

Dynamic, reactivity and catalytic behavior of pseudo-undercoordinated ruthenium and rhodium complexes stabilized by intramolecular solvents¹

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Abstract

The fluxional behavior of pseudo-undercoordinated ruthenium complexes provided with bifunctional ether–phosphine ligands which compete for a common coordination site at the metal center is reviewed. The quantitative determination of this dynamic exchange by temperature-dependent ³¹P NMR spectroscopy and line-shape analyses gives access to kinetic and thermodynamic data. From these, valuable information concerning the different chelating

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¹Dedicated to Professor Dr. Kees Vrieze on the occasion of his 25th anniversary as professor of inorganic chemistry.

abilities of various ether–phosphines is available in dependence on both O-nucleophilicity and phosphorus basicity. Based on these experimental results, appropriate (ether–phosphine)-ruthenium and rhodium complexes are presented showing high reactivity toward the activation of small molecules like hydrogen, sulfur dioxide, carbon dioxide, carbon disulfide, ethene and phenylacetylene. Moreover, their catalytic properties with respect to hydrogenations, carbonylations and carbon dioxide hydrogenation are discussed.

1. Introduction

Coordinatively unsaturated transition metal complexes play a crucial role in catalytically operating processes, because they represent very reactive intermediates promoting several important steps, e.g. oxidative addition or simple substrate complexation. A remarkable improvement concerning the isolation and thus the examination of such undercoordinated species has been achieved by the introduction of bifunctional or so-called ‘hemilabile’ [1] ether–phosphines (O,P) instead of ‘classical’ tertiary phosphines [2]. These O,P ligands are provided with oxygen atoms incorporated in open-chain or cyclic ether moieties which form a weak metal–oxygen contact while the phosphorus atom is strongly coordinated to the central atom. From this ‘hemilabile’ nature, it has been reported that the ether oxygen donor may be regarded as an intramolecular solvent molecule stabilizing the empty coordination site and due to the chelate effect these complexes are much more stable than simple solvent adducts [2]. In contrast, the easy cleavage of the metal–oxygen bond guarantees a high reactivity of such complexes in the case of an incoming substrate.

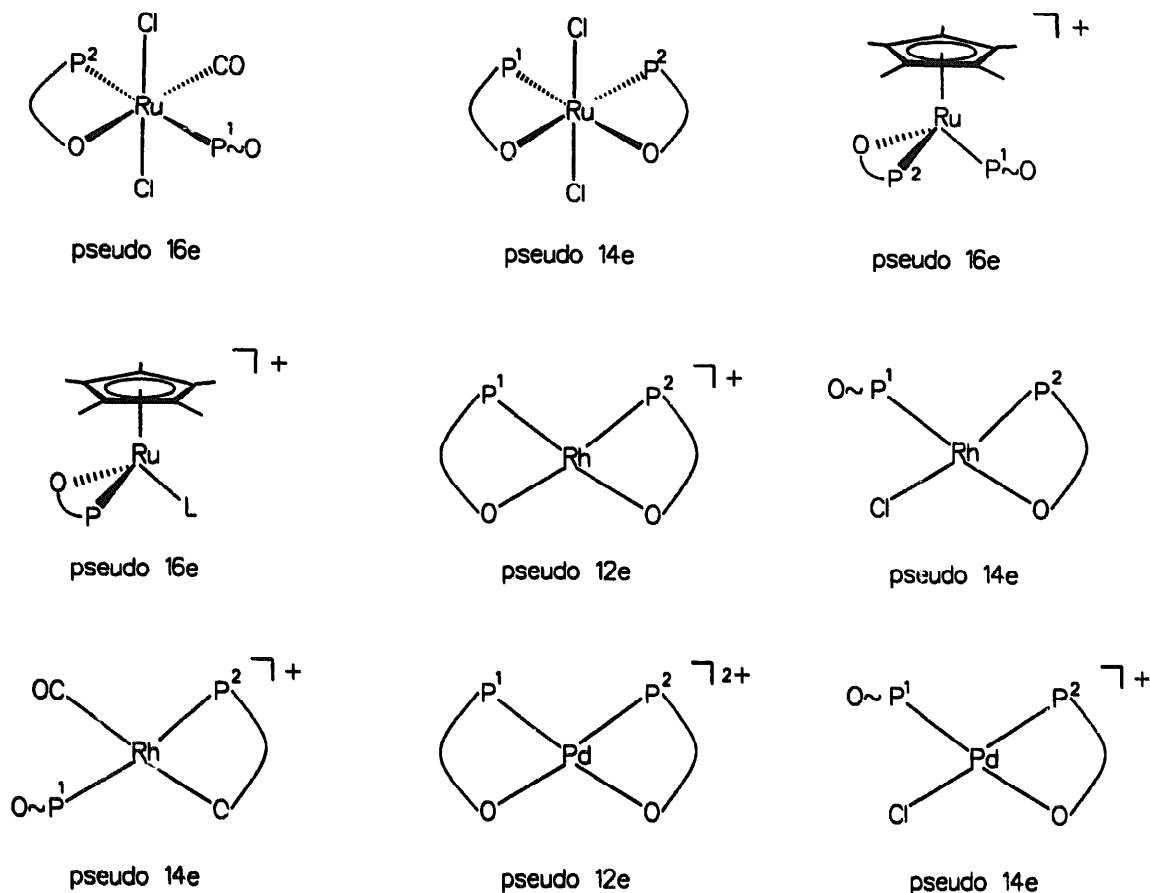
In this regard, extensive research has been carried out in the synthesis and characterization of highly undercoordinated ether–phosphine complexes of late transition metals. As a result of these investigations, ample precedents of octahedral [3,4] and half-sandwich ruthenium [5–8], as well as square-planar rhodium [9–11] and palladium [12–14] complexes are presently known (Scheme 1).

One of the main targets in recent years was to study in detail the dynamic behavior of systems containing monodentate ($P \sim O$) and bidentate ($P \cap O$) ether–phosphines ($P \sim O = \eta^1(P)$ -coordinated ligand, $P \cap O = \eta^2(O,P)$ -chelated ligand) in order to obtain the thermodynamic parameters ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger [4,6,11,13]. They are valuable data to obtain some knowledge of the exchange mechanism, and hence of the reactivity of the complex. Therefore, on the basis of these results, appropriate ether–phosphines for certain catalytic processes can be designed.

This review reports on the fluxional behavior of pseudo-undercoordinated ruthenium complexes and the application of (ether–phosphine)ruthenium and rhodium complexes to important types of stoichiometric and catalytic reactions.

2. Dynamic investigations

Fluxional isomerization is an important property of complexes containing ‘hemilabile’ ligands in their coordination sphere [2,15,16]. Especially advantageous are



$\text{O,P} = \text{R}_2\text{P}-\text{CH}_2-\text{Ether}$ ($\text{R} = \text{Alkyl-}, \text{Aryl-}$)

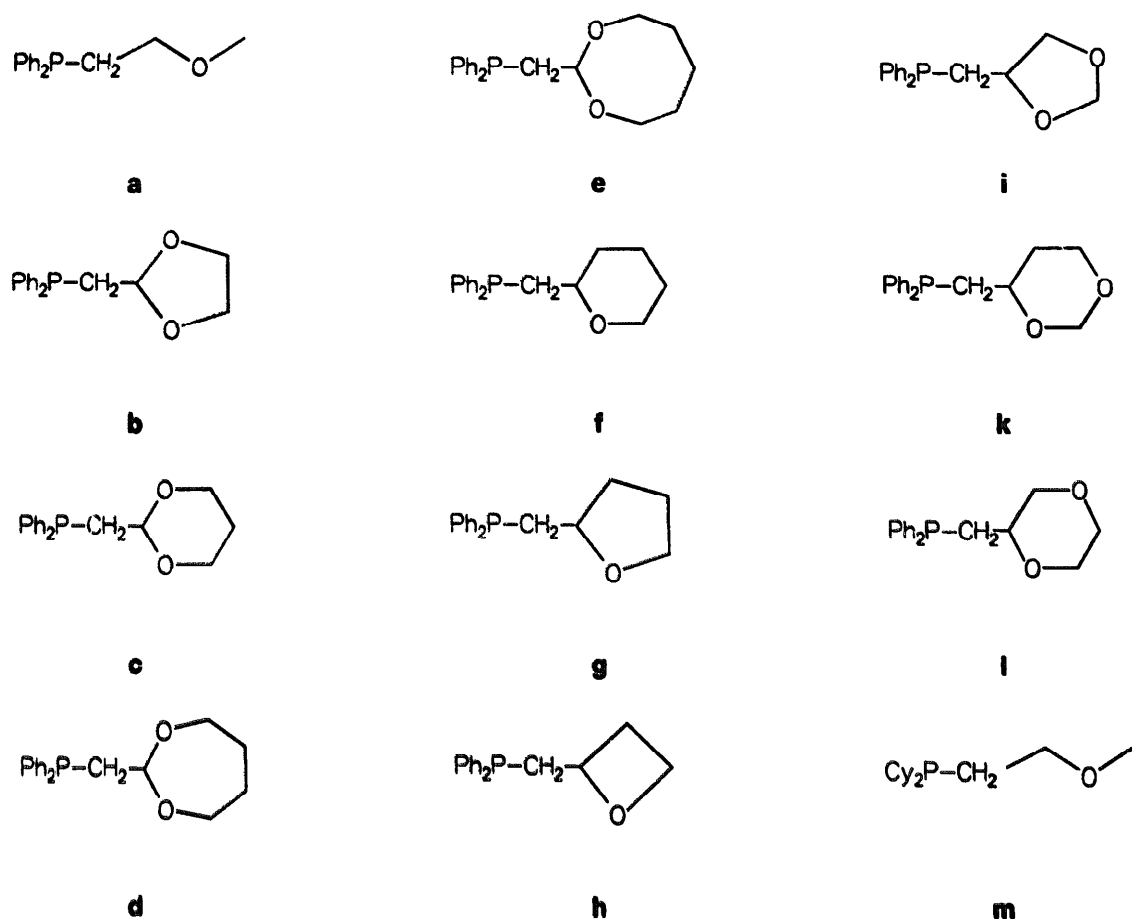
$\text{P}\sim\text{O} = \eta^1(\text{P})\text{-coordinated}$

$\text{P}\curvearrowright\text{O} = \eta^2(\text{O,P})\text{-coordinated}$

$\text{L} = \text{CO}, \text{P}(\text{OEt})_3$

Scheme 1. Schematic representation of the various types of pseudo-undercoordinated ruthenium, rhodium and palladium complexes.

compounds with at least two bifunctional O,P ligands in which the weak oxygen donors compete for a common coordination site. This leads to an exchange of the chelated and acyclic phosphorus and therefore reveals a dynamic behavior in solution that can be studied by variable-temperature ^{31}P NMR spectroscopy. A line-shape analysis gives access to kinetic and thermodynamic data which offers an insight into the isomerization mechanism. Thus, from the knowledge of a variety of different types of ether-phosphine ligand (Scheme 2), dynamic investigations and line-shape



Scheme 2. Schematic representation of the employed ether-phosphine ligands a–m.

analyses were carried out to establish the different chelating abilities of these ligands in dependence on the O-nucleophilicity [4,6].

2.1. Octahedral ruthenium complexes

Octahedral monocarbonyl complexes like *trans*-Cl₂Ru(CO)(P~O)(P∩O) (**1**) represent one type of known undercoordinated ruthenium complex which meets the above-mentioned requirements for fluxionality [2]. In order to determine the influence of different kinds of ether moieties on the strength of the Ru–O contact, the dynamic behavior of **1a–l** has been studied via temperature-dependent ³¹P{¹H} NMR spectroscopy [4]. The ³¹P{¹H} NMR spectra of these complexes show typical AB patterns at low temperatures. Owing to the presence of chiral C atoms in the ether-phosphines, two AB systems are found in the case of **1f–i**, **1l**. According to the ring contribution of the chemical shift Δ_R [17], the low- and high-field signals are assigned to the η²(O,P)- and η¹(P)-coordinated ligands. The large coupling constants ²J_{PP} ≈ 334–346 Hz are in agreement with the mutual trans position of the P atoms. When the temperature is raised, the lines first broaden, then coalesce and finally become a sharp singlet, indicating fluxional behavior in all cases with the

exception of **1h**, which decomposes below the coalescence temperature [4]. This averaging of magnetic environments on the NMR time scale indicates mutual exchange of the two O,P ligands. The rate constants of the exchange-broadened $^{31}\text{P}\{^1\text{H}\}$ NMR spectra and the thermodynamic parameters ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger of **1a–g** and **1i–l** were obtained by using the DNMR 5 program followed by the graphic application of the Eyring equation to the kinetic data.

All calculated ΔH^\ddagger values are positive (ca. 24–69 kJ mol $^{-1}$), indicating the rupture of a bond in the transition state. The ΔH^\ddagger data correlate with the O-nucleophilicity in noncoordinated ethers which increases with decreasing ring size of the cyclic ether moiety ($4 > 5 > 7 \approx 8 > 6$) [18]. The ΔS^\ddagger values are small and negative in most cases, pointing to an intramolecular process [4]. Therefore, we propose a simple ‘opening and closing’ mechanism depicted in Scheme 3. Primarily the Ru–O bond cleavage results in a five-coordinate species. Following recombination of the Ru–O contact, the oxygen donor of the second ether–phosphine regenerates the octahedral ruthenium complex.

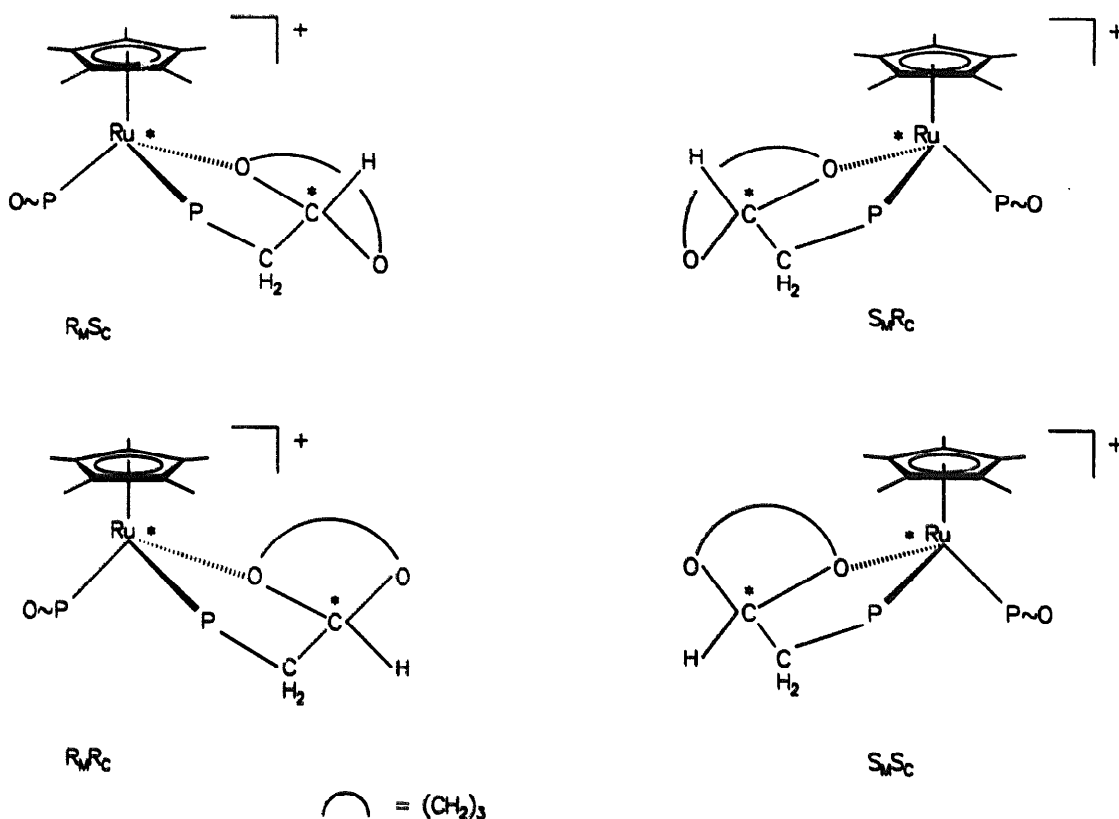
It should be mentioned that an ‘opening and closing’ mechanism is hindered in complexes in which the $\eta^1(\text{P})$ -coordinated O,P ligand is trans-positioned to the ether–oxygen donor. This structural situation requires a rearrangement of the coordination sphere for fluxional isomerization resulting in higher coalescence temperatures and ΔG^\ddagger values [4].

2.2. Half-sandwich ruthenium complexes

This section refers to the steric and dynamic properties of recently developed monochelated half-sandwich complexes of the type $[\text{Cp}^*\text{Ru}(\text{P} \sim \text{O})(\text{P} \cap \text{O})]^+$ (**2a–d**, **2g**, $\text{Cp}^* = \eta^5\text{-C}_5\text{Me}_5$) provided with the ether–phosphine ligands **a–d**, **g** [6]. Owing to the $\eta^2(\text{O,P})$ -chelating and the $\eta^1(\text{P})$ -coordinated ligand the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2a** reveals an AB pattern. The use of the cyclic ether substituents with oxygen atoms in 1,3-positions (**b–d**) in the complexes **2b–d** leads to the possible formation of two diastereomeric forms; this is caused by chirality at the ruthenium center in addition to C chirality of the $\eta^2(\text{O,P})$ -chelated ligand (Scheme 4). However, $^{31}\text{P}\{^1\text{H}\}$ NMR spectra at low temperature shows that the formation of the two diastereomers is strongly dependent on the ring size of the cyclic ether moiety. Whereas the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **2b** exhibits two AB systems, only the



Scheme 3. Exchange mechanism of the fluxional behavior of *trans*-Cl $_2$ Ru(CO)(P \sim O)(P \cap O) (**1a–l**).



Scheme 4. Possible diastereomeric forms of **2b–d** caused by C chirality, resulting from the η^2 -complexation of the ether–phosphine ligand.

sterically favored $R_M S_C/S_M R_C$ form is present in the case of **2c,d** [6]. This is a consequence from an interference of the six- or seven-membered ether-ring with the large Cp^* ligand. It is noteworthy, that there is a remarkable chemical shift difference (ca. 12–17 ppm) between the resonances of the respective $\eta^2(\text{O,P})$ -chelating ligands in the low field range of the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. Compared with the situation in solution, compound **2c** shows the inverse diastereomeric composition in the solid state, as deduced from an X-ray structural determination and ^{31}P CP MAS NMR measurements [19]. In the case of complex **2g** provided with the chiral ether–phosphine ligand **g**, only two of four possible diastereomers are observed in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at -30°C (Fig. 1).

Variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR examinations of the cationic, monochelated compounds $[\text{Cp}^*\text{Ru}(\text{P}\sim\text{O})(\text{P}\curvearrowright\text{O})]^+$ (**2a–d**, **2g**) indicate that they are fluxional in solution [6]. An illustration of the exchange-broadened $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of the two diastereoisomers of **2g** is depicted in Fig. 1. The calculated ΔH^\ddagger (ca. 42–56 kJ mol^{-1}) and ΔS^\ddagger values are in the same range as the corresponding data for the monocarbonyl ruthenium complexes. Therefore, we proposed the same mechanism for the O,P fluxionality in the half-sandwich ruthenium complexes as for the octahedral ruthenium compounds mentioned in Section 2.1 [6].

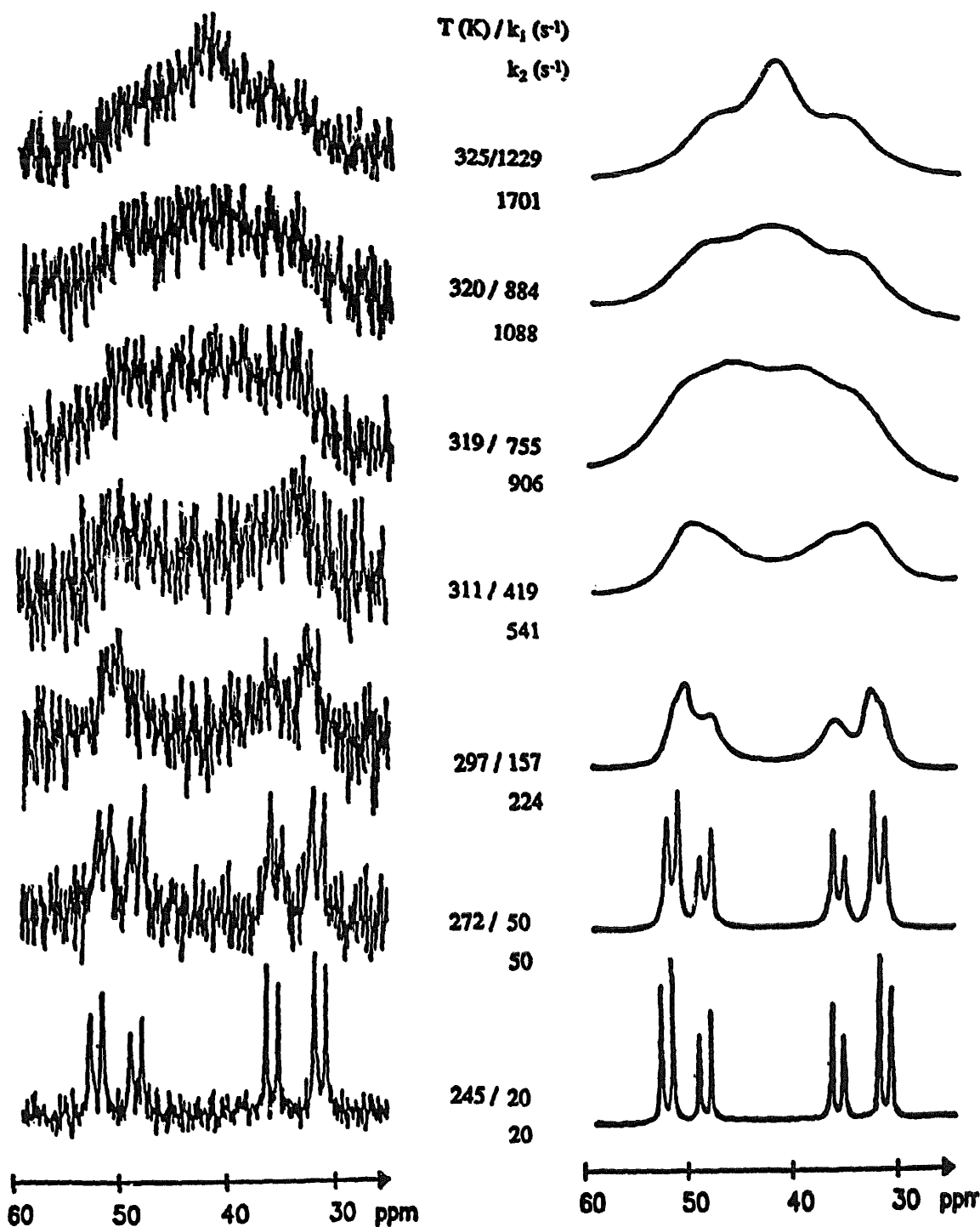


Fig. 1. Experimental and computer-simulated variable-temperature $^{31}\text{P}\{^1\text{H}\}$ NMR spectra for the O,P exchange in **2g** (k_1/k_2 are the rate constants of the corresponding diastereomers).

3. Reactivity

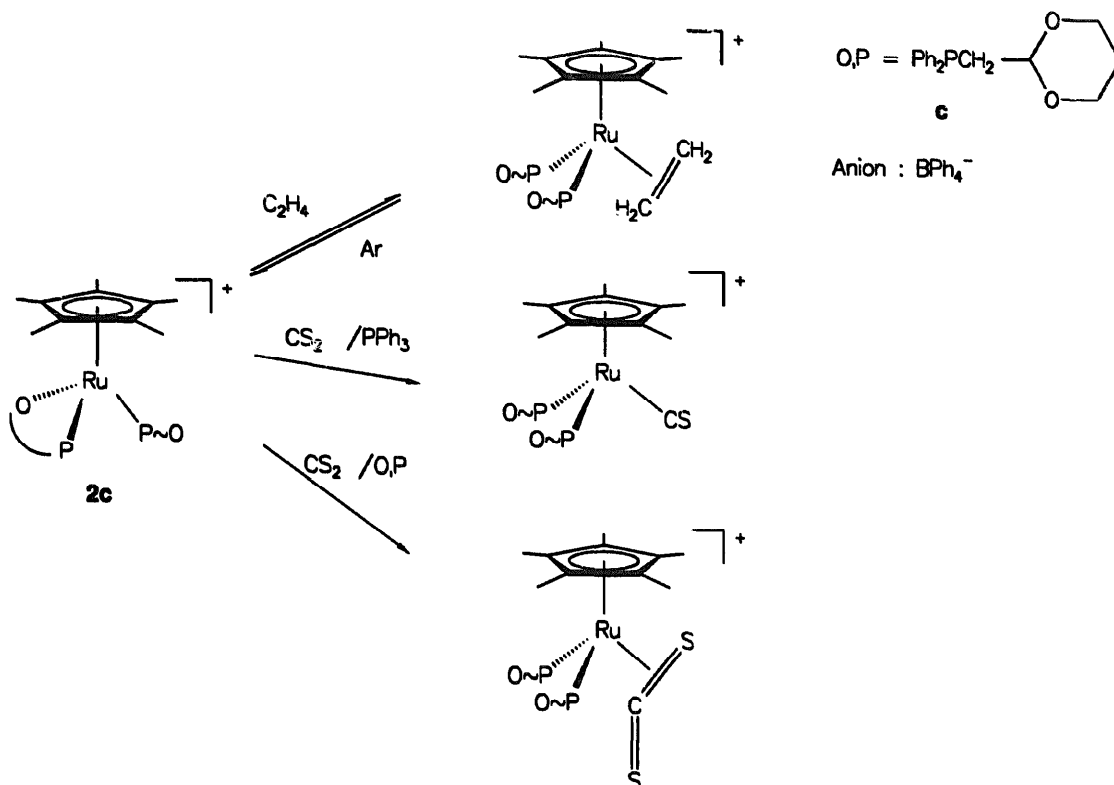
The coordination of a substrate to an undercoordinated transition metal center represents a key step in catalytically operating processes. In this regard, the interest

in $\eta^2(\text{O,P})$ -chelated ether–phosphine complexes having one or more pseudo-vacant coordination sites at the metal center (Scheme 1) is plausible, because they are expected to act as suitable precursors promoting this important pathway. The ease of substrate binding of such types of complex strongly depends on the nature of the O,P ligands employed, and stems from the fact that the incoming molecule has to compete with the oxygen donor of the chelating ether moiety. In this regard, knowledge of the especially weak coordinating ether–phosphines is advantageous in order to generate highly reactive compounds. In the case of half-sandwich [6] and octahedral ruthenium complexes [4], quantitative information concerning the different chelating abilities of various ether–phosphine ligands has been obtained as a result of the thermodynamic data based on line-shape analyses. With this in mind, the reactivity of these systems toward a wide range of small molecules has been studied recently [7,8,20,21].

3.1. Half-sandwich ruthenium complexes

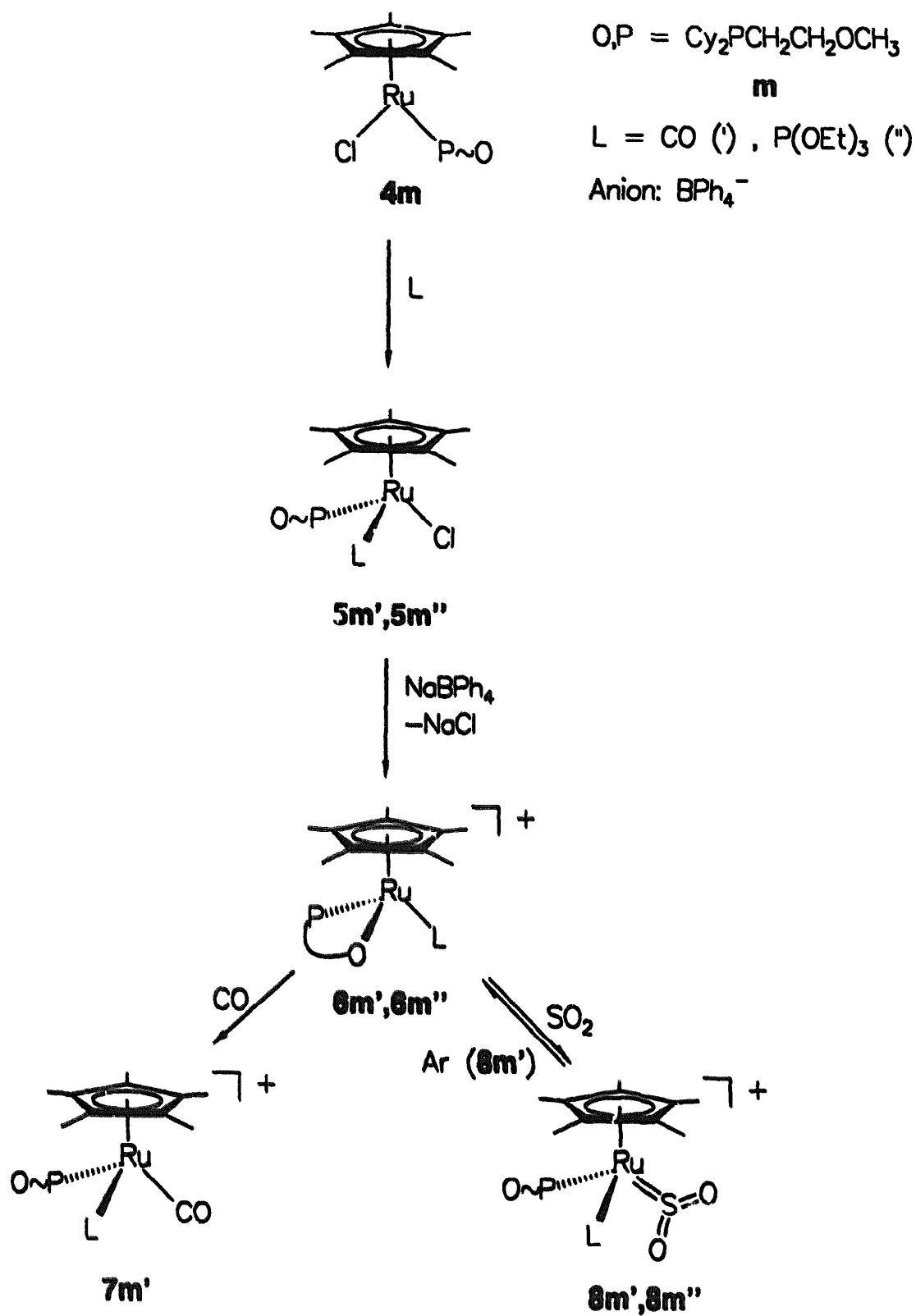
The use of the (1,3-dioxan-2-ylmethyl)diphenylphosphine ligand (**c**, Scheme 2) in the cationic, monochelated complex $[\text{Cp}^*\text{Ru}(\text{P}\sim\text{O})(\text{P}\cap\text{O})]^+$ (**2c**) has led to a relatively low coalescence temperature [6], from which it has been anticipated that **2c** should undergo a facile cleavage of its intramolecular ether moiety by treatment with substrates. Indeed, complex **2c** is capable of coordinating simple molecules such as carbon monoxide, ethene, phenylacetylene, diphenyldiazomethane, oxygen, sulfur dioxide and carbon disulfide under mild reaction conditions [6,20]. Among these examples, the reversibility of the reaction between **2c** and ethene (Scheme 5) reflects the outstanding property of the O,P ligand employed. Thus, if a CH_2Cl_2 solution of **2c** is stirred under an atmosphere of C_2H_4 , the η^2 -ethene complex $[\text{Cp}^*\text{Ru}(\text{P}\sim\text{O})_2(\eta^2\text{-C}_2\text{H}_4)]^+$ is formed quantitatively. This conversion is accompanied by a color change from dark red to yellow. Upon stirring under an argon atmosphere the color of the solution turns to dark red again, resulting in the re-formation of **2c**. The oxygen donor of the ether–phosphine ligand prevents the ruthenium complex from decomposition by occupation of the vacant coordination site after ethene dissociation. The treatment of **2c** with carbon disulfide and additional triphenylphosphine affords the stable thiocarbonyl derivative $[\text{Cp}^*\text{Ru}(\text{P}\sim\text{O})_2(\text{CS})]^+$ (Scheme 5) [20], whereas if the O,P ligand (**c**) is added to the reaction mixture instead of PPh_3 , the $\eta^2\text{-CS}_2$ complex $[\text{Cp}^*\text{Ru}(\text{P}\sim\text{O})_2(\eta^2\text{-CS}_2)]^+$ (Scheme 5) is obtained as the main product.

It has already been reported that the strong electron-donating nature of the dialkyl-substituted phosphorus function in $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ (**m**) reduces the Lewis-acidity of the metal center in $\eta^2(\text{O,P})$ -coordinated Rh(III) complexes and leads to a weaker metal–oxygen bond compared with the diphenyl analogs [10]. According to this, the introduction of this ligand in half-sandwich ruthenium complexes has been regarded as also gaining a further labilization of the Ru–O contact. However, owing to the steric constraint of $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$, oligomeric $[\text{Cp}^*\text{RuCl}_2]_n$ [22], which has been used for the preparation of bis(ether–phosphine) derivatives $\text{Cp}^*\text{RuCl}(\text{P}\sim\text{O})_2$ ($\text{P}\sim\text{O}=\eta^1(\text{P})$ -coordinated diphenyl(ether–phos-



Scheme 5. Representative examples for the reversible and irreversible coordination of small molecules to the Cp^*Ru fragment in **2c**.

phine)) [6] reacts with **m** and excess Zn to give the monosubstituted 16-electron compound $\text{Cp}^*\text{RuCl}(\text{P}\sim\text{O})$ (**4m**, Scheme 6) [7]. Despite the presence of a vacant coordination site at the ruthenium center in **4m**, an $\eta^2(\text{O},\text{P})$ -chelating mode of the bifunctional O,P ligand is prevented which is deduced by means of NMR spectroscopy [7]. It should be mentioned that the $\text{C}=\text{O}$ oxygen of the corresponding derivative provided with the phosphinoester $^i\text{Pr}_2\text{PCH}_2\text{CO}_2\text{CH}_3$ as a 'hemilabile' ligand is bound to the ruthenium center [23]. The stabilization of the undercoordinated, and hence reactive, complex $\text{Cp}^*\text{RuCl}(\text{P}\sim\text{O})$ (**4m**) is successful by treatment with carbon monoxide or triethylphosphite and affords the stable 18-electron complexes $\text{Cp}^*\text{RuCl}(\text{CO})(\text{P}\sim\text{O})$ (**5m'**) and $\text{Cp}^*\text{RuCl}(\text{P}\sim\text{O})(\text{P}(\text{OEt})_3)$ (**5m''**, Scheme 6) respectively [7,8]. Chloride abstraction with NaBPh_4 from these complexes results in the formation of the $\eta^2(\text{O},\text{P})$ -chelated cationic complexes $[\text{Cp}^*\text{Ru}(\text{P}\cap\text{O})(\text{L})]^+$ (**6m'**, **6m''**, Scheme 6). If carbon monoxide is used as an ancillary ligand, the cleavage of the intramolecular Ru–O bond in **6m'** has been achieved by reaction with carbon monoxide (Scheme 6). However, the quantitative conversion into the dicarbonyl species **7m'** requires more rigorous reaction conditions (2 bar, 30 min) compared with the fast coordination of CO to the corresponding bis(phosphine) derivative **2c**; this may be explained by the decreased electron density at the ruthenium metal in **7m'** compared with **2c** [6,7]. In this regard, the reversible reaction between **6m'** and sulfur dioxide (Scheme 6) is plausible and is a consequence of the weak donating

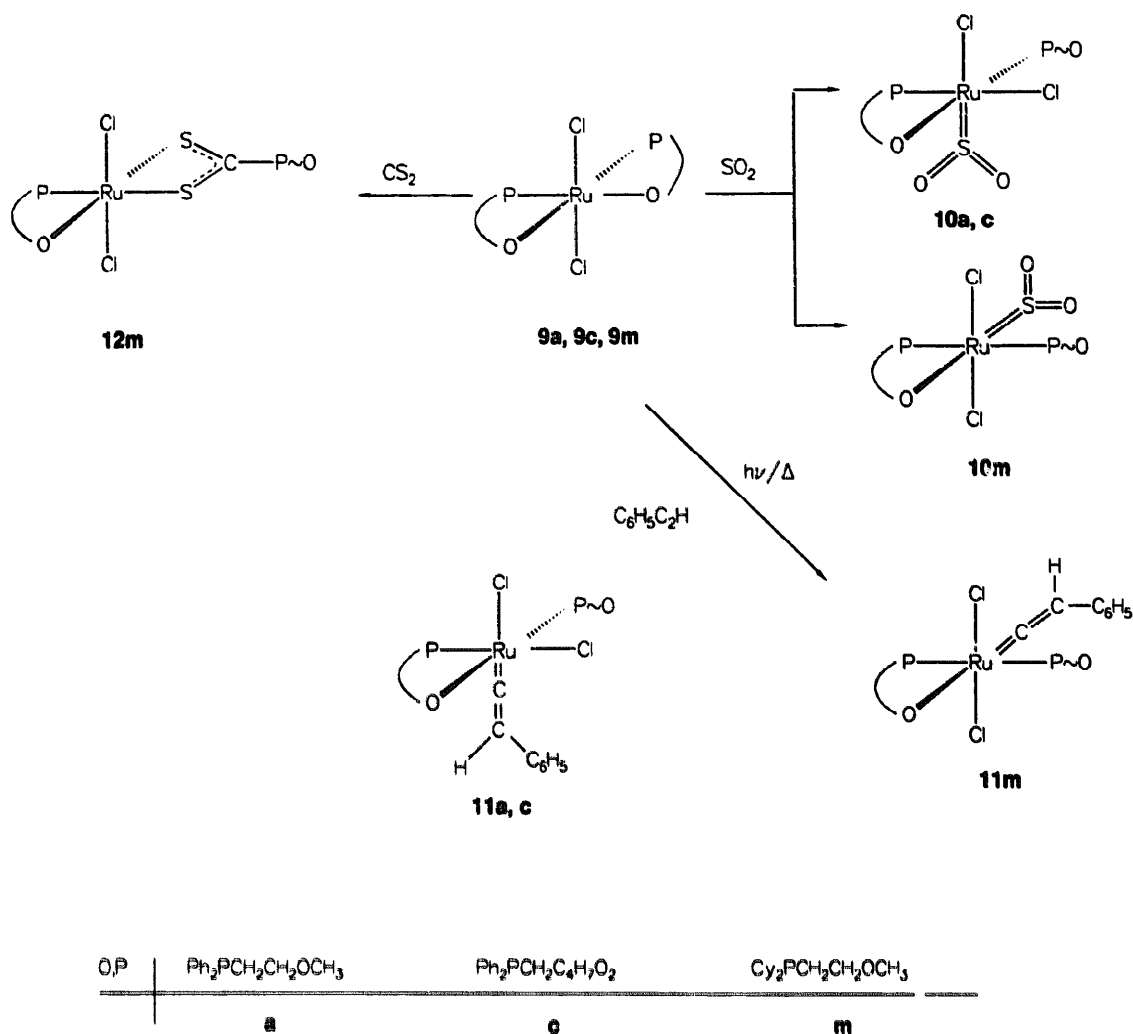


Scheme 6. Synthesis and reactivity of the cationic monochelated complexes $[\text{Cp}^*\text{Ru}(\text{P}(\text{O})(\text{L}))]^+$ (**6m'**, **6m''**).

ability of electrons from the central atom into the b_1 -orbital of the SO_2 ligand [8]. The employment of $\text{P}(\text{OEt})_3$ instead of CO in **6m** increases the electron density at the ruthenium and therefore demands a higher stability of the sulfur dioxide complex **8m** [8].

3.2. Octahedral ruthenium complexes

From dynamic investigations concerning the fluxional behavior of the octahedral ruthenium(II) complexes *trans*- $\text{Cl}_2\text{Ru}(\text{CO})(\text{P}\sim\text{O})(\text{P}\cap\text{O})$ (**1**, vide infra) containing both monodentate ($\text{P}\sim\text{O}$) and bidentate ($\text{P}\cap\text{O}$) ether–phosphines it is known that six-membered ether moieties with oxygen atoms in 1,3-positions generally show lower coalescence temperatures compared with the open-chain methoxy ethyl ether [4]. Based on these experimental results, a very recent study investigated the chemical reactivity of pseudo 14-electron bis(chelate)ruthenium(II) complexes *trans*- $\text{Cl}_2\text{Ru}(\text{P}\cap\text{O})_2$ (**9a**, **9c**, **9m**, Scheme 7) toward the activation of small molecules in order to evaluate the influence of the Lewis basicity at the ruthenium center and the different chelating abilities of the ligands **a**, **c** and **m** [21]. In this regard, these complexes were provided with a selection of O,P ligands with respect to different oxygen and phosphorus basicity. A facile cleavage of one or both ruthenium–oxygen bonds has been achieved by reaction of **9a**, **9c**, **9m** with sulfur dioxide, carbon disulfide, acetonitrile, phenylacetylene and isonitrile [21]. However, the ease of the Ru–O bond rupture of the bis(chelates), as well as the arrangement and the stability of the received substrate complexes, strongly depends on the chelating ability and the steric demand of the O,P ligands employed. This is nicely reflected by the different reaction pathways if **9a**, **9c**, **9m** are treated with SO_2 , CS_2 and phenylacetylene (Scheme 7). The bis(chelate) complexes **9a,c** react with sulfur dioxide resulting in the formation of the stable η^1 -coplanar SO_2 complexes **10a,c** (Scheme 7). However, whereas **9a** coordinates sulfur dioxide at ambient temperature almost instantaneously, refluxing THF is necessary to gain the quantitative conversion of **9c** into the η^1 - SO_2 derivative **10c**. Both complexes are isostructural showing a cis-geometry of the phosphine ligands. Owing to a chelated O,P ligand and an open-chain ether–phosphine the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10a,c** reveal AB patterns at low temperatures. When the temperature is raised, coalescence phenomena are observed which are a consequence of the competition between the ether dentates for a coordination site at the central atom. From the temperature-dependent $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **10a**, the activation barrier ($\Delta G^\ddagger = 69.8 \text{ kJ mol}^{-1}$) of this dynamic exchange has been determined using the approximate equation: $\Delta G^\ddagger = RT_c(22.96 + \ln T_c/\delta\nu)$ [22]. This relatively high energy barrier is due to the rearrangement of the ligands in the coordination sphere of the central atom, which requires additional energy as for the ‘opening and closing’ mechanism [15]. The cleavage of the Ru–O bond in **9m** with SO_2 occurs at significantly lower temperature (-15°C) compared with the corresponding reactions of **9a,c** with sulfur dioxide. In contrast to **10a,c**, the unstable η^1 - SO_2 complex **10m** undergoes marked loss of SO_2 at room temperature. The *trans*-configuration of the phosphine ligands in **10m** (Scheme 7) is evidenced by the large coupling constants ($^2J_{\text{PP}} \approx 290 \text{ Hz}$) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum and stems



Scheme 7. Representative examples for the potential use of the bis(chelate)ruthenium(II) complexes (**9a**, **9c**, **9m**) toward the activation of small molecules.

from the fact that this arrangement is more favorable for sterically demanding phosphines [25]. The treatment of **9a, c** with phenylacetylene demands the cleavage of one Ru–O bond affording the moderately air-stable η^1 -vinylidene complexes **11a, c** (Scheme 7) [21]. In agreement with the reaction of **9a, c** and SO_2 , the formation of **11c** requires more rigorous reaction conditions (refluxing toluene) compared with the reaction between **9a** and phenylacetylene (40°C , CH_2Cl_2). The structure of **11a, c** with *cis*-chlorines, *cis*-phosphines and the η^1 -vinylidene unit trans to chlorine has been ensured by spectroscopic means and an additional X-ray structural determination of **11a**. In contrast to the generation of **11a, c**, compound **11m** is prepared starting from a solution of **9m** and phenylacetylene in toluene, which is irradiated at ambient temperature with a mercury lamp. Complex **11m** represents an air-stable solid which displays an AB pattern with large coupling constants ($^2J_{\text{PP}} \approx 360 \text{ Hz}$) in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at low temperatures. This is consistent with a *trans*-arrangement of the bulky phosphines (Scheme 7). When the temperature is raised,

both doublets first broaden, then coalesce with final averaging in a sharp single peak. The origin of this dynamic process stems from the ‘opening and closing’ mechanism of the oxygen donors of the ether–phosphines competing for the vacant coordination site. The calculated activation energy ($\Delta G^\ddagger = 41.8 \text{ kJ mol}^{-1}$ [24]) is significantly lower than the dynamic exchange of the cis-configured O,P ligands in **10a** (vide infra). The major difference between the reactivity of **9a,c** and **9m** is reflected by the reaction of these compounds with carbon disulfide. Whereas **9a,c** are inert toward CS_2 , a solution of **9m** in toluene undergoes a ready insertion of CS_2 into the ruthenium–phosphorus bond to yield the phosphoniodithiocarboxylato compound **12m** (Scheme 7) as a dark purple, air-stable solid [21]. In agreement with this result, it is already known that such a type of insertion reaction requires the presence of basic phosphine ligands [26]. Concerning the capability of pseudo 14-electron bis(chelate)ruthenium(II) complexes *trans*- $\text{Cl}_2\text{Ru}(\text{P}\curvearrowright\text{O})_2$ (**9a**, **9c**, **9m**) to activate small molecules, in summary of these studies, it can be said that the ease of the Ru–O bond cleavage of these compounds and the stability of the respective substrate complexes obtained, is in the order $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ (**a**) $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ (**m**) $\text{Ph}_2\text{PCH}_2\text{C}_4\text{H}_7\text{O}_2$ (**c**) [21]. The result of this investigation is in contrast to our expectations which are based on studies of the dynamic behavior of (ether–phosphine)metal complexes. This may be a consequence of the increasing steric demand on going from **a** to **c** shielding the metal center from being attacked by the incoming substrate. Further investigations will be necessary for a better understanding of this discrepancy.

4. Catalytic behavior

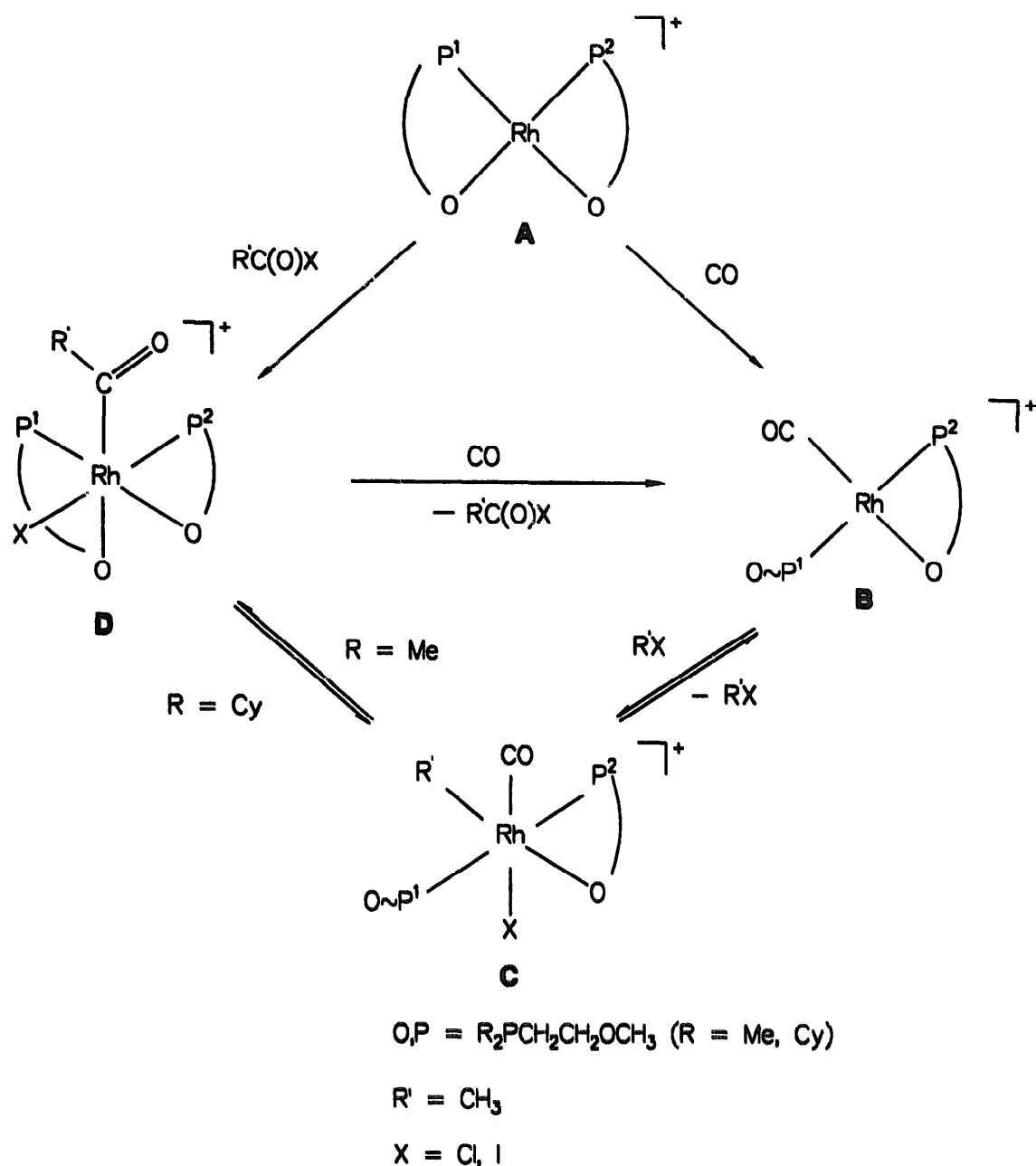
4.1. Hydrogenations

Spurred by the successful use of the well-known Wilkinson complex $\text{RhCl}(\text{PPh}_3)_3$ as an efficient homogenous hydrogenation catalyst, much effort has been expended in elucidating the mechanistic background [27]. The solvent complex $\text{RhCl}(\text{PPh}_3)_2(\text{S})$ ($\text{S} = \text{solvent}$) has been postulated to be a reactive species in the catalytic cycle but cannot be isolated [28]. In this regard, the monochelated rhodium complex $\text{ClRh}(\text{P}\sim\text{O})(\text{P}\curvearrowright\text{O})$ (**3m**) plausibly represents an isolable analog of unstable $\text{RhCl}(\text{PPh}_3)_2(\text{S})$ and should therefore be active in the hydrogenation of olefins. Recent experiments have indeed shown that neat 1-hexene is effectively hydrogenated to *n*-hexane over **3m** with 100% selectivity and excellent activity (turnover number 7920 h^{-1}) [11].

The cationic half-sandwich complex $[\text{Cp}^*\text{Ru}(\text{P}\sim\text{O})(\text{P}\curvearrowright\text{O})]^+$ (**2c**) has been anticipated to act as a suitable ruthenium derivative promoting the catalytic hydrogenation of olefins. The results of the hydrogenation experiments show that **2c** is able to hydrogenate 1-hexene to *n*-hexane at moderate H_2 pressures, but in contrast to the experiments with **3m** as a catalyst elevated temperatures (80°C) and long reaction times (4 h) are required to achieve a complete conversion [20].

4.2. Reversible alkyl migration

Alkyl migration, in which carbon monoxide is involved, has been intensively studied because of its significance for the formation of carbon–carbon bonds in transition-metal-catalyzed processes [29]. The introduction of ‘hemilabile’ ether–phosphine ligands has been very successful in the cobalt-catalyzed hydrocarbonylation of methanol to acetaldehyde. Methanol conversions and selectivities to acetaldehyde rose to 90% and 85% respectively [30]. To get an insight into the catalytic cycle, a rhodium-based model has been established [9]. This process is composed of three steps: oxidative addition of methyl iodide, methyl migration and reductive elimination of acetyl iodide. Starting from the pseudo 12-electron bis(chelate)rhodium complex $[\text{Rh}(\text{P}\cap\text{O})_2]^+$ (**13**, species A, Scheme 8), carbonylation to species B followed by oxidative addition of methyl iodide affords the alkyl rhodium derivative $[\text{trans}-(\text{P}\sim\text{O})(\text{P}\cap\text{O})\text{Rh}(\text{CO})(\text{CH}_3)(\text{I})]^+$ (**C**). The methyl migration step leading to the bis(chelate) species $[\text{cis}-(\text{P}\cap\text{O})_2\text{Rh}(\text{C}(\text{O})\text{CH}_3)(\text{I})]^+$ (**D**) is promoted by the ether–phosphine ligands. Rhodium(III) is more oxophilic than rhodium(I); hence, bis(chelate) complexes are usually more preferred [9]. Recently, it has been reported that the basicity of O,P ligands plays a key role in the course of alkyl migration [10]. Whereas with ligands of lower basicity ($\text{O,P}=\text{Me}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$, Scheme 8) ‘CO insertion’ is favored [9], reverse alkyl migration takes place if stronger basic ether–phosphines are used. This has been demonstrated by introduction of the basic O,P ligand $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ (**m**) into the cationic bis(chelate)rhodium complex $[\text{Rh}(\text{P}\cap\text{O})_2]^+$ (**13m**, Scheme 8, species A). If **13m** is treated with acyl halides of the general formula $\text{R}'\text{C}(\text{O})\text{X}$, octahedral bis(chelate) complexes $[\text{cis}-(\text{P}\cap\text{O})_2\text{Rh}(\text{C}(\text{O})\text{R}')(\text{X})]^+$ (**D**) are formed via oxidative addition. The small coupling constants $^2J_{\text{PP}}$ of approximately 20 Hz in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of complexes **D** are interpreted with a cis-configuration of the two $\eta^2(\text{O,P})$ -chelated ether–phosphines [10]. It should be mentioned that the corresponding acyl complex (**D**) obtained by reaction of **13m** with $^1\text{C}_3\text{H}_7\text{C}(\text{O})\text{Cl}$ ($\text{R}'=^1\text{C}_3\text{H}_7$) shows an unusual stability and therefore can be isolated. The proposed structure as depicted in Scheme 8 has been ensured by an X-ray structural determination of this compound. A reasonable explanation for this unexpected stability is that the large substituent R' ($^1\text{C}_3\text{H}_7$) shields the acyl group from being subjected to reverse alkyl migration. Moreover, six-coordinate complexes of the type $[\text{trans}-(\text{P}\sim\text{O})(\text{P}\cap\text{O})\text{Rh}(\text{CO})(\text{R}')(\text{X})]^+$ (**C**) would undoubtedly be more crowded than complexes of the type $[\text{cis}-(\text{P}\cap\text{O})_2\text{Rh}(\text{C}(\text{O})\text{R}')(\text{X})]^+$ (**D**) [31]. These arguments are further evidenced by the fact that a solution of the acetyl rhodium complex ($\text{R}'=\text{CH}_3$, **D**) undergoes a spontaneous reverse methyl migration when heated from -20 to 20°C yielding the mono(chelated) alkyl species **C** which represents an intermediate in the reductive elimination of alkyl halides from **D**. This conversion has been monitored by $^{31}\text{P}\{^1\text{H}\}$ NMR spectroscopy and GC-MS [10]. To sum up these examinations, it can be said that the employment of the basic O,P ligand $\text{Cy}_2\text{PCH}_2\text{CH}_2\text{OCH}_3$ (**m**) labilizes the Ru–O contact in oxophilic Rh(III) complexes and therefore forces the reverse alkyl migration step, especially in the case of small substituents R' .

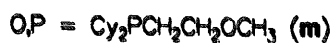
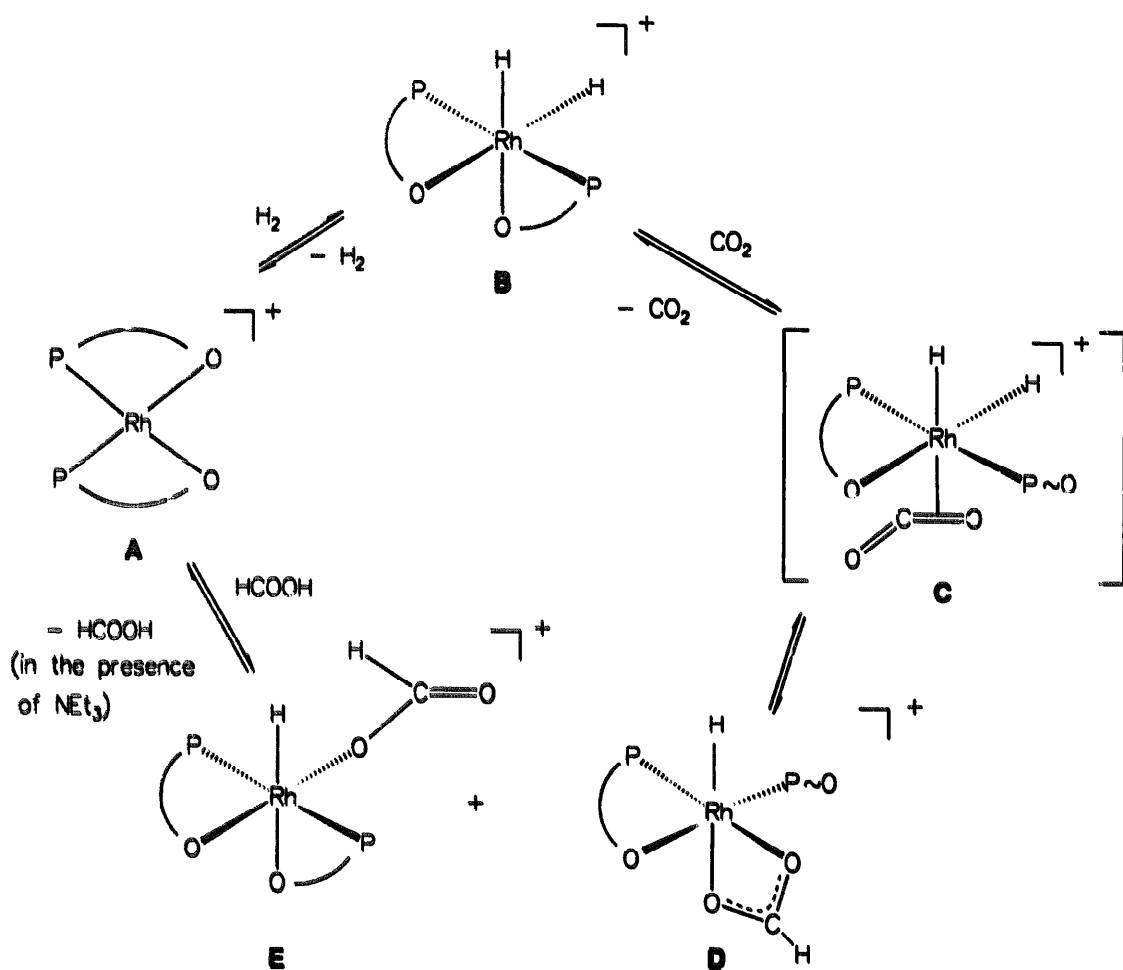


Scheme 8. Reversible alkyl migration in dependence on the phosphorus basicity of the employed ether-phosphine ligand.

4.3. Catalytic hydrogenation of carbon dioxide

The hydrogenation of CO_2 to formic acid represents an area of current research interest, because it appears to be a straightforward approach to the utilization of carbon dioxide as a chemical feedstock [32]. One of the main targets of these investigations was the creation of suitable catalysts which are able to decrease the large kinetic barrier for this reaction, and therefore make the hydrogenation of

carbon dioxide an economically interesting process. With reference to this, rhodium(I) phosphine complexes have been evaluated to act as valuable precatalysts leading to excellent conversion rates at moderate temperatures [33–35]. A detailed mechanistic study of this catalytic process was carried out by Tsai and Nicholas defining a cationic dihydride complex of rhodium stabilized by an external solvent molecule (THF, H₂O) as the active species [33]. With this in mind, the pseudo 12-electron bis(chelate)rhodium(I) derivative [Rh(P(O)CH₂CH₂CH₃)₂]⁺ (**13m**, species **A**, Scheme 9) should be predestined to catalyze the hydrogenation of carbon dioxide, and therefore an interesting study in our group examined the potential activity of this compound [36]. In a typical experiment, a solution of **13m** in methanol and NEt₃ is transferred to a stainless steel autoclave. The autoclave is purged three times with carbon dioxide and pressurized first to 25 bar with CO₂ and then to a total of



Anion: BPh₄⁻

Scheme 9. Proposed mechanism for the rhodium-catalyzed hydrogenation of carbon dioxide over complex **13m** (**A**).

50 bar with H₂. After a reaction time of 2 h (at 60 °C) the conversion was determined by GC analysis of the reaction mixture. The concentration of formic acid which is usually observed under these conditions is consistent with 860 turnovers in 2 h [36]. The proposed mechanism of CO₂ hydrogenation over **13m** is depicted in Scheme 9. Preliminary oxidative addition of H₂ leads to the generation of the already known *cis*-dihydridorhodium(III) complex [Rh(P(O)H)₂(H)₂]⁺ (**B**) [37]. Subsequent CO₂ insertion into the metal–hydride bond results in the formation of the formato complexes **D** and **E**. This insertion step may involve the η²-CO₂-coordinated intermediate **C**. Reductive elimination of formic acid from **D** and **E**, respectively, produces the undercoordinated η²(O,P)-chelated starting compound **13m** (**A**). It is noteworthy that the reaction of a CH₂Cl₂ solution of **13m** with HCOOH at –40 °C affords a mixture of the formato complexes **D** and **E**, as deduced by ³¹P{¹H} NMR and ¹H NMR spectroscopic investigations at low temperatures which show a double set of hydride resonances in the range of –18 to –21 ppm in the case of the latter method [36]. From this, the presence of **D** and **E** during the catalytic cycle can be undoubtedly evidenced.

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