(1) (PE = 11.2 and 11.6 kcal·mol$^{-1}$). Furthermore, the distance between these terminal H atoms was too short (1.64 Å) as well as some other H-H distances.

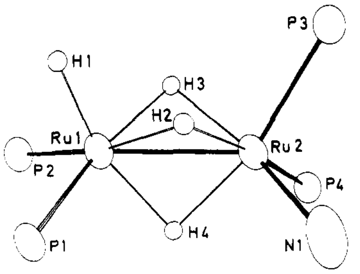

Figure 2. Perspective view of bond disposal around the Ru atoms in compound 1.

These results forced us to reconsider the $^1$H NMR experiments. New recordings of $^1$H spectra using longer interpulse delays (60 s) showed that the intensities of the three signals were actually in the 2:1:1 proportion (vide infra), thus implying the existence of only four hydrido H atoms. In this case, new calculations gave much more reasonable results that are reported in Table I.

If four hydrido H atoms are included in the structure (for determination of the number of hydrides and location, vide infra), the framework of the molecule (Figure 2) can be described as a two face-sharing distorted octahedra, with the two Ru atoms hexacoordinated. It can be seen that the four H atoms play their full steric role.

Indeed, in the absence of bridging H atoms (provided that the Ru(1)-Ru(2) link remains) the molecule would be expected to present a staggered conformation with the phosphorus atoms located in opposite directions due to the steric hindrance of the bulky $PPh_3$ groups. The sharing of the three bridging H atoms implies for both octahedra the sharing of the H(2)-H(3)-H(4) face which, in its turn, implies an eclipsed conformation in which at least two phosphorus atoms bonded to distinct ruthenium atoms occult one another. Because of steric hinderance, two phosphorus atoms only are eclipsed. Thus, the localization of the bridging H atoms is consistent with the structure found by X-ray techniques, independently of the more sophisticated molecular mechanics calculations. A Newman projection along the Ru(1)-Ru(2) axis illustrates these results (Figure 3). The eclipsing of two $P(Ph_3)$ groups is probably a constraint of the molecule in the solid state whose release may allow, in solution and at ambient temperature, the fluxional molecule to change one of its octahedra into a trigonal prism (vide infra).

Another interesting feature of the structure is the short Ru(1)-Ru(2) distance (2.553 (5) Å) which has to be examined in relation with the electronic distribution around the Ru atoms.

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(24) Orpen, A. G. *J. Chem. Soc., Dalton Trans.* **1980**, 2509.

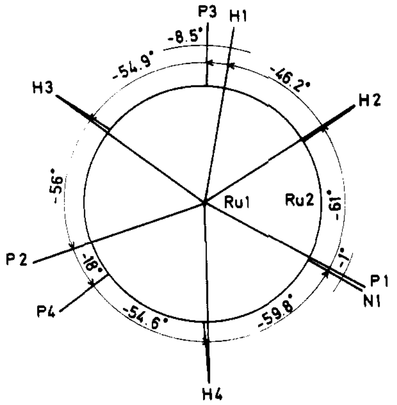

**Figure 3.** Newman projection for compound 1.

**Table IV. NMR Data for Hydride Compounds 1-6**

| compd | formula | $^1$H NMR$^a$ $\delta$ ($J$, Hz) | $^{31}$P NMR $\delta$ |
|---|---|---|---|
| 1 | $Ru_2H_4N_2(PPh_3)_4$ | -8.0 d (64), -15.0 quin (13), -18.2 t (35) | 82 |
| 2 | $RuH_6(PPh_3)_2$ | -7.1 br | 79.5 |
| 3 | $Ru_2H_6(PPh_3)_4$ | -10.6 br | 60.1 |
| 4 | $Ru_2H_6(P\text{-}i\text{-}Pr_3)_4$ | -12.8 br | 88.2 |
| 5 | $Ru_2H_6(PCy_3)_4$ | -12.4 br | 81.1 |
| 6 | $Ru_2H_4N_2(PCy_3)_4$ | -12.4 br | 81 |

$^a$Hydride resonances at room temperature.

To achieve an 18-electron configuration around each ruthenium atom, we propose the existence of a triple metal-metal bond. Although this distance seems somewhat long,[25] it is in the range found for similar triply hydrido-bridged, metal-metal bonded complexes (e.g., 2.538 (4) Å[2] for $Re_2H_8$ $P(Et_2Ph)_4$ and 2.558 (Å) for $[Os_2H_3(PMe_2Ph)_6]^+$[14]). In a closely related complex, $[Ru_2H_3(PMe_3)_6]^+$,[15] Wilkinson et al. suggest that a metal-metal distance of 2.540 (1) Å could indicate the presence of a metal-metal double bond, but as this complex is isostructural and isoelectronic with the osmium complex, we suggest in this case the existence of a metal-metal triple bond.

**Spectroscopic Properties.** The chemistry in solution of these complexes is complicated because of their instability which makes the study of their NMR spectra rather difficult (NMR results are listed in Table IV, together with compound numbering and formula). Nevertheless, the case of $Ru_2H_4N_2(PPh_3)_4$ is the easiest since it is the most stable. Its $^{31}$P NMR spectrum shows a single peak at room temperature at $\delta$ 82 which splits at -75 °C into two broad peaks at $\delta$ 87.1 and 78.05. Each of these two signals seem to split into two at 193 K, but no limit spectrum is obtained.

These data indicate the fluxionality of the complex at room temperature. The $^1$H NMR spectrum at room temperature is more informative. It consists of three sets of peaks (Figure 4): a broad doublet at $\delta$ -8.0 ($H_{a,b}$, $J_{PH}$ = 64 Hz), a quintet at $\delta$ -15.0 ($H_c$, $J_{PH}$ = 13 Hz), and a triplet at $\delta$ -18.2 ($H_d$, $J_{PH}$ = 35 Hz). As quoted above, an incorrect integration ratio had led us to propose an erroneous formulation in which the complex would contain six hydride ligands. A careful reexamination showed the integration ratio to be actually 2:1:1 which means that only four hydrides are present in the molecule, in agreement with the molecular mechanics calculation (vide supra). Lowering the temperature causes only broadening of the signals for $H_{a,b}$ and $H_c$. The interpretation of the NMR data is rather puzzling. $H_d$ is most probably the terminal hydride on $Ru_1$ (Figure 5), $H_{a,b}$ and $H_c$ are bridging. The molecular structure in the solid state (Figures 1 and 2) clearly shows that the molecule in such fixed conformation belongs to the $C_1$ symmetry group. There is no reason thus for the phosphorus nuclei and hydrogen nuclei to be isochronous or chemically equivalent, provided that in solution the molecules keep the rigid structure found in the crystal. At very low temperature (lower than 193 K) this seems to be the case because the four phosphorus nuclei become *distinguishable*.

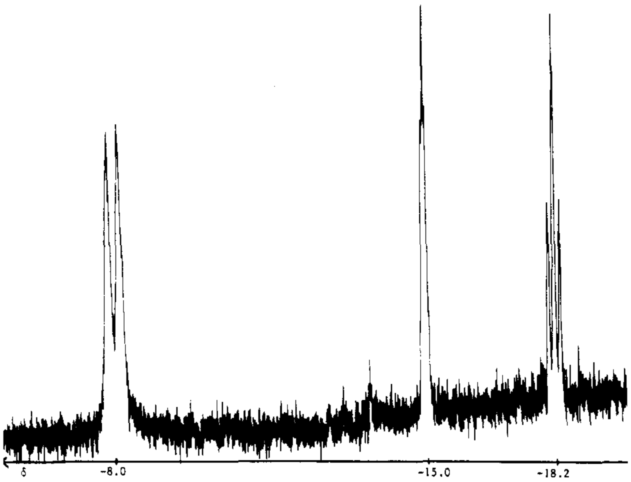

**Figure 4.** High-field $^1$H NMR spectrum of $Ru_2H_4N_2(PPh_3)_4$ (1).

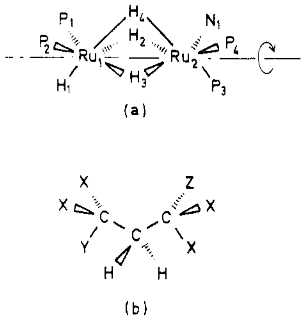

**Figure 5.** Fluxionality of $Ru_2H_4N_2(PPh_3)_4$ (see text).

At room temperature, the fact that phosphorus nucleu are chemically equivalent by pairs and that two hydrido atoms also are equivalent led us to consider a fluxionality for the molecule.

As the hydrogen nuclei remain in three distinct groups, a complex mechanism involving alternative bridging and *unbridging* of the hydrido atoms one by one cannot be considered for this would mean that the four H atoms are equivalent.

A rotation of the three bridging H atoms block relative to the fixed $Ru_1(P_1P_2H_1)$ and $Ru_2(P_3P_4N_1)$ moieties is also to be excluded as it would mean that the three bridging H atoms are equivalent.

On the contrary, if we assume the possibility of a free rotation of either $P_1$, $P_2$, and $H_1$ or $P_3$, $P_4$, and $N_1$ atoms around the $Ru_1$-$Ru_2$ axis, two of the bridging H atoms become equivalent because, as shown in Figure 5, the complex molecule 5a is topologically equivalent to the molecule 5b in which the H atoms are enantiotopic or prochiral.

Let us consider that, starting from the conformation represented in Figure 5a, $P_1$, $P_2$, and $H_1$ being fixed, the atoms $N_1$, $P_3$, and $P_4$ rotate around the $Ru_1$-$Ru_2$ axis. $H_2$

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[25] See, for example: Cotton, F. A.; Walton, R. A. In "Multiple Bonds between Metal Atoms"; Wiley-Interscience: New York, 1982; Chapter 5, p 183.

and $H_3$ exchange their magnetic sites as well as $P_1$ and $P_2$, on the one hand, and $P_3$ and $P_4$, on the other hand. If $P_3$, $P_4$ and $N_1$ are fixed and $P_1$, $P_2$, and $H_1$) rotate, starting from the same conformation, then $H_2$ and $H_4$ become equivalent.

In such a process, the phosphorus nuclei theoretically remain distinct by pairs. Observance of only one large peak in the $^{31}P\{^1H\}$ spectrum at room temperature is probably due to the anisotropy being too small compared to the line width. The atom $H_1$ remains coupled to the $P_1$ and $P_2$ equivalent nuclei in a cis position and gives rise to a single 1:2:1 triplet which is in good agreement with the signal observed at −18 ppm ($H_d$). In the same process, one H bridging atom, viz., $H_4$, remains in a cis position relative to two fixed equivalent P atoms but is further coupled to two more rotating P atoms and thus gives rise to a complex multiplet that looks like a quintet because of the line width but in which the relative intensities should not be 1:4:6:4:1, which is verified for the $H_c$ signal at −15 ppm.

The signal given by the equivalent bridging Hatoms, e.g., $H_2$ and $H_3$, corresponds to the AA′ pat of an AA′XX′ system modified by the coupling with the rotation of $P_3$ and $P_4$ nuclei which must remain symmetrical. It corresponds to the complex symmetrical doublet which is observed ($H_{a,b}$ signal) at −8.0 ppm.

We still have to identify the compounds present in the crude reaction mixture prio to recrystallization. Analytical data suggest the composition "$RuHx(PPh_3)_2$". The $^{31}P$ NMR spectrum shows the presence of two fluxional compounds ($\delta$ 79.5 and 60.1) and also shows their instability since after a while in solution, new peaks appear which were not identified. The $^1H$ NMR data are in agreement with these observations since two broad singlets are observed at $\delta$ −7.1 and −10.6. The first complex (**2**) that is fluxional at any temperature is most probably the hexahydride $RuH_6(PPh_3)_2$ analogous to $RuH_6(PCy_3)_2$,[19] but it is apparently much less stable. As quoted above, the other complex (**3**) shows a peak at $\delta$ −10.6 in its room-temperature $^1H$ NMR spectrum that splits into four peaks at −75 °C: a broad doublet at $\delta$ −8.4 [$J_{PH}$ = 65.5 Hz (apparent coupling constant)] ($H_a$), two broad peaks at $\delta$ −10.3 ($H_b$) and −12.4 ($H_c$), and a triplet at $\delta$ −19.2 ($H_d$). Unfortunately, due to the low solubility and reactions in solution, we could not obtain an accurate integration of these peaks. Nevertheless, this spectrum resembles very much that of $Ru_2H_4N_2(PPh_3)_4$ except for the presence of an extra peak. By analogy with **1**, this complex could be dinuclear with the formulation $Ru_2H_6(PPh_3)_4$; $H_d$ could be the unique terminal hydride on one ruthenium whereas $H_a$ would represent two bridging hydrides. $H_b$ and $H_c$ would be the remaining bridging hydride and the two terminal hydrides on the other ruthenium (Figure 5). The reaction with $N_2$ would then only be the substitution of two hydrides by $N_2$ which is known for mononuclear ruthenium polyhydride complexes.[26]

**Reactivity of the New Dinuclear Complexes.** The new species described above have shown a rather disappointing reactivity. Thus, reaction with an olefin, an acid, or chloroform leads to decomposition of the complexes. **1** and **3** are unstable in solution and decompose (**3** rapidly and **1** more slowly) to brown solutions showing no evidence for the presence of hydrides.

**Conclusion.** This study shows that it is definitely possible to obtain triply hydrido-bridged and triply metal–metal bonded dinuclear polyhydride complexes of ruthenium. With this method, we have not been able to obtain hydride clusters of ruthenium but, in the case of rhodium, only phosphite clusters are known. The same reactions do not work with phosphines.

**Table V. Physical and Crystallographic Data of Compound 1. Experimental Conditions of Crystallographic Measurements**

Physical and Crystallographic Data

formula: $Ru_2P_4N_2C_{72}H_{64}$
cryst system: monoclinic
$a$ = 14.7968 (21) Å
$b$ = 20.8167 (20)
$c$ = 21.4421 (21)
$\beta$ = 96.5791 (13)°
$\rho_{exptl}$ = not determined (see text)
mol wt: 1283.36
space group: $P2_1/n$
$V$ = 6561.1 Å$^3$
$Z$ = 4
$F(000)$ = 2631.7
$\rho_{calcd}$ = 1.30 g·cm$^{-3}$
$\mu[\lambda(Mo)]$ = 5.27 cm$^{-1}$

Data Collection

temp: 20 °C
radiat: molybdenum; $\lambda(K\alpha)$ = 0.710 69 Å
monochromatizatn: oriented graphite crystal
cryst-detector dist: 208 mm
detector window:[a] height = 4 mm; width[a] = 4.00 + 0.00 tan $\theta$ mm
takeoff angle:[a] 2.25°
scan mode: $\theta/\omega$
max bragg angle: 21.5°
values determining the scan speed: first shell (1.5° < $A$ < 17.5°), SIGPRE[a] = 0.70, SIGMA[a] = 0.018, VPRE = 10° min$^{-1}$ for $\theta$(TMAX)[a] = 5 s; second shell (17.5° < $\theta$ < 20.0°); third shell (20.0° < $\theta$ 21.5°)
intensity controls: 550, 080, 105 measd every 7200 s of iradiatn
orientatn controls: 080, 008, 800 measd every 200 reflctns

Conditions for Refinement

reflctns for the refinement of the cell dimens: 25
recorded reflctns: 7514
independent reflctns: 7514
utilized reflctns ($F > 6\sigma(F)$) = 2541
reliability factors: $R = \sum|k|F_o| - |F_c||/\sum k|F_o|$ and $R_w = \sum w|k|F_o| - |F_c||/\sum wk|F_o|$

[a] Values specified in ref 1.

Finally, in contrast with the structural features, the chemistry of these complexes has proved somewhat deceiving and seems far less rich than the corresponding rhenium chemistry.

## Experimental Section

Microanalyses were performed by the Centre de Microanalyse du CNRS and by Miss Magna in the laboratory. Infrared spectra were obtained as Nujol mulls by using a Perkin-Elmer PE 577 or PE 225 grating diffractometer, and NMR spectra were obtained by using a Bruker WH90 (90 MHz) or WM250 (250 MHz) spectrometer operating in the Fourier transform mode with proton noise decoupling when $^{31}P$ NMR spectra were recorded and a Perkin-Elmer R12 (60 MHz) spectrometer.

All solvents were thoroughly degassed before use, and all operations were carried out in nitrogen or argon atmosphere.

$Ru(C_8H_8)_2(PPh_3)_2$[22] was prepared according to published methods. $RuCl_3{\cdot}3H_2O$ was purchased from Johnson Matthey Ltd., and $PCy_3$ and P-*i*-$Pr_3$ were purchased from Alpha.

**Preparation of the Complexes. Hydrogenation of Ru$(C_8H_8)_2(PPh_3)_3$ and Production of $Ru_2H_4N_2(PPh_3)_4$.** $Ru(C_8H_8)_2(PPh_3)_2$ (0.400 g, 4.8 mmol) was suspended in hexane (40 mL), and hydrogen was passed for 2 h through the rapidly stirred suspension. The color changed from purple to brown, and eventually a pink precipitate was obtained which was filtered off and dried in vacuo (yield ca. 75%). It was shown to be composed of a mixture of $RuH_6(PPh_3)_2$ and $Ru_2H_6(PPh_3)_4$ (see text). This

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[26] Harris, R. O.; Hota, N. K.; Sadavoy, L.; Yuen, J. M. C. *J. Organomet. Chem.* **1973**, *54*, 259.

precipitate was dissolved in toluene (20 mL) at 50 °C under nitrogen. Hexane was added to the red solution (ca. 20 mL), and the resulting solution was filtered and cooled at −15 °C. Red crystals were obtained over a period of 2 weeks: total yield ca. 20%. Anal. Calcd for $C_{72}H_{64}N_2P_4Ru_2$: C, 69.0; H, 5.5; N, 2.0; P, 8.1. Found: C, 68.2; H,5.2; N, 2.0; P,8.1.

**Crystallographic Study.** Owing to its air sensitivity, the crystal of $Ru_2N_2H_4(PPh_3)_4$ chosen for the study was protected by a Lindemann capillary.

Preliminary photographic studies with Weissenberg and precession cameras showed that the compound crystallizes in a monoclinic system. The observed systematic absences ($h0l$, $h + l = 2n + 1$; $0k0$, $k = 2n + 1$) are consistent with the $P2_1/n$ space group.

The setting angles of 25 *hkl* reflections, regularly distributed in the half sphere, automatically centered on a Enraf-Nonious CAD4 diffractometer, were used in a least-squares calculation which led to the cell constants (Table V). On the assumption of four formula units per cell, the calculated density $\rho_{calcd} = 1.30$ $g\cdot cm^{-3}$ was found to be of the order of magnitude for that type of compound. Owing to the instability of the compound, we were not able to get a value for $\rho_{exptl}$.

**Data Collection.** Table V gives pertinent details concerning the experimental data collection conditions. Reflections have been recorded in three shells with the same crystal. No significantly deviation from the average value of any of the intensity control reflections was observed. Data were thus processed in the usual way[27] using a value of 0.02 for $p$.

**Structure Determination and Refinement.** The structure has been solved by standard Patterson and Fourier methods with the help of the SHELX program.[28] Conditions of refinement and used agreement indices, $R$ and $R_w$, are defined in Table V. Values of the atomic scattering factors and the anomalous terms used for P, N, C, and H are those included in the SHELX program. For Ru, they come from the ref 29.

From the Patterson function, the two Ru atoms were located, and on a subsequent Fourier map, the four phosphorus and 10 carbon atoms were found (C(1), C(2), C(3), C(5), C(6), C(7), C(8), C(13), C(14), and C(15)). Alternation of full-matrix least-squares refinements of isotropic atoms and difference Fourier maps then led to the location of all non-hydrogen atoms. At that point, two supplementary cycles of full-matrix least-squares refinements of the position of the Ru and P atoms (anisotropic), N (isotropic), and carbon atoms (isotropic) as phenyl rigid groups led to $R = R_w = 8.6\%$. Further refinements with introduction of all the hydrogen atoms of the 12 phenyl groups (as rigid group atoms with a fixed $U_{iso}$ equal to the $U_{iso}$ of the carbon bearing atom) led to $R = 8.3\%$ and $R_w = 7.5\%$ with a weighting scheme of the type $w = k/\sigma^2(F)$ ($k = 1.454$; 217 parameters). Any further attempt to improve the resolution failed probably due to the smallness and poor quality of the crystal (lack of intense reflections). A subsequent difference Fourier map did not permit a reliable location of the hydrido atoms. One of the phenyl groups presents rather high $U_{iso}$ thermal parameters, which is probably the sign of a slight disorder, but we were not able to solve it.

**Registry No.** 1, 97570-08-6; 2, 87800-34-8; 3, 97570-07-5; 4, 97570-10-0; 5, 97570-09-7; 6, 97570-11-1; $Ru(C_8H_8)_2(PPh_3)_2$, 68088-93-7.

**Supplementary Material Available:** Tables of final anisotropic thermal parameters (Å × $10^2$) with estimated standard deviations in parentheses, atomic positional and thermal parameters for hydrogen, and structure factors (16 pages). Ordering information is given on any current masthead page.

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# Asymmetric Catalyses. 16. Catalysts (cod)RhNN′ and [(cod)RhNN″]PF₆ (NN′ and NN″ = Optically Active Pyrrole and Pyridine Imines)[1]

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A single-crystal X-ray analysis of $[(cod)RhNN'']PF_6$, **2**, was carried out, NN″ = Schiff base derived from 2-pyridinealdehyde and (*S*)-1-phenylethylamine. The solution conformations of **2** and complexes **1** and **3**, containing the corresponding pyrrole imine ligand, were determined by $^1H$ NMR NOE difference spectroscopy. The arrangement of the chiral N-substituent C*HMePh with respect to chelate ring and Rh coordination plane is compared with that of compounds studied previously. Good agreement is found between solid-state and solution conformations.

In the enantioselective hydrosilylation of ketones, rhodium(I) complexes of optically active pyrrole and pyridine imines of type **1–3** give optical inductions superior to those obtained with optically active phosphanes, the ligands usually used in asymmetric catalysis.[1,2] These imine and phosphane ligands differ in the way chirality is transmitted to the metal sites, where the prochiral substrates are transformed into the chiral products.[3,4]

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[1] Asymmetric Catalysis, Part 15: Brunner, H.; Becker, R. *Angew. Chem.* **1984**, *96*, 221; *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 222.

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