Inorg. Chem. **1980**, *19*, 375-383

Contribution from the Laboratoire de Chimie Quantique, E.R. No. 139 du CNRS,
Institut Le Bel, Université Louis Pasteur, 67000 Strasbourg, France

Hydrogenation of Olefins Catalyzed by the Chlorotris(triphenylphosphine)rhodium(I) Complex. A Theoretical Study of the Structural Aspects

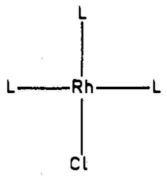
A. DEDIEU

Received June 28, 1979

Ab initio LCAO–MO–SCF calculations are reported for the complexes $RhClL_2$, H_2RhClL_3, H_2RhClL_2, $H_2RhClL_2(C_2H_4)$, and $HRhClL_2(C_2H_5)$ ($L = PH_3$), which stand as models for the possible intermediates involved in the hydrogenation of olefins catalyzed by the chlorotris(triphenylphosphine)rhodium complex or by other related rhodium complexes. For each intermediate the most probable stereoisomers have been considered and their relative stabilities determined. On this basis it is shown that two different pathways (with respect to the geometry of the corresponding intermediates) are likely for the reaction, depending on the nature (i.e., with or without chelating phosphine ligands) and on the formation of the catalyst. From the relative stabilities of the different stereoisomers for $HRhClL_2(C_2H_5)$ it is concluded that the transfer of the first hydrogen to the coordinated olefin in $H_2RhClL_2(C_2H_4)$ is not a simple hydride migration but more likely a rather complex process involving rearrangements of the nonreacting ligands.

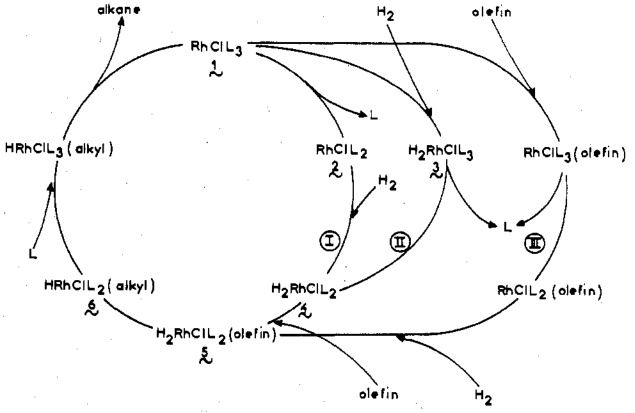
Introduction

The homogeneous hydrogenation of olefins catalyzed by the chlorotris(triphenylphosphine)rhodium(I) complex (the so-called Wilkinson catalyst $RhCl(PPh_3)_3$) has been the subject of many experimental studies since the first report of the hydrogenation of cyclohexene.[1,2] Many investigations have been devoted to the scope of this hydrogenation reaction[1,2e] and to its mechanism.[1,3–17] From these mechanistic studies, the following picture has emerged: olefin hydrogenation catalyzed by the Wilkinson complex $RhClL_3$ (**1**) may operate through three different routes denoted I, II, and III in Scheme I ($L = PPh_3$). Route I, which begins by a complete dissociation of L from $RhClL_3$ (**1**) to give $RhClL_2$ (**2**) and is followed by oxidative addition of molecular hydrogen yielding the coordinatively unsaturated five-coordinate intermediate H_2RhClL_2 (**4**), was originally proposed by Wilkinson et al.[1] Following studies[3–7] have shown that this dissociation is far from being complete. On this basis and on the basis of the 16- and 18-electron rule[8] Tolman originally concluded[8] that the hydrogenation reaction is taking place through route II. In this pathway the first step is believed to be an oxidative addition of H_2 on the catalyst leading to the intermediate H_2RhClL_3 (**3**). Support for this comes from the fact that the major species observed spectrophotometrically in solutions of $RhClL_3$ and H_2 are $RhClL_3$ and H_2RhClL_3[9] and from the isolation of H_2RhClL_3.[10] A subsequent dissociation of a phosphine ligand leads to the same five-coordinate intermediate **4**. However it was then shown[9,11] that both the dissociative pathway (route I) and the associative pathway (route II) could operate for the hydrogenation of $RhCl(PPh_3)_3$ depending on the concentration of free PPh_3. On the basis of calculated rate constants, $RhCl(PPh_3)_2$ was found to be more reactive toward H_2 than $RhCl(PPh_3)_3$ and other dimeric species[9,11] and is likely to be the reactive intermediate in this part of the catalytic cycle. Both routes I and II are characterized by H_2 addition prior to olefin addition (and therefore called the "hydride route"). They have the H_2RhClL_2 intermediate **4** and the next steps in common. The substrate (i.e., the olefin) adds to the H_2RhClL_2 (**4**) complex to form a six-coordinate adduct H_2RhClL_2(olefin) (**5**). This ethylene–dihydrido complex is a key intermediate in the hydrogenation since the two hydrogen atoms coordinated to the rhodium atom are then transferred stepwise[12,13] to the substrate (see the Scheme I). Once the first transfer has been completed, it is believed that a phosphine



1

Scheme I



---

(1) (a) F. H. Jardine, J. A. Osborn, G. Wilkinson, and J. F. Young, *Chem. Ind.* (*London*), 560 (1965); (b) M. A. Bennett and P. A. Longstaff, *ibid.*, 846 (1965); (c) J. A. Osborn, F. H. Jardine, J. F. Young, and G. Wilkinson, *J. Chem. Soc. A*, 1711 (1966).

(2) For recent reviews on homogeneous hydrogenation of olefins see: (a) B. R. James, "Homogeneous Hydrogenation", Wiley, New York, 1973; (b) R. E. Harmon, S. K. Gupta, and D. J. Brown, *Chem. Rev.*, **73**, 21 (1973); (c) G. Dolcetti and N. W. Hoffman, *Inorg. Chim. Acta*, **9**, 269 (1974); (d) B. R. James, *Adv. Organomet. Chem.*, **17**, 319 (1979); (e) A. J. Birch and D. H. Williamson, *Org. React.*, **24**, 1 (1976).

(3) D. R. Eaton and S. R. Stuart, *J. Am. Chem. Soc.*, **90**, 4170 (1968).

(4) D. D. Lehman, D. F. Shriver, and I. Wharf, *Chem. Commun.*, 1486 (1970).

(5) H. Arai and J. Halpern, *Chem. Commun.*, 1571 (1971).

(6) P. Meakin, J. P. Jesson, and C. A. Tolman, *J. Am. Chem. Soc.*, **94**, 3240 (1972).

(7) Y. Demortier and I. de Aguirre, *Bull. Soc. Chim. Fr.*, 1614, 1619 (1974).

(8) C. A. Tolman, *Chem. Soc. Rev.*, **1**, 337 (1972).

(9) C. A. Tolman, P. Z. Meakin, D. L. Lindner, and J. P. Jesson, *J. Am. Chem. Soc.*, **96**, 2762 (1974).

(10) A. Sacco, R. Ugo, and A. Moles, *J. Chem. Soc. A*, 1670 (1966).

(11) J. Halpern and C. S. Wong, *J. Chem. Soc., Chem. Commun.*, 629 (1973).

(12) G. C. Bond and R. A. Hillyard, *Discuss. Faraday Soc.*, **46**, 20 (1968).

(13) A. S. Hussey and Y. Takeuchi, *J. Am. Chem. Soc.*, **91**, 672 (1969).

(14) Y. Ohtani, M. Fujimoto, and A. Yamagishi, *Bull. Chem. Soc. Jpn.*, **49**, 1871 (1976); **50**, 1453 (1977); **52**, 69 (1979).

(15) J. Halpern, T. Okamoto, and A. Zakhariev, *J. Mol. Catal.*, **2**, 65 (1976).

(16) S. Siegel and D. Ohrt, *Inorg. Nucl. Chem. Lett.*, **8**, 15 (1972).

(17) C. Rousseau, M. Evrard, and F. Petit, *J. Mol. Cat.*, **3**, 309 (1977); **5**, 163 (1979).

0020-1669/80/1319-0375$01.00/0 © 1980 American Chemical Society

ligand will coordinate to the unsaturated five-coordinate intermediate $HRhClL_2$(alkyl) (**6**) and that the second transfer will then occur. Route III (the so-called "substrate route") involving a prior addition of the olefin to the Wilkinson catalyst has been found to be very slow[1c] and does not contribute appreciably to the hydrogenation.

In addition to the starting catalyst $RhClL_3$ (**1**) there are five other species which are important in delineating the mechanism of this homogeneous hydrogenation, namely, $RhClL_2$ (**2**), H_2RhClL_3 (**3**), H_2RhClL_2 (**4**), H_2RhClL_2(olefin) (**5**), and $HRhClL_2$(alkyl) (**6**). None of them has been characterized by an X-ray crystal structure except the Wilkinson catalyst $RhCl(PPh_3)_3$.[18] The structure of the $[Rh(PPh_3)_3]^+$ cation which may be considered as a model for the tricoordinate intermediate $RhClL_2$ (**1**) has been recently published.[19] From NMR studies the molecular structure of the H_2RhClL_3 complex has been inferred for L = PPh_3[6] and L = P-*t*-BuMePh.[20] Both complexes gave the same stereochemistry. Conversely the stereochemistry of the five-coordinate intermediate H_2RhClL_2 seems to be dependent on the solvent and on the size of the ligand L.[6,9,20,21] The existence of the intermediates **5** and **6** has been deduced from kinetic studies only, and these two species have not been observed even with spectroscopic techniques. Their structure is therefore unknown. Very recently some dihydrido(olefin)iridium complexes closely related to the intermediate **5** have been isolated and their structures deduced from NMR and IR spectra.[22-24] Also an equilibrium between an (ethylene)hydridometal complex and an ethylmetal complex has been reported.[25]

There have been only a few theoretical studies devoted to catalytic reactions,[26-34] most of them using semiempirical techniques.[26-29,32,34] We present here the first part of a theoretical study of the hydrogenation of olefin catalyzed by $RhCl(PPh_3)_3$ using LCAO-MO-SCF calculations. We proceed first through a detailed analysis of the geometry and of the electronic structure of the intermediates **2**-**6**. We then discuss different possible pathways of the catalytic cycle by using as a criterion the relative stabilities of the different stereoisomers for each intermediate. The determination of the reaction path leading from **5** to **6**, i.e., the transfer of the first hydrogen atom, will appear in a forthcoming publication.[35]

Table I. Total SCF Energies of the Most Stable Stereoisomers

molecule	isomer[a]	total energy,[b] au
$RhCl(PH_3)_2$	**2b**	−5816.4836
$H_2RhCl(PH_3)_3$	**3a**	−6159.5084
$H_2RhCl(PH_3)_2$	**4a**	−5817.6065
$H_2RhCl(PH_3)_2(C_2H_4)$	**5cp**	−5895.5440
$HRhCl(PH_3)_2(C_2H_5)$	**6a**	−5895.5809

[a] See the text for the definition of these stereoisomers. [b] 1 au = 627.7 kcal/mol.

Calculations

LCAO-MO-SCF calculations have been carried out on the systems $RhClL_2$ (**2**), H_2RhClL_3 (**3**), H_2RhClL_2 (**4**), $H_2RhClL_2(C_2H_4)$ (**5**), and $HRhClL_2(C_2H_5)$ (**6**) where L = PH_3 stands as a model for the triphenylphosphine ligand PPh_3 and C_2H_4 and C_2H_5 stand as models for the olefin and the alkyl ligands, respectively. For each system we have considered all stereoisomers corresponding to the following idealized geometries: T-shaped for the three-coordinate $RhClL_2$ complex (on the basis of the X-ray crystal structure of $[Rh(PPh_3)_3]^+$[19] and on theoretical grounds, too[36]), octahedral for the six-coordinate complexes H_2RhClL_3 and $H_2RhClL_2(C_2H_4)$, and flat square pyramid for the five-coordinate complexes H_2RhClL_2 and $HRhClL_2(C_2H_5)$ (most of the pentacoordinate d^6 metal complexes have a square-pyramid geometry[37] and we do not think that the assumption of a flat base will change drastically our conclusions since our purpose here is to compare the stability of the different stereoisomers for each system).

The Rh-Cl, Rh-P, and Rh-H distances were set to 2.40, 2.37, and 1.65 Å, respectively, for the H_2RhClL_3 system (the Rh-Cl and Rh-P bond lengths were taken from the X-ray crystal structure of the related complex $RhCl(PPh_3)_3(O_2)$[38,39] and the Rh-H bond is found to be 1.66 Å in the $RhH(N_2)[P(C_6H_5)(C_4H_9)_2]_2$ complex[48,49]). For the sake of computational economy the same bond lengths were kept for the other systems considered here. The Rh-C distances were set to 2.15 and 2.05 Å in $H_2RhClL_2(C_2H_4)$ and $HRhClL_2(C_2H_5)$, respectively, this choice being based on the X-ray crystal structures of some olefinic[53-60] and alkyl complexes.[61-65] The C_2H_4 geometry was set as

---

(18) (a) P. B. Hitchcok, M. McPartlin, and R. Mason, *Chem. Commun.*, 1367 (1969). (b) M. J. Bennett and P. B. Donaldson, *Inorg. Chem.*, **16**, 655 (1977). (c) There is also an EXAFS structure of $RhCl(PPh_3)$ in solution: J. Reed, P. Eisenberger, B. K. Teo and B. M. Kincaid, *J. Am. Chem. Soc.*, **99**, 7076 (1977).

(19) Y. W. Yared, S. L. Miles, R. Bau, and C. A. Reed, *J. Am. Chem. Soc.*, **99**, 7076 (1977).

(20) C. Masters and B. L. Shaw, *J. Chem. Soc. A*, 3679 (1971).

(21) H. L. M. Van Gaal, J. M. Verlaak, and T. Posno, *Inorg. Chim. Acta*, **23**, 43 (1977).

(22) R. H. Crabtree, H. Felkin, and G. E. Morris, *J. Chem. Soc., Chem. Commun.*, 716 (1976).

(23) R. H. Crabtree, H. Felkin, T. Fillebeen-Khan, and G. E. Morris, *J. Organomet. Chem.*, **168**, 183 (1979).

(24) S. Hietkamp, D. J. Stufkens, and K. Vrieze, *J. Organomet. Chem.*, **152**, 347 (1978).

(25) H. Werner and R. Feser, *Angew. Chem., Int. Ed. Engl.*, **18**, 157 (1979).

(26) K. S. Wheelock, J. H. Nelson, J. D. Kelly, H. B. Jonassen, and L. C. Cusachs, *J. Chem. Soc., Dalton Trans.*, 1457 (1973).

(27) S. Sakaki, H. Kato, H. Kanai, and K. Tamara, *Bull. Chem. Soc. Jpn.*, **47**, 377 (1974).

(28) S. Sakaki, H. Kato, H. Kanai, and K. Tamara, *Bull. Chem. Soc. Jpn.*, **48**, 813 (1975).

(29) D. R. Armstrong, R. Fortune, and P. G. Perkins, *J. Catal.*, **42**, 435 (1976).

(30) J. Ph. Grima, F. Choplin, and G. Kaufmann, *J. Organomet. Chem.*, **129**, 221 (1977).

(31) L. Salem, O. Eisenstein, N. T. Anh, H. B. Bürgi, A. Devaquet, G. Segal, and A. Veillard, *Nouv. J. Chim.*, **1**, 335 (1977).

(32) D. L. Thorn and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 2079 (1978).

(33) (a) G. Giunchi, E. Clementi, M. E. Ruiz-Vizcaya, and O. Novaro, *Chem. Phys. Lett.*, **49**, 8 (1977); (b) O. Novaro, E. Blaisten-Barojas, E. Clementi, G. Giunchi, and M. E. Ruiz-Vizcaya, *J. Chem. Phys.*, **68**, 2337 (1978).

(34) F. Cassoux, F. Crasnier, and J. F. Labarre, *J. Organomet. Chem.*, **165**, 303 (1979).

(35) A. Dedieu and A. Rossi, to be submitted for publication.

(36) (a) J. K. Burdett, *J. Chem. Soc., Faraday Trans. 1*, **70**, 1599 (1974); *Inorg. Chem.*, **14**, 375 (1974); (b) M. Elian and R. Hoffmann, *ibid.*, **14**, 1058 (1975); (c) S. Komiya, T. A. Albright, R. Hoffmann, and J. K. Kochi, *J. Am. Chem. Soc.*, **98**, 7255 (1976).

(37) P. R. Hoffman and K. G. Caulton, *J. Am. Chem. Soc.*, **97**, 4221 (1975), and references therein.

(38) M. J. Bennett and P. B. Donaldson, *Inorg. Chem.*, **16**, 1581 (1977).

(39) Similar Rh-P and Rh-Cl bond lengths are also found in other hexacoordinated Rh(III) complexes[40-44] and in five-coordinate square-pyramid complexes.[45-47]

(40) A. C. Skapski and F. A. Stephens, *J. Chem. Soc., Dalton Trans.*, 1789 (1973).

(41) B. Cetinkaya, M. F. Lappert, G. M. McLaughlin, and K. Turner, *J. Chem. Soc., Dalton Trans.*, 1591 (1974).

(42) K. Itoh, I. Matsuda, F. Ueda, Y. Ishii, and J. A. Ibers, *J. Am. Chem. Soc.*, **99**, 2118 (1977).

(43) M. Cowie and J. A. Ibers, *Inorg. Chem.*, **15**, 559 (1976).

(44) P. D. Frisch and G. P. Khare, *J. Am. Chem. Soc.*, **100**, 8267 (1978).

(45) T. E. Nappier, Jr., D. W. Meek, R. M. Kirchner, and J. A. Ibers, *J. Am. Chem. Soc.*, **95**, 4194 (1973).

(46) K. W. Muir and J. A. Ibers, *Inorg. Chem.*, **9**, 440 (1970).

(47) S. Z. Goldberg, G. Kubiak, C. D. Meyer, and R. Eisenberg, *Inorg. Chem.*, **14**, 1650 (1975).

(48) P. R. Hoffman, T. Yoshida, T. Okano, S. Otsuka, and J. A. Ibers, *Inorg. Chem.*, **15**, 2462 (1976).

(49) Ru(II)-H bond lengths (Ru(II) is isoelectronic with Rh(III)) ranging from 1.58 to 1.68 Å have been found in distorted octahedral complexes.[50-52]

(50) L. D. Brown, S. D. Robinson, A. Sahajpal, and J. A. Ibers, *Inorg. Chem.*, **16**, 2728 (1977).

(51) L. J. Guggenberger, *Inorg. Chem.*, **12**, 1317 (1973).

(52) A. C. Skapski and F. A. Stephens, *J. Chem. Soc., Dalton Trans.*, 390 (1974).

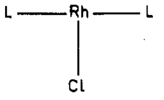
follows: C–C = 1.38 Å,[66] C–H = 1.10 Å, $\angle$C–C–H = 120°, and $\angle$H–C–H = 113.372° (this corresponds to bending back the hydrogen atoms at 0.25 Å from their original position). For the alkyl ligand, the staggered geometry was assumed, all angles were set to 109°28′ (including the Rh–C–C angle), and the C–C bond length was set to 1.54 Å. For the PH_3 ligand the experimental geometry[68] was chosen.

Calculations were carried out with the system of programs Asterix[69] using the following Gaussian basis set: (13,9,7) contracted to [5,4,3] for Rh,[70] (10,6) contracted to [4,3] for phosphorus and chlorine,[71] (8,4) contracted to [3,2] for the first-row atoms,[72] and (4) contracted to [2] for hydrogens[73] (the contracted basis set is a minimal set for the inner shells and the 5s and 5p shells of rhodium and a double-ζ set for the valence shells).

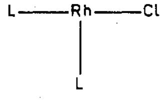
For each system we hereafter report the total energy of the most stable stereoisomer (Table I) and the calculated relative energies of the other stereoisomers (in kcal/mol under the corresponding structures).[74]

Results

$RhClL_2$ System. For this system there are two T-shaped stereoisomers **2a** and **2b**. The trans isomer **2a** is the result of the dissociation in $RhClL_3$ (**1**) of a phosphine ligand L trans to the chlorine atom whereas dissociation of L trans to another phosphine ligand gives the cis isomer **2b**. The results of the SCF calculations indicate that both isomers are of comparable energy.[75] Note that in both geometries the π-donor orbitals of the chlorine atom can always find a rhodium d orbital with which to interact. The cis isomer **2b** is found slightly more stable, but the difference is too small to allow any definite conclusion regarding the $RhCl(PPh_3)_2$ system because no geometry optimization has been performed: the crystal structure of the $[Rh(PPh_3)_3]^+$ system[19] shows a distorted T-shaped geometry with one P–Rh–P angle of 159.3°. Moreover the two rhodium phosphorus bond lengths of the cis isomer are probably unequal (due to a different trans influence of the chlorine and the phosphine ligands). The relative stability of these two limiting conformations may be governed by steric interactions since ^{31}P NMR experiments indicate the structure **2a** when L is a bulky ligand such as PCy_3 (Cy = cyclohexyl) in $RhClL_2$ (X = F, Cl, Br, I).[76,77]

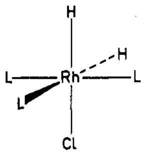


2a (3.5)

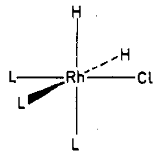


2b (0.)

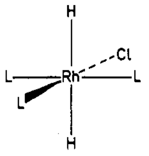
H_2RhClL_3 System. Three stereoisomers are possible for this system, namely, **3a**, **3b**, and **3c**. Their relative stabilities have been discussed previously in the context of the oxidative addition of H_2 on $RhClL_3$ (which is the first step of route II).[79]



3a (0.)



3b (11.8)



3c (16.9)

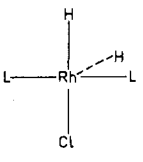
The SCF results are reported here for the sake of completeness and point to **3a** being the most stable stereoisomer. This is in agreement with the conclusions derived from NMR experiments[9,20,22,80,81] and with some X-ray crystal structures of the closely related complexes $[H_2Rh(CO)(PPh_3)_3]^+$[82] and $[H_2Re(NO)(PPh_3)_3]$.[83] The structure **3c** (with trans hydrogen atoms) has been found for $RuH_2[(C_6H_5)P(OC_2H_5)_2]_4$, but this may be a consequence of the four bulky phosphine ligands.[51] (Note, however, that this complex is predominantly cis at room temperature like several other H_2RuL_4 systems.[84])

Deviations from idealized geometries have been observed in complexes which mix bulky phosphines and small hydrides.[85] Structures of the *cis*-H_2ML_4 complexes are generally midway between an octahedron and a bicapped tetrahedron. The major distortion consists of the bending of the two axial ligands toward the hydrido ligands and increases with the bulkiness of the ligands of L.[83,85] The geometry optimization of the isomer **3a** of the $H_2RhCl(PH_3)_3$ system was performed, yielding a value of 164° for the P–Rh–P axial angle and 85 and 88° for the H–Rh–H and P–Rh–Cl equatorial angles, respectively. This rather limited deviation gives some support to our choice of idealized geometries throughout this study.

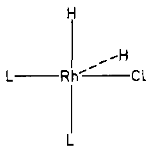
H_2RhClL_2 System. The six possible flat square-pyramid stereoisomers can be obtained from the dissociation of one of the coordinated ligands of the H_2RhClL_3 parent system. They may be classified through the nature of the apical ligand. **4a**

---

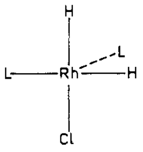
(53) L. J. Guggenberger and R. Cramer, *J. Am. Chem. Soc.*, **94**, 3779 (1972).
(54) M. O. Visscher, J. C. Huffman, and W. E. Streib, *Inorg. Chem.*, **13**, 792 (1974).
(55) V. W. Day, B. R. Stults, K. J. Reimer, and A. Shaver, *J. Am. Chem. Soc.*, **96**, 1227 (1974).
(56) R. R. Ryan, R. Schaeffer, P. Clark, and G. Hartwell, *Inorg. Chem.*, **14**, 3039 (1975).
(57) R. R. Ryan, P. G. Eller, and G. J. Kubas, *Inorg. Chem.*, **15**, 797 (1976).
(58) D. R. Russell and P. A. Tucker, *J. Chem. Soc., Dalton Trans.*, 841 (1976).
(59) R. Mason, G. Scollary, B. Moyle, K. I. Hardcastle, B. L. Shaw, and C. J. Moulton, *J. Organomet. Chem.*, **113**, C49 (1976).
(60) K. D. Tau, D. W. Meek, T. Sorrell, and J. A. Ibers, *Inorg. Chem.*, **17**, 3454 (1978).
(61) M. R. Churchill, *Inorg. Chem.*, **4**, 1734 (1965).
(62) P. G. H. Troughton and A. C. Skapski, *Chem. Commun.*, 575 (1968).
(63) A. C. Skapski and P. G. H. Troughton, *Chem. Commun.*, 666 (1969).
(64) A. Takenaka, S. K. Syal, Y. Sasada, T. Omura, H. Ogoshi, and Z. I. Yoshida, *Acta Crystallogr., Sect. B*, **32**, 62 (1976).
(65) J. P. Collman, P. A. Christian, S. Current, P. Denisevich, T. R. Halbert, E. R. Schmittou, and K. O. Hodgson, *Inorg. Chem.*, **15**, 223 (1976).
(66) The first X-ray crystal structure determination of a six-coordinate d^6 metal complex containing ethylene as one of its ligands, namely, $RuCl_2(C_2H_4)(PMe_2Ph)_2$, has been very recently reported.[67] Our chosen value for the C–C bond length is in good agreement with the reported value of 1.376 Å.
(67) L. D. Brown, C. F. J. Barnard, J. A. Daniels, R. J. Mawby, and J. A. Ibers, *Inorg. Chem.*, **17**, 2932 (1978).
(68) M. H. Sirvetz and R. E. Weston, Jr., *J. Chem. Phys.*, **21**, 898 (1953).
(69) M. Bênard, A. Dedieu, J. Demuynck, M. M. Rohmer, A. Strich, and A. Veillard, "Asterix: a system of programs for the Univac 1110", unpublished work; M. Bênard, *J. Chim. Phys.*, **73**, 413 (1976).
(70) J. Demuynck and A. Dedieu, unpublished results.
(71) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, **17**, 209 (1970).
(72) D. R. Whitman and C. H. Hornback, *J. Chem. Phys.*, **51**, 398 (1969).
(73) S. Huzinaga, *J. Chem. Phys.*, **42**, 1293 (1965).
(74) The complete list of total energies may be obtained upon request.
(75) We have also verified that a rotation of the two phosphine ligands in the trans isomer around the P–Rh–P axis hardly changed the total energy (by less than 0.001 au).
(76) H. L. M. Van Gaal and F. L. A. Van den Bekerom, *J. Organomet. Chem.*, **134**, 237 (1977).
(77) In their report on the existence of the compounds $RhH(P\text{-}t\text{-}Bu_3)_2$ and $RhH(PCy_3)_2$ Otsuka et al.[78] suggest (on the basis of NMR results) that a considerable distortion from a regular trigonal structure occurs but do not discuss these two limiting T-shaped structures.
(78) T. Yoshida, T. Okano, and S. Otsuka, *J. Chem. Soc., Chem. Commun.*, 855 (1978).
(79) A. Dedieu and A. Strich, *Inorg. Chem.*, **18**, 2940 (1979).
(80) M. A. Bennett and D. L. Milner, *J. Am. Chem. Soc.*, **91**, 6983 (1969).
(81) R. Craig Taylor, J. F. Young, and G. Wilkinson, *Inorg. Chem.*, **5**, 20 (1966).
(82) P. Bird, J. F. Harrod, and K. A. Than, *J. Am. Chem. Soc.*, **96**, 1222 (1974).
(83) G. Ciani, D. Giusto, M. Manassero, and A. Albinati, *J. Chem. Soc., Dalton Trans.*, 1943 (1976).
(84) P. Meakin, E. L. Mutterties, and J. P. Jesson, *J. Am. Chem. Soc.*, **95**, 75 (1973).
(85) B. A. Frenz and J. A. Ibers, *Transition Met. Hydrides*, 33 (1971).



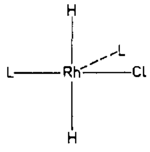
4a (0.)



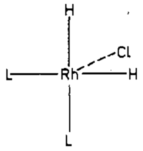
4b (12.6)



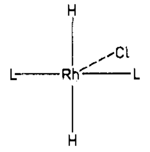
4c (18.1)



4d (37.3)

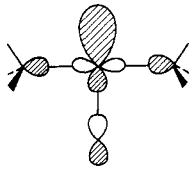


4e (28.2)

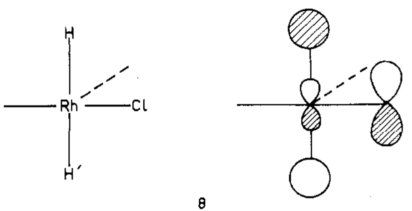


4f (34.6)

and **4b** have a hydride ligand in the apical position and can be considered as resulting from the dissociation of a phosphine ligand trans to it in **3a** and **3b**, respectively. In **4c** and **4d** the apical ligand is a phosphine ligand: this now results from the dissociation of a phosphine ligand trans to another phosphine ligand in **3a** and **3c**, respectively. Finally dissociation of a phosphine ligand trans to the chlorine atom in **3b** and **3c** leads to the stereoisomers **4e** and **4f**, respectively, leaving the chlorine atom as the apical ligand. The results of the SCF calculations indicate unambiguously that **4a** is the most stable isomer. This result is in agreement with ^{31}P NMR studies on $H_2RhCl(PPh_3)_3$ which have shown that the phosphine ligand trans to a hydride is the most labile.[6,9] The difference in stability between **4a** and **4b** (12.6 kcal/mol) cannot be traced to the relative positions of the phosphine ligands, either cis or trans to each other, since the corresponding conformations of the $RhClL_2$ system are roughly of the same energy. However they differ slightly through their lowest unoccupied molecular orbital (LUMO). For the trans stereoisomer **2a** of $RhClL_2$ the LUMO (shown in **7**) is more polarized toward the in-plane missing site and slightly lower in energy. The stabilizing interaction with the basal hydride ligand in H_2RhClL_2 is therefore probably enhanced when H is trans to Cl (as in **4a**). Both isomers **4d** and **4f**, which are of high energy, are characterized by two hydrogen atoms trans to each other and cis to the chlorine atom. This results in the highest occupied molecular orbital (HOMO, **8**) being rather destabilized since it consists mainly of an unfavorable interaction between the out-of-plane combination S_H–$S_{H'}$ with the 4p orbital of the rhodium atom *and* the 3p orbital of the chlorine atom.



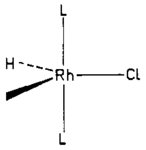
7



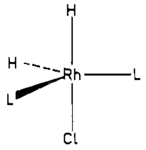
8

The SCF results also point to a general trend in the stability of the H_2RhClL_2 stereoisomers when the apical ligand is varied: there is an increase of destabilization in the series H, PH_3, and Cl (this is specially true for **4a**, **4c**, and **4e**). This may be related to H being a better σ donor than PH_3 and Cl being a cylindrical π donor.[86] In the crystal structure of $RhI_2(PPh_3)_2(CH_3)$ the methyl ligand, which is a better σ donor than the triphenylphosphine ligand, is found at the apex of a square pyramid.[62] The preference for a basal position in the case of a π-donor ligand has also been found through Fenske–Hall type calculations performed on $Mn(CO)_5Br$.[87] The ordering found in Table III may be modified if bulky phosphine ligands are used: from NMR and IR spectra trans equivalent phosphine ligands and two equivalent hydridic hydrogens have been inferred for H_2RhClL_2 with L = $P(t\text{-}Bu_3)$[20] and L = PCy_3[21] (Cy = cyclohexyl). This corresponds to the structure **4f**. However a trigonal-bipyramidal structure has also been proposed for this latter complex and the corresponding iridium complex.[24] The complex $H_2RhCl(P(t\text{-}Bu_3))_2$ has been reported[88] to have a distorted trigonal-bipyramidal configuration with a bent P–Rh–P axial bond (but no further details were given).

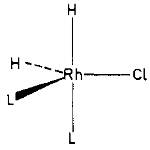
We have tested this possibility for our $H_2RhCl(PH_3)_2$ model system by carrying out calculations on some trigonal-bipyramidal stereoisomers[89] **4g**, **4h**, and **4i** which are also of interest in connection with intramolecular rearrangements between **4a**, **4b**, and **4c** (see the Discussion). They are of higher energy than the **4a** isomer, as it would be expected[37,90] for d^6 five-coordinate complexes.



4g (29.4)

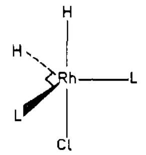


4h (45.8)

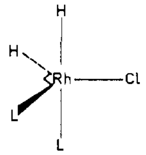


4i (43.4)

We also considered the two stereoisomers **4j** and **4k** (of pseudosymmetry C_{2v}) since these geometries may be preferred (for a metal d^6 electronic configuration[87,93]) over the trigonal-bipyramidal geometries **4h** and **4i**, respectively, and may



4j (25.6)



4k (22.8)

---

(86) A. Rossi and R. Hoffmann, *Inorg. Chem.*, **14**, 365 (1975).

(87) D. L. Lichtenberger and T. L. Brown, *J. Am. Chem. Soc.*, **100**, 366 (1978).

(88) Reference 42 from S. Otsuka, T. Yoshida, M. Matsumoto, and K. Nakatsu, *J. Am. Chem. Soc.*, **98**, 5850 (1976).

(89) Preliminary extended Hückel calculations which were carried out on all possible trigonal-bipyramidal and flat square-pyramidal stereoisomers of $H_2RhCl(PH_3)_2$ indicated that the trigonal-bipyramidal isomers were less stable than **4a** by at least 32 kcal/mol.

(90) Theoretical calculations performed on the $Cr(CO)_5$ system with different degrees of sophistication (with the angular overlap model,[36a] extended Hückel calculations,[36b] and ab initio calculations at the SCF[91] and at the CI level[92]) predict a square-pyramid geometry for this system in the singlet ground state. However since ligand–ligand repulsions favor a trigonal-bipyramid arrangement, one could think that bulky ligands might lead to this geometry.

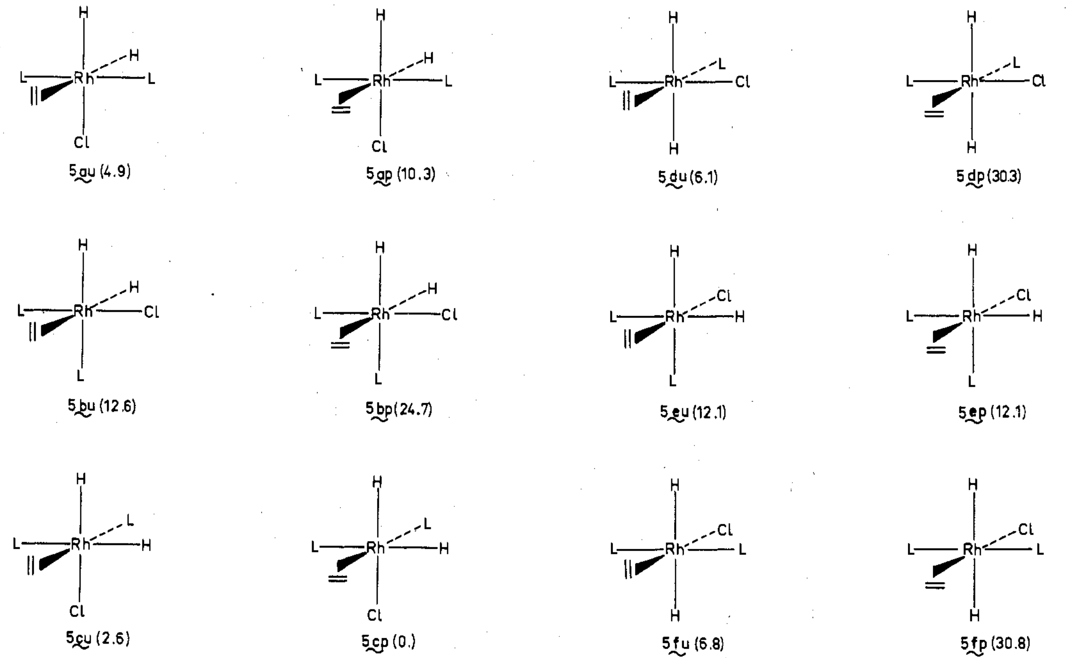
(91) J. Demuynck, A. Strich, and A. Veillard, *Nouv. J. Chim.*, **1**, 217 (1977).

(92) P. J. Hay, *J. Am. Chem. Soc.*, **100**, 2411 (1978).

(93) This geometry was first proposed by Burdett et al.[36a] on the basis of extended Hückel calculations on $M(CO)_5$. CI calculations on $Cr(CO)_5$ also show this behavior for the $^1A_1$ electronic state.[94]

(94) See Table III and Figure 9 of ref 92.

Chart I



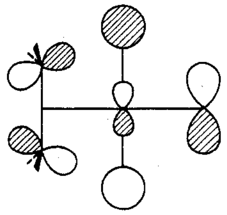
5au (4.9)
5ap (10.3)
5du (6.1)
5dp (30.3)
5bu (12.6)
5bp (24.7)
5eu (12.1)
5ep (12.1)
5cu (2.6)
5cp (0.)
5fu (6.8)
5fp (30.8)

therefore be transition states in intramolecular rearrangements between the square-pyramid isomers. The results of the corresponding SCF calculations show that this turns out to be the case but that these two isomers are still higher in energy than the **4a** isomer by at least 23 kcal/mol.[95]

$H_2RhClL_2(C_2H_4)$ System. The coordination of C_2H_4 to the six flat square-pyramid stereoisomers of $H_2RhCl(PH_3)_2$ gives rise to 12 geometries (hereafter denoted **5au**–**5fp** (Chart I)) for the $H_2RhCl(PH_3)_2(C_2H_4)$ system. We have considered only the eclipsed geometries (eclipsed meaning that C_2H_4 is eclipsed with respect to two basal ligands of the $H_2RhCl(PH_3)_2$ fragment) since they have been shown to be more stable than the staggered ones both on experimental[96] and on theoretical[97] grounds. For each $H_2RhCl(PH_3)_2$ fragment there are therefore two possible orientations for the incoming ethylene ligand which we shall denote upright (u) and planar (p).

The total energies and the relative stabilities of these 12 stereoisomers are controlled by three main factors: the steric interaction and the two orbital interactions of the Dewar–Chatt–Duncanson model,[98] one between the $3d_{z^2}$ empty orbital of the $H_2RhCl(PH_3)_2$ fragment and the filled π_g orbital of C_2H_4 and one between the filled d_π orbital of the $H_2RhCl(PH_3)_2$ fragment and the π_u empty orbital of C_2H_4. Separating the three factors is a very difficult task. We note simply that in many instances the u conformers are more stable than their p analogues, and we trace this trend to less steric repulsion: all the u conformers have a hydride ligand (which is not of high steric demand) in the plane of the ethylene ligand. In the case of the isomers **5cu** and **5cp** one will notice that they both have a hydride ligand in the plane of the ethylene ligand, the other ligand being either PH_3 or Cl which are probably similar with respect to steric demand. The difference in energy is small (2.6 kcal/mol) and may not be significant, since no geometry optimization was performed. Moreover the ordering may also change since more bulky phosphine ligands (like PPh_3) would probably favor the u conformation.

One may also ask why the two stereoisomers **5du** and **5fu** are not highly destabilized (since they have two trans hydrogen atoms cis to a chlorine atom) as it is the case for the five-coordinate parent complexes. There is first a favorable situation in terms of steric interactions since the ethylene lies in the plane of two hydride ligands. Moreover the HOMO of the $H_2RhCl(PH_3)_2$ fragment, which is also the HOMO in the ethylene adduct $H_2RhCl(PH_3)_2(C_2H_4)$, is stabilized by the π_u empty orbital of C_2H_4 as shown in **9** for **5fu**. Note that the corresponding p isomers where these two effects no longer operate are highly destabilized.



9

From the SCF results and taking into account that we did not optimize the geometries, the most stable stereoisomer for the $H_2RhCl(PH_3)_2(C_2H_4)$ intermediate may be **5cp**, **5cu**, **5au**, **5du**, or **5fu**, originating from **4c**, **4a**, **4d**, and **4f**. We shall take advantage of this origin in the discussion to predict the geometry of this intermediate in the catalytic cycle.

$HRhCl(PH_3)_2(C_2H_5)$ System. The nine possible stereoisomers[99] corresponding to a flat square pyramid for this intermediate are **6a**–**6i** and may be classified (as for the $H_2RhCl(PH_3)_2$ system) through the nature of the apical ligand. The trends found for the other flat square-pyramid system $H_2RhCl(PH_3)_2$ are also operative here: destabilization when

---

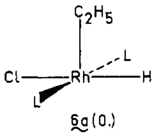
[95] The same result was obtained through preliminary extended Hückel calculations. Other pseudo-C_{2v} geometries were also considered and found to be higher in energy than the **4a** geometry.

[96] (a) C. G. Kreiter and H. Strack, *Z. Naturforsch. B*, **30**, 748 (1975); (b) U. Koemm, C. G. Kreiter, and H. Strack, *J. Organomet. Chem.*, **148**, 179 (1975).

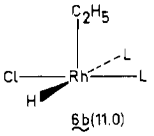
[97] T. A. Albright, R. Hoffmann, J. C. Thibeault, and D. L. Thorn, *J. Am. Chem. Soc.*, **101**, 3801 (1979).

[98] (a) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C79 (1951); (b) J. Chatt and L. Duncanson, *J. Chem. Soc.*, 2339 (1953).

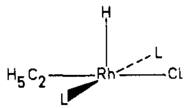
[99] For each isomer the orientation of the alkyl ligand was chosen to minimize the steric contacts: for **6a** and **6b** the C–C bond was eclipsing the Rh–H bond and for all other isomers (where C_2H_5 is in a basal position) the C–C bond staggered the apical bond (eclipsing the apical bond resulted in a destabilization of 4.1 kcal/mol for the **6c** isomer).



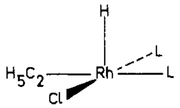
6a (0.)



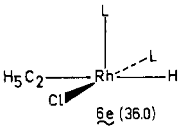
6b (11.0)



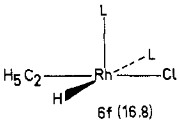
6c (0.3)



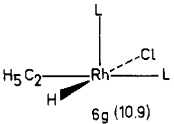
6d (6.7)



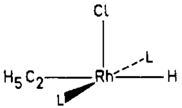
6e (36.0)



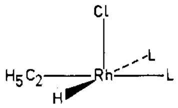
6f (16.8)



6g (10.9)



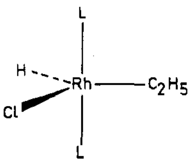
6h (35.3)



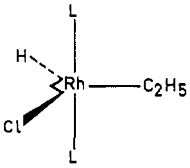
6i (21.8)

going in the series strong σ donor (H^-, $C_2H_5^-$), moderate σ donor (PH_3), and π donor (Cl^-). Also the isomers which have two strong σ donors trans to each other and cis to a chlorine atom (i.e., **6e** and **6h**) are strongly destabilized.

We have considered two other stereoisomers which may be of interest in connection with the determination of the reaction path leading from $H_2RhClL_2(C_2H_4)$ to $HRhClL_2(C_2H_5)$. The trigonal-bipyramidal stereoisomer **6j** may be also an intermediate or a transition state in a Berry pseudorotation which could lead from **6a** to **6c** or to **6h**. As expected,[37,90] this isomer is found to be higher in energy (by about 28 kcal/mol) than the most stable square-pyramidal isomers **6a** and **6c**. A somewhat similar destabilization (31 kcal/mol) has been found for the isomer **6k** of pseudosymmetry C_{2v}.



6j (28.2)



6k (30.8)

Discussion

We shall now attempt to use the preceding results to derive some insight into the mechanistic details of the hydrogenation reaction catalyzed by $RhClL_3$. Our discussion is based on the relative stabilities of the possible intermediates and therefore deals with the thermodynamics of the reaction rather than with its kinetics. Two schemes (hereafter referred as Schemes II and III) are tentatively put forth to describe the stereochemical course of the hydrogenation process depending on the mutual position of the two phosphine ligands—trans for Scheme II and cis for Scheme III) in the intermediates **2**, **4**, and **5**.

Both pathways shown in Scheme II have the **4a** and the **5au** intermediates in common. The first one (commonly called associative pathway, route II of Scheme I) involves the oxidative addition of H_2 on $RhClL_3$ yielding H_2RhClL_3 and is followed by a dissociation of a phosphine ligand. The present calculations indicate that the preferred geometries of the H_2RhClL_3 and H_2RhClL_2 systems are **3a** and **4a**, respectively (the corresponding solvated analogue of **4a**, $H_2RhClL_2(S)$, would then be **11a**), in complete agreement with the well-established experimental results. From this result it can be suggested (cf. Halpern et al.[15]) that **5au** is the structure for the dihydrido–olefin complex obtained either by the coordination of the olefin to **4a** or by the displacement of the solvent molecule in **11a** by an olefin. This is confirmed by our calculations which show that **5au** is one of the most stable stereoisomers of the $H_2RhCl(PH_3)_2(C_2H_4)$ system.

The second pathway (the so-called dissociation pathway, route I of Scheme I) consists in a dissociation of one phosphine ligand from $RhClL_3$ followed by the oxidative addition on the tricoordinate complex $RhClL_2$. In Scheme II we have considered the dissociation of the phosphine ligand (L) trans to the chlorine ligand which gives the trans isomer **2a** for $RhClL_2$. This structure has been found to be slightly less stable than the cis structure **2b** for the $RhCl(PH_3)_2$ system. However we have already pointed out that no geometry optimization was performed. In addition the interconversion between the cis and trans T-shaped structures of the $[HPt(PH_3)_2]^+$ system (which is isoelectronic to $RhCl(PH_3)_2$) via the Y-shaped structure has been shown (through EH calculations) to be an easy rearrangement.[32] Structure **2a** may therefore be favored on steric grounds for nonchelating phosphine ligands which are much bulkier than PH_3 (PPh_3 and PH_3 have ligand cone angles which are 145 and 87°, respectively).[100] The H_2 oxidative addition on **2a** may be either cis or trans. The trans addition would lead to the isomer **4f** for H_2RhClL_2 which is very high in energy. Moreover the least-motion pathway for the trans addition of **2a** is symmetry forbidden although a non-least-motion pathway could be envisioned.[101] The cis addition (keeping the $RhClL_2$ skeleton rigid) leads to isomer **4a** which is also obtained through the associative pathway discussed previously.

Solvation of **2a**[102] would likely lead to the isomer **10a** for $RhClL_2(S)$. In this isomer the solvent S is trans to the chlorine ligand. Oxidative addition of H_2 on **10a** will be cis[103] and the geometry **11a** is expected to result (by analogy to the oxidative addition on $RhClL_3$[79]). The isomer **11a** is the solvated analogue of **4a**, and displacement of the solvent by the olefin will yield **5au**.

The next step after the coordination of the olefin is the transfer of the first hydrogen atom. We shall assume (and this will hold for both Schemes II and III) that the transferred hydrogen atom is in the plane of the coordinated olefin[22,32] and is cis to it (in **5au** both hydrogen atoms are in the plane of the olefin). We can then think of two different processes, either migration of the hydrogen atom toward the olefin or insertion of the olefin into the Rh–H bond. Starting from **5au** (Scheme II) migration of the hydrogen ligand would lead to the **6h** isomer of $HRhClL_2$(alkyl) which has been found to be very high in energy. In this structure the second hydrogen atom is trans to the coordinated alkyl, and this stereochemistry, as pointed out by Schrock and Osborn[104] for cationic complexes, would not permit facile reductive elimination of the alkane in the next step unless some rapid rearrangement occurs. Moreover this process appears (from preliminary calculations[35]

---

[100] C. A. Tolman, *Chem. Rev.*, **77**, 313 (1977).

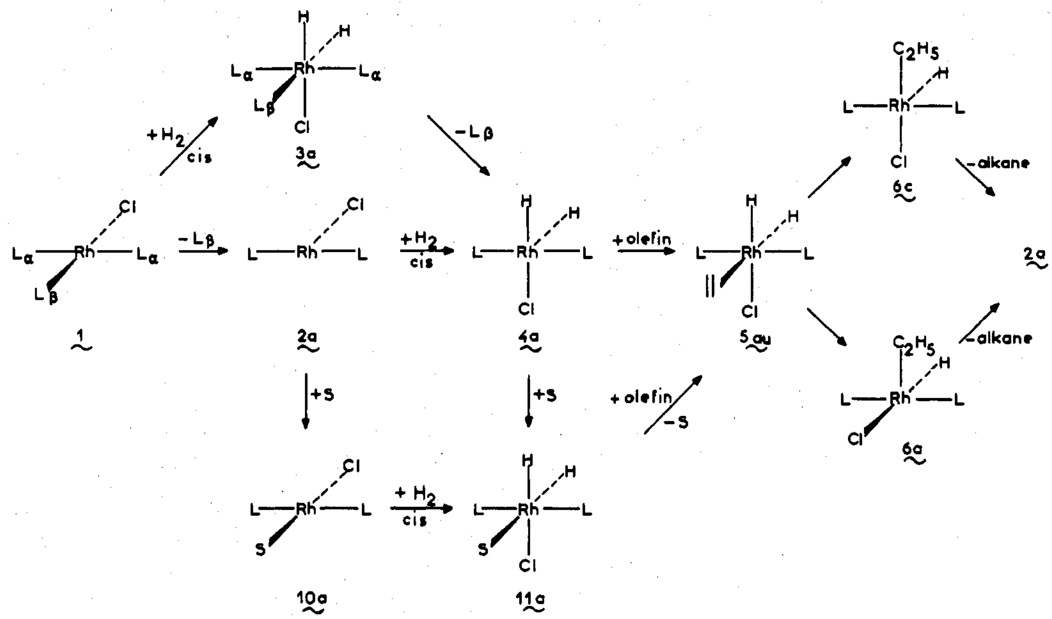
[101] As an example of a nonleast motion pathway operating, see J. M. Howell, *J. Am. Chem. Soc.*, **99**, 7447 (1977).

[102] M. H. J. M. de Croon, P. F. M. T. van Nisselroij, H. J. A. M. Kuipers, and J. W. E. Coenen, *J. Mol. Catal.*, **4**, 325 (1978).

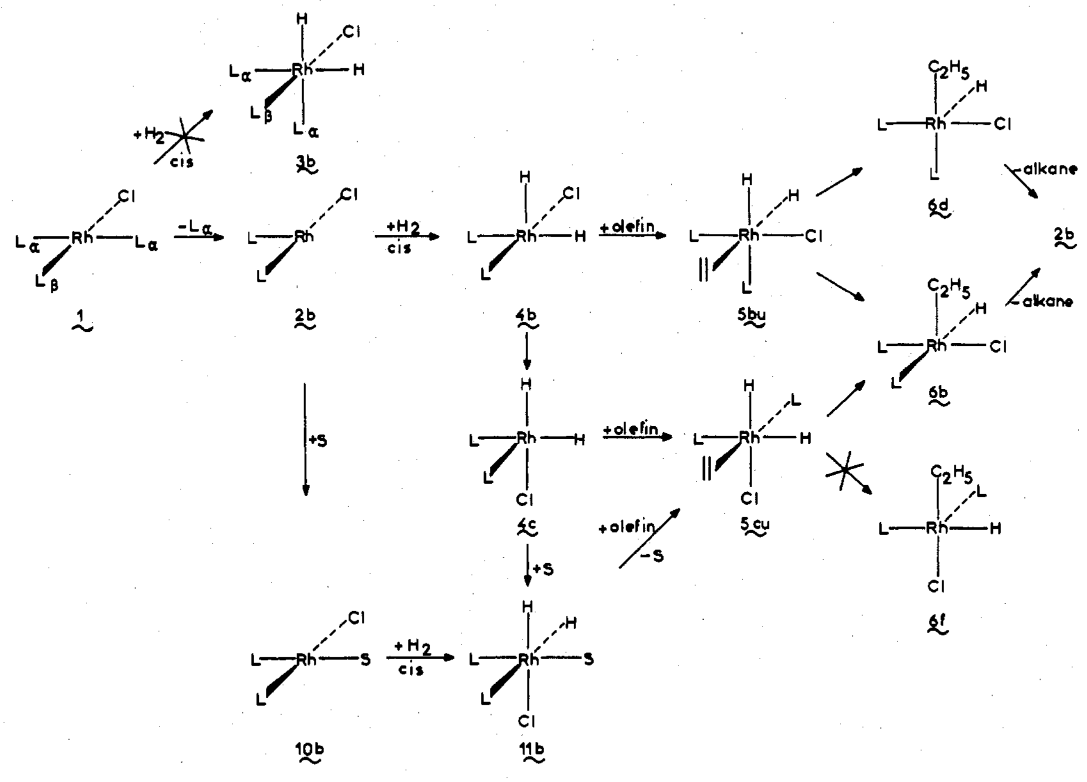
[103] (a) J. P. Collmann, *Acc. Chem. Res.*, **1**, 136 (1968); (b) L. Vaska, *ibid.*, **1**, 335 (1968); (c) J. Halpern, *ibid.*, **3**, 386 (1970); (d) R. G. Pearson, "Symmetry Rules for Chemical Reactions", Wiley, New York, 1976, pp 292–4.

[104] R. R. Schrock and J. A. Osborn, *J. Am. Chem. Soc.*, **98**, 2134 (1976).

Scheme II



Scheme III



on the reaction path between $H_2RhCl(PH_3)_2(C_2H_4)$ and $HRhCl(PH_3)_2(C_2H_5)$) to be energetically very unfavorable. This is no longer true for the insertion of the olefin into the Rh–H bond leading to the **6c** isomer (when keeping the rest of the skeleton of the molecule rigid): the process is exothermic (by about 24 kcal/mol)[105] and **6c** is one of the most stable isomers for the $HRhClL_2$(alkyl) system. This isomer has been suggested by Halpern et al.[15] One has to note however that the **5au** isomer of $H_2RhCl(PH_3)_2(C_2H_4)$ and the isomers **6j** and **6k** of $HRhCl(PH_3)_2(C_2H_5)$ are roughly of the same energy. One can therefore conceive another reaction path in which some rearrangement in the insertion plane (involving the chlorine ligand and the second hydrogen atom) would occur simultaneously with the insertion. The corresponding transition state would probably have a geometry similar to **6j** or **6k**, and the resulting alkyl intermediate would be **6a** (which has been computed to have the lowest energy for the $HRhCl(PH_3)_2(C_2H_5)$ system). **6a** and **6c** are too close in energy to make a definite choice between them on energy grounds only. Both have the alkyl ligand cis to the second hydrogen atom which is a favorable arrangement for the second hydrogen transfer. Clearly only the determination of the reaction path will indicate whether **6a** or **6c** is the geometry of the alkyl intermediate when the hydrogenation process is going along Scheme II. Such a determination is now in progress.[35]

---

[105] We consider here a geometry where the C–C bond eclipses the Rh–H bond.[99]

Only the dissociative pathway (route I) needs to be considered in Scheme III (we have shown in a previous paper[79] that the corresponding associative pathway was unlikely). Dissociation of the phosphine ligand trans to another phosphine (L_α in Scheme III) gives the cis isomer **2b** for $RhClL_2$. As with **2a**, trans addition of H_2 on this system should probably be ruled out since it would lead to the isomer **4d** of H_2RhClL_2 which is very high in energy. The cis addition yields the isomer **4b**. This isomer has been computed to be 13 kcal/mol higher in energy than **4a**. Moreover the olefin–dihydrido intermediate **5bu** is also rather high in energy. The five-coordinate complex H_2RhClL_2 may rather undergo an intramolecular rearrangement from **4b** to **4a**. However this cannot be achieved through a single-step process, either through the inverse of a Berry pseudorotation or through an intermediate (more likely a transition state) of C_{2v} pseudosymmetry but may be done through a two-step process, **4c** being an intermediate between **4b** and **4a**. The SCF results indicate that this rearrangement would take place through the sequence **4b** $\rightleftarrows$ **4k** $\rightleftarrows$ **4c** $\rightleftarrows$ **4j** $\rightleftarrows$ **4a**, the highest energy difference being 10.2 kcal/mol between **4b** and **4k** (somewhat greater than the 7.5 kcal/mol between **4c** and **4j**). Coordination of the olefin to either **4c** or **4a** would yield respectively the **5cu** and **5au** isomers of the H_2RhClL_2(olefin) intermediate which are more stable than **5bu**.

There is less ambiguity when the solvent molecule replaces the dissociated phosphine ligand. The cis oxidative addition on **10b** will likely yield the **11b** isomer (this is also based on the analogy with the oxidative addition on $RhClL_3$[79]). Displacement of the solvent molecule by the olefin then leads to the **5cu** isomer. Experimental work on asymmetric hydrogenation,[106] where the catalyst is generated in situ from a rhodium complex with a chelating diphosphine ligand[107] or from a dirhodium species,[108–110] has led us to postulate the structure **5cu** for the olefin–dihydrido intermediate. (As already pointed out by Kagan,[106a] the **5cu** isomer is chiral even if the ligands are achiral. Note that this is not true for the **5au** isomer.) This structure was also deduced from space-filling molecular models for the (+)(DIOP)$RhClH_2$(olefin) intermediate[111] (the DIOP ligand is a chelating diphosphine[112]). Since a chelating diphosphine imposes the two L's to be cis to each other, the isomers **4a** or **11a** which have two trans phosphine ligands cannot be formed.[113] Our calculations, which give **5cu** as one of the most stable isomers, give therefore support to these proposals.[115]

As in the case of **5au**, hydrogen transfer from **5cu** may occur through hydrogen migration or olefin insertion. Hydrogen migration would lead to the isomer **6i** which is high in energy (as in the case of **5au**, the migration process must be rather endothermic). Insertion of the olefin yields either **6f** (keeping the rest of the molecule rigid) or **6b** (in the case of a simultaneous relaxation of the two in-plane ligands). The latter isomer **6b** is to be preferred over **6f** on the basis of the relative stabilities (the insertion process is then computed to be exothermic by about 15 kcal/mol). It is interesting to note that since the second hydrogen was out of the insertion plane in **5cu** (and on the contrary to **5au**), one has to postulate a rotation around the Rh–C(alkyl) bond prior to the second hydrogen transfer.

Conclusion

The limitations of this study are obvious: since it was not possible to optimize all structures, idealized geometries were kept throughout the calculations. As a consequence, we have not reported energies of reaction. Also the use of PH_3 (which has the smallest ligand cone angle[100]) as a model of the actual phosphine ligand may not give rise to the same steric effects. It has also been suggested that the utility of a triphenylphosphine ligand over other phosphines might be the result of the stabilization of the $RhClL_2$ intermediate through partial metal–phenyl group interaction.[19] We have already pointed out that our reasoning is based on the relative stabilities for each isomer although we are well aware that a more complete discussion, in particular the comparison with the known kinetic data, requires the determination of the reaction path or at least the transition state (if any) for each elementary step of the whole reaction pathway.

In spite of these limitations the SCF ab initio results do agree with the experimental results for the determination of the structure of the H_2RhClL_3 (**3**) and H_2RhClL_2 (**4**) intermediates. This gives us some confidence for predicting the unknown structures of some other intermediates. We have pointed out that depending on the nature of the phosphine ligand (i.e., chelating or not) and on the precursor of the catalyst, one could expect different structures for the olefin–dihydrido intermediate H_2RhClL_2(olefin) and alkyl–hydrido intermediate $HRhClL_2$(alkyl). For the Wilkinson complex $RhCl(PPh_3)_3$ and other complexes $RhClL_3$, where L is a nonchelating phosphine, our calculations favor the structures **5au** for H_2RhClL_2(olefin) and **6a** or **6c** for $HRhClL_2$(alkyl). When $RhClL_2$ is the actual catalyst and when its structure is restricted either by formation or by a chelating diphosphine, the corresponding structures seem to be **5cu** and **6b**. We have also shown that the transfer of the first hydrogen cannot be reduced to a simple hydride migration but is rather a complex process which probably involves some rearrangements of the nonreacting ligands.[116]

Further theoretical work is needed first on the reactivity of $RhClL_3$ and $RhClL_2$ toward the oxidative addition of H_2 to determine and compare factors accounting for the feasibility of the reaction on these two complexes. The addition of the olefin to $RhClL_2$ and to the corresponding cationic complex $[RhL_2]^+$ is also of interest since it has recently been inferred that the substrate route was operating in the case of a chelating diphosphine ligand.[117] One should extend the present study to incorporate kinetic aspects especially in determining the reaction path between $H_2RhCl(PH_3)_2(C_2H_4)$ and $HRhCl(PH_3)_2(C_2H_5)$ (the hydrogenation of the coordinated olefin has been found to be the rate determining step for the Wilkinson complex[14–16]). This would allow us to choose between **6a** and

---

(106) For a review on asymmetric hydrogenation see: (a) H. B. Kagan, *Pure Appl. Chem.*, **43**, 401 (1975); (b) J. D. Morrison, W. F. Masler, and M. K. Neuberg, *Adv. Catal.*, **25**, 81 (1976); (c) H. B. Kagan and J. C. Fiaud, *Top. Stereochem.*, **10**, 175 (1978).

(107) (a) H. B. Kagan and T. P. Dang, *J. Am. Chem. Soc.*, **94**, 6429 (1972); (b) T. P. Dang, J. C. Poulin, and H. B. Kagan, *J. Organomet. Chem.*, **91**, 105 (1975); (c) S. Brunie, J. Mazan, N. Langlois, and H. B. Kagan, *ibid.*, **114**, 225 (1976).

(108) W. S. Knowles, M. J. Sabacky, and B. D. Vineyard, *Chem. Commun.*, 10 (1972).

(109) L. Horner, H. Siegel, and H. Buthe, *Angew. Chem., Int. Ed. Engl.*, **7**, 942 (1968).

(110) J. D. Morrison, R. E. Burnett, A. M. Aguiar, C. J. Morrow, and C. J. Phillips, *J. Am. Chem. Soc.*, **93**, 1301 (1971).

(111) R. Glaser, *Tetrahedron Lett.*, 2127 (1975).

(112) DIOP = 2,3-*O*-isopropylidene-1,4-bis(diphenylphosphino)butane-2,3-diol.[107]

(113) When a chelating triphosphine ligand has been used, no catalytic activity of $RhClL_3$ under mild conditions was observed. This was explained by the lack of a vacant site obtained through the dissociation of a phosphine.[114]

(114) D. L. Dubois and D. W. Meek, *Inorg. Chim. Acta*, **19**, L29 (1976).

(115) We have restricted ourselves to the case of neutral intermediate, i.e., noncationic.

(116) For an intramolecular reaction involving a transition-metal complex the terminology "hydride migration and olefin insertion" refers to the structure of the product compared to that of the starting complex once the reaction has been completed rather than to the actual movement either of the hydride or of the olefin. This is especially true when some rearrangement of the nonreacting ligands occurs.

(117) J. Halpern, D. P. Riley, A. S. C. Chan, and J. J. Pluth, *J. Am. Chem. Soc.*, **99**, 8055 (1977).

6c for the structure of the alkyl intermediate (when L is a nonchelating phosphine) and to rationalize the substituent effects (on L and the olefin) by singling out the factors which control the corresponding energy barrier. Work along these lines is currently in progress.

Acknowledgment. Calculations have been carried out at the Centre de Calcul du CNRS in Strasbourg-Cronenbourg. We thank the staff of the Centre for their cooperation. This work has been supported through A.T.P. No. 3790 of the CNRS.

Registry No. **1** (L = PPh_3), 14694-95-2; **2**, 72152-06-8; **3a**, 71213-98-4; **3b**, 71213-97-3; **3c**, 71171-41-0; **4a**, 72152-07-9; **4b**, 72173-73-0; **4c**, 72173-74-1; **4d**, 72173-75-2; **4e**, 72173-76-3; **4f**, 72173-77-4; **4g**, 72173-78-5; **4h**, 72173-79-6; **4i**, 72173-80-9; **5a**, 72152-08-0; **5b**, 72257-15-9; **5c**, 72257-16-0; **5d**, 72257-17-1; **5e**, 72257-18-2; **5f**, 72257-19-3; **6a**, 72152-09-1; **6b**, 72173-81-0; **6c**, 72173-82-1; **6d**, 72173-83-2; **6e**, 72173-84-3; **6f**, 72173-85-4; **6g**, 72173-86-5; **6h**, 72173-87-6; **6i**, 72173-88-7; **6j**, 72173-89-8.

Contribution from the Department of Chemistry and Materials Research Center,
Northwestern University, Evanston, Illinois 60201

Octakis(alkylthio)tetraazaporphyrins

CHARLES J. SCHRAMM and BRIAN M. HOFFMAN*

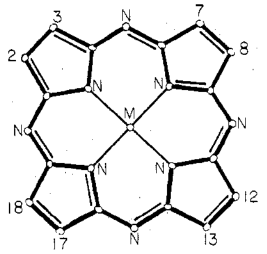
Received July 30, 1979

Free-base and metal-substituted 2,3,7,8,12,13,17,18-octakis(methylthio)tetraazaporphyrins have been synthesized and characterized. The Mg, Ni, and Cu derivatives are discussed. The method of preparation presents a synthetic procedure for a range of (alkylthio)- or (arylthio)tetraazaporphyrins. Electron paramagnetic resonance measurements are reported for copper octakis(methylthio)tetraazaporphyrin ($g_{\parallel} = 2.14$, $g_{\perp} = 2.06$, $\langle a_{Cu} \rangle = 95$; $A_{\parallel}^{Cu} = 215$; $A_N = 19.9$, $C_N = 15.0$) and for the $S = 1$ dimer ($D = 400$ G).

The template reaction, in which four molecules of phthalonitrile condense about a divalent metal ion to form a metallophthalocyanine, M(Pc), is well-known. Metallotetraazaporphyrins, M(TAP), can be prepared by the analogous template condensation of maleonitrile.[2] However, peripherally substituted tetraazaporphyrins are synthesized much more conveniently than the parent macrocycle because disubstituted maleic dinitriles are more stable than the parent compound. Since the substituted tetraazaporphyrins may prove valuable as pigments[3] or catalysts,[4] a convenient route to a diverse set of such complexes is desirable.

The action of alkyl or aryl iodides or diiodides on disodium maleonitrile, $Na_2(mnt)$,[5] yields a wide variety of cis-substituted maleic dinitriles. These provide a rich source of starting materials for the synthesis of substituted tetraazaporphyrins. A few cis-substituted maleic dinitriles, notably 1,2-dicyano-3,6-dithiacyclohexene[6] and 1,2-dicyano-3,6-dithia-4-phenylcyclohexene,[7] have been condensed to form substituted tetraazaporphyrins, respectively the free base and copper derivatives. However, preparations of such relatively unstable metal derivatives as the magnesium macrocycle from free-base tetraazaporphyrin or of any other metal derivative from the stable copper complex are not trivial procedures. Thus, the above syntheses do not present a convenient route to the full variety of metal-substituted tetraazaporphyrins.

We find that the template condensation of disubstituted maleonitriles in the presence of magnesium propoxide leads directly to the magnesium derivative of the octasubstituted tetraazaporphyrins and that these materials provide a convenient route to the preparation of parent macrocycle and thence to other metal derivatives. Several disubstituted maleonitriles have been condensed by this procedure: 1,2-dicyano-3,6-dithiocyclohexane, 1,2-dicyano-3,6-dithiocyclopentane, and 1,2-dicyano-1,2-bis(methylthio)ethylene. We illustrate the technique by presenting the synthesis and properties of metal 2,3,7,8,12,13,17,18-octakis(methylthio)tetraazaporphyrin, M(OMTTAP), where M = Mg, "H_2", Cu, or Ni.



M(OMTTAP)

Experimental Section

All solvents and chemicals used in the experiments were obtained commercially and were of reagent grade. They were used without further purification except for drying with molecular sieves.

Visible spectra were recorded on a Beckman ACTA III spectrophotometer in the range of 350-750 nm. X-Band electron paramagnetic resonance, EPR, measurements were carried out by using a highly modified Varian E-4 X-band EPR spectrometer, with 100-kHz field modulation. For **g**-tensor measurements, 2,2-diphenyl-1-picrylhydrazyl (DPPH, $g = 2{,}0036$) was used to provide absolute field calibration. The cavity resonance frequency was measured to an accuracy of 5 ppm by a transfer oscillator technique.

Elemental analyses were performed by Miss H. Beck, Northwestern Analytical Services Laboratory.

Synthesis. **$C_6H_6N_2S_2$.** 1,2-Dicyano-1,2-bis(methylthio)ethylene (**I**) was prepared by reacting methyl iodide with Na_2mnt by the method of Bähr et al.[8]

Mg(OMTTAP). Magnesium, 1.0 g (41 mmol), was dissolved in 20 mL of refluxing 1-propanol during 8 h with the aid of a crystal of iodine as initiator. To the resulting magnesium propoxide suspension was added 3.5 g (21 mmol) of I as a slurry in 40 mL of 1-propanol. The combined mixture was refluxed for 18 h. The reaction mixture was filtered hot. The residual solid was discarded after washing with

---

(1) A. B. P. Lever, *Adv. Inorg. Chem. Radiochem.*, **7**, 28-114 (1965).
(2) R. P. Linstead and M. Whalley, *J. Chem. Soc.*, 4839-45 (1952).
(3) H. France, Wm. O. Jones, and Imperial Chemical Industries Ltd., British Patent 689387 (1953); *Chem. Abstr.*, **47**, 9023*h* (1953).
(4) M. Kaneko, M. Georg, and Nissan Chemical Industries, Ltd., Japan Kokai 75132098 (1975); *Chem. Abstr.*, **84**, 74883 (1975).
(5) A. Davison and R. H. Holm, *Inorg. Synth.*, **6**, 8-25 (1967).
(6) V. G. Manecke and D. Worhle, *Makromol. Chem.*, **120**, 176-91 (1968).
(7) W. E. Hahn and A. Kujawski, *Soc. Sci. Lodz., Acta Chim.*, **16**, 129-36 (1971).
(8) G. Bahr and G. Schleitzer, *Chem. Ber.*, **90**, 438-43 (1957).

0020-1669/80/1319-0383$01.00/0