Comparative Studies on Ether−Phosphine-Assisted Exchange Processes in the Rhodium(III) and Iridium(III) Complexes ClMH$_2$(P$\frown$O)(P$\sim$O)[†]

Ekkehard Lindner,* Karlheinz Gierling,[‡] Berthold Keppeler, and
Hermann A. Mayer

*Institut für Anorganische Chemie der Universität Tübingen, Auf der Morgenstelle 18,
D-72076 Tübingen, Germany*

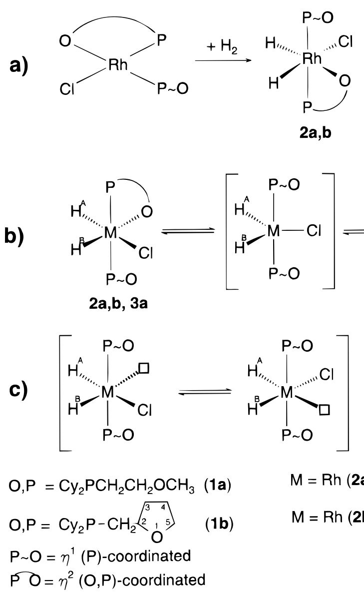
Received February 11, 1997[⊗]

The rhodium and iridium complexes ClRhH$_2$(P$\frown$O)(P$\sim$O) (**2a**,**b**) and ClIrH$_2$(P$\frown$O)(P$\sim$O) (**3a**) (P$\frown$O = η^2(P,O) coordination, P$\sim$O = η^1(P) coordination of Cy$_2$PCH$_2$CH$_2$OCH$_3$ (**a**) and Cy$_2$PCH$_2$C$_4$H$_7$O (**b**); C$_4$H$_7$O = tetrahydrofuranyl) were subjected to dynamic NMR studies. They exhibit a fast fluxional behavior both of the two ether oxygen donors and of the two *cis* hydrides at room temperature. The exchange of the hydrides is assisted by the fact that one of the ether moieties simulates an external solvent. The complexes **2a**,**b** show the same behavior as is suggested for the coordinatively unsaturated species ClRhH$_2$(PPh$_3$)$_2$, which is generally postulated to be an active intermediate in the catalytic hydrogenation of olefins. In the course of the formation of **3a** from its ortho-metalated precursor ClIrH($\overline{\mathrm{POC}}\mathrm{H_2}$)(P$\frown$O) (**4a**; $\overline{\mathrm{POC}}\mathrm{H_2}$ = η^2(P,CH$_2$) coordination of Cy$_2$PCH$_2$CH$_2$OCH$_2$) and dihydrogen, one C−H bond of the methoxy group and an additional Ir−H bond were formed. This was confirmed by the corresponding reaction of **4a** with D$_2$ to give the analogous dideuterium complex **3a′**. The opposite behavior was observed when **4a** was treated with DCl: one C−D and one Ir−Cl bond were formed in the complex Cl$_2$IrH(P$\frown$O)(P$\sim$O) (**5a**; one Cy$_2$PCH$_2$CH$_2$OCH$_2$D ligand) while the hydride remained at the metal. The ^{103}Rh chemical shift has been determined for compound **2b**.

Introduction

In 1966 Wilkinson et al. discovered the rapid homogeneous hydrogenation of olefins catalyzed by ClRh(PPh$_3$)$_3$;[1] since then, numerous mechanistic studies have led to an improved understanding of the functioning of this catalyst on a molecular level. Some authors postulated that solvent complexes such as ClRh(PPh$_3$)$_2$(S) (S = solvent) and ClRhH$_2$(PPh$_3$)$_2$(S) are reactive intermediates in the catalytic cycle.[2] These species are usually present only in solution and cannot be isolated. The introduction of ether−phosphine ligands instead of simple tertiary phosphines, however, rendered it possible to prepare and to investigate intramolecular solvent complexes which, due to P,O chelation, are much more stable than adducts with external solvents and can therefore be isolated and examined in detail.[3] A further advantage of phosphines with an additional ether function is a hindered dimerization of the coordinatively unsaturated species, which reduces the catalytic activity of the “classical” systems.[2−5]

Scheme 1



Recently we reported on the fluxional behavior of the (ether−phosphine)rhodium complex ClRh(P$\frown$O)(P$\sim$O) (P$\sim$O = η^1(P) coordination, P$\frown$O = η^2(P,O) coordination of Cy$_2$PCH$_2$CH$_2$OCH$_3$).[6] In this work, compounds of the general formula ClMH$_2$(P$\sim$O)(P$\frown$O) (M = Rh (**2a**,**b**), Ir (**3a**); P$\sim$O = η^1(P) coordination, P$\frown$O = η^2(P,O) coordination of the ether−phosphines Cy$_2$PCH$_2$CH$_2$OCH$_3$ (**a**) and Cy$_2$PCH$_2$C$_4$H$_7$O (**b**)) (Scheme 1) are presented as a

---

[†] Dedicated to Professor Max Herberhold on the occasion of his 60th birthday.

[‡] E-mail: karlheinz.gierling@uni-tuebingen.de.

[⊗] Abstract published in *Advance ACS Abstracts,* June 15, 1997.

(1) Osborn, J. A.; Jardine, F. H.; Young, J. F.; Wilkinson, G. *J. Chem. Soc. A* **1966**, 1711.

(2) (a) Tolman, C. A.; Meakin, P. Z.; Lindner, D. L.; Jesson, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 2762. (b) Halpern, J. *Inorg. Chim. Acta* **1981**, *50*, 11. (c) Dedieu, A. *Inorg. Chem.* **1980**, *19*, 375. (d) Hussey, A.; Takeuchi, Y. *J. Org. Chem.* **1970**, *35*, 643.

(3) Bader, A.; Lindner, E. *Coord. Chem. Rev.* **1991**, *108*, 27.

(4) Duckett, S. B.; Newell, C. L.; Eisenberg, R. *J. Am. Chem. Soc.* **1994**, *116*, 10548.

(5) Lindner, E.; Schneller, T.; Auer, F.; Wegner, P.; Mayer, H. A. *Chem. Eur. J.*, in press.

(6) Lindner, E.; Wang, Q.; Mayer, H. A.; Kühbauch, H.; Wegner, P. *Organometallics* **1993**, *12*, 3291.

model for $ClRhH_2(PPh_3)_2S$ with a view to study the properties and the ether−phosphine-assisted dynamic behavior of complexes derived from the Wilkinson catalyst by reaction with dihydrogen. In the course of these investigations a chemical exchange of the hydrides as well as of the ether−phosphine ligands was observed. By using three complexes (**2a**,**b** and **3a**) with different strengths of the metal−ether oxygen interaction, we hoped to find a mechanism for the hydride and phosphine exchange. Solvent complexes can be expected to behave similarly in the catalytic cycle.

The preparation of $ClIrH_2(P{\sim}O)(P\frown O)$ (**3a**) from its ortho-metalated precursor $ClIrH(\overline{POC}H_2)(P\frown O)$ (**4a**; $\overline{POC}H_2 = \eta^2(P,CH_2)$ coordination of $Cy_2PCH_2CH_2OCH_2$)[7] and dihydrogen raised the question of whether the methoxy group is rebuilt by the hydride already present or by dihydrogen. For this reason a mechanistic study comparing the reaction of **4a** with D_2 and DCl, respectively, was performed.

Experimental Section

General Comments. All manipulations were carried out under an atmosphere of argon by use of standard Schlenk techniques. Solvents were dried over appropriate reagents and stored under argon. IR spectra were recorded on a Bruker IFS 48 FT-IR spectrometer. FD mass spectra were recorded on a Finnigan MAT 711 A instrument (8 kV, 333 K), modified by AMD. Elemental analyses were performed with a Carlo Erba 1106 analyzer and Perkin-Elmer Model 4000 atomic absorption spectrometer. Cl analyses were carried out according to the method of Schöniger[8] and analyzed as described by Dirschel and Erne.[9] Rh was determined on a Perkin-Elmer Model 4000 atomic absorption spectrometer. ^1H, $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^{103}Rh NMR spectra were recorded on a Bruker DRX 250 spectrometer at 250.13, 101.25, 62.90, and 7.90 MHz. ^1H and ^{13}C chemical shifts were measured relative to partially deuterated solvent peaks and to deuterated solvent peaks, respectively, which are reported relative to TMS. ^{31}P chemical shifts were measured relative to 85% H_3PO_4 (δ 0). The ^{103}Rh NMR resonances were measured using a 2D (^{31}P,^{103}Rh)$\{^1H\}$ experiment.[10] Chemical shift values are referred to $\Xi(Rh) = 3.16$ MHz.[11] The ligand $(C_6H_{11})_2PCH_2CH_2OCH_3$[12] and the complex **2a**[6] were prepared as previously described. The iridium complexes **3a** and **4a** were synthesized according to the method of Werner et al.[7]

^1H and $^{31}P\{^1H\}$ DNMR. DNMR experiments were performed on a Bruker DRX 250 spectrometer using a 5 mm NMR sample tube. The temperature was measured with a temperature control unit (Eurotherm) and an external thermocouple (PT 100). The NMR probe temperature was calibrated by the method of van Geet[13] and is considered accurate to ±1 K (about 20 min was required for the temperature equilibration of the NMR sample). $\Delta G^{\ddagger}$ values have been calculated according to the method of Günther.[14]

Dicyclohexyl(tetrahydrofurfuryl)phosphine (1b). A solution of 20.0 g (100.0 mmol) of dicyclohexylphosphine in 100 mL of THF was treated at 273 K with 100.0 mmol of *n*-butyllithium (62.5 mL of a 1.6 m *n*-hexane solution). The red mixture was stirred for 1 h at ambient temperature, and subsequently 12.0 g (100.0 mmol) of tetrahydrofurfuryl chloride in 20 mL of THF was added dropwise. After 120 mL of a saturated solution of NH_4Cl in water was added, the organic phase was separated, and finally the solvent was removed in vacuo. The product was distilled from the residue under reduced pressure to yield 16.0 g (60%) of a colorless air-sensitive oil, mp 4 °C. MS (FD, 35 °C): *m/e* 282 [M^+]. Anal. Calcd (found) for $C_{17}H_{31}OP$: C, 72.30 (72.27); H, 11.06 (10.77). IR (KBr, cm^{-1}): $\nu_{as}(C_2O)$ 1100 (s). $^{31}P\{^1H\}$ NMR (101.25 MHz, $CDCl_3$, 22 °C): δ −10.3 (s). $^{13}C\{^1H\}$ NMR (62.9 MHz, $CDCl_3$, 22 °C): δ 79.4 (d, $^2J_{PC} = 24.9$ Hz, CHO), 68.0 (s, OCH_2), 34.3 (d, $^1J_{PC} = 10.5$ Hz, PCH), 32.9 (d, $^1J_{PC} = 10.5$ Hz, PCH), 32.7 (d, $^1J_{PC} = 6.7$ Hz, PCH_2), 29.0−25.2 (m, Cy). ^1H NMR (250.13 MHz, $CDCl_3$, 22 °C): δ 3.8 (m, 2H, OCH_2), 3.6 (m, 1H, OCH), 1.6−0.9 (m, 28H, Cy and CH_2).

Chloro[dicyclohexyl(tetrahydrofurfuryl)phosphine-*P*][dicyclohexyl(tetrahydrofurfuryl)phosphine-*P,O*]-*cis*-dihydridorhodium(III) (2b). A solution of 100.0 mg (0.14 mmol) of $[RhCl(COE)_2]_2$ in 15 mL of toluene was treated at ambient temperature with 158.0 mg (0.56 mmol) of **1b**. After 3 h the solution was stirred under 1 bar of H_2 for 10 min. The solvent was removed under vacuum, and the residue was washed with 5 mL of *n*-pentane and dried in vacuo to yield 69.0 mg (70%) of **2b**, mp 120 °C dec. MS (FD, 35°C): *m/e* 702 [$M^+ - H_2$]. Anal. Calcd (found) for $C_{34}H_{64}ClO_2P_2Rh$: C, 57.91 (56.07);[15] H, 9.15 (8.83); Cl, 5.03 (5.01); Rh, 14.59 (14.46). IR (KBr, cm^{-1}): $\nu(RhH_2)$ 2072 (m), 2134 (m); $\nu_{as}(C_2O)$ of $P{\sim}O$ 1099 (s), $\nu_{as}(C_2O)$ of $P\frown O$ 1047 (m). $^{31}P\{^1H\}$ NMR (101.25 MHz, acetone-d_6, 22 °C): δ 49.2 (d, $^1J_{RhP} = 112.3$ Hz). $^{13}C\{^1H\}$ NMR (62.9 MHz, acetone-d_6, 22 °C): δ 79.2 (s, CHO), 68.2 (s, OCH_2). ^1H NMR (250.13 MHz, acetone-d_6, 22 °C): δ −22.8 (dt, $^1J_{RhH} = 26.8$, $^2J_{PH} = 15.5$ Hz, RhH_2). ^{103}Rh NMR (7.90 MHz, acetone-d_6, 22 °C): δ 780.

Chloro[dicyclohexyl(methoxyethyl)phosphine-*P*][dicyclohexyl(methoxyethyl)phosphine-*P,O*]-*cis*-dideuteridoiridium(III) (3a′). A solution of 100.0 mg (0.14 mmol) of **4a** in 15 mL of toluene was stirred for 10 min under 1 bar of D_2. The solvent was removed under vacuum, and the residue was washed with 5 mL of *n*-pentane and dried in vacuo to yield 83.0 mg (80%) of **3a′**. This complex, which is analogous to **3a**, was characterized by MS and IR and $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectroscopy. MS (FD, 35 °C): *m/e* 740 [$M^+ - D_2$]. IR (KBr, cm^{-1}): $\nu_{as}(C_2O)$ of $P{\sim}O$ 1110 (s), $\nu_{as}(C_2O)$ of $P\frown O$ 1052 (m). $^{31}P\{^1H\}$ NMR (101.25 MHz, acetone-d_6, 22 °C): δ 32.2 (s). $^{13}C\{^1H\}$ NMR (62.9 MHz, acetone-d_6, 22 °C): δ 73.5 (s, OCH_2), 60.8 (s, OCH_3). ^1H NMR (250.13 MHz, acetone-d_6, 22 °C): δ −28.9 (t, $^2J_{PH} = 15.5$ Hz, weak signal of non-deuterated IrH_2).

***cis*-Dichloro[dicyclohexyl((deuteriomethoxy)ethyl)-phosphine-*P*][dicyclohexyl(methoxyethyl)phosphine-*P,O*]hydridoiridium(III) (5a).** A solution of 100.0 mg (0.14 mmol) of **4a** in 15 mL of toluene was treated with 0.5 mmol of DCl (0.1 mL of a 20% solution in D_2O). The solvent was removed under vacuum, and the residue was washed with 5 mL of *n*-pentane and finally dried in vacuo to yield 82.0 mg (75%) of **5a**. This complex, which is analogous to the corresponding non-deuterated compound,[7] was characterized by MS and IR and $^{31}P\{^1H\}$, $^{13}C\{^1H\}$, and ^1H NMR spectroscopy. MS (FD, 35 °C): *m/e* 778 [M^+]. IR (KBr, cm^{-1}): $\nu(IrH)$ 2299 (w), $\nu_{as}(C_2O)$ of $P{\sim}O$ 1102 (s), $\nu_{as}(C_2O)$ of $P\frown O$ 1046 (m). $^{31}P\{^1H\}$ NMR (101.25 MHz, acetone-d_6, 22 °C): δ 11.0 (s). $^{13}C\{^1H\}$ NMR (62.9 MHz, acetone-d_6, 22 °C): δ 71.4 (s, OCH_2), 60.1 (s, OCH_3), 59.8 (t, $^1J_{CD} = 21.0$ Hz, OCH_2D). ^1H NMR (250.13 MHz, acetone-d_6, 22 °C): δ −34.7 (t, $^2J_{PH} = 13.0$ Hz).

---

[7] Werner, H.; Schulz, M.; Windmüller, B. *Organometallics* **1995**, *14*, 3659.

[8] (a) Schöniger, W. *Microchim. Acta* **1955**, 123. (b) Schöniger, W. *Microchim. Acta* **1956**, 869.

[9] Dirschel, A.; Erne, F. *Microchim. Acta* **1961**, 866.

[10] Benn, R.; Brevard, C. *J. Am. Chem. Soc.* **1986**, *108*, 5622.

[11] Mann, B. E. In *Transition Metal Nuclear Magnetic Resonance*; Pregosin, P. S., Ed.; Elsevier: Amsterdam, 1991.

[12] Lindner, E.; Meyer, S.; Wegner, P.; Karle, B.; Sickinger, A.; Steger, B. *J. Organomet. Chem.* **1987**, *335*, 59.

[13] (a) Van Geet, A. L. *Anal. Chem.* **1968**, *40*, 2227. (b) Van Geet, A. L. *Anal. Chem.* **1970**, *42*, 679.

[14] Günther, H. *NMR Spectroscopy*; Georg Thieme Verlag: Stuttgart, Germany, 1992.

[15] (a) Although high temperature and V_2O_5 (catalyst) were used for C, H analyses, the carbon values remained low. This is probably due to incomplete combustion, which may be caused by rhodium. (b) Nappier, T. E.; Meek, D. W.; Kirchner, R. M.; Ibers, J. A. *J. Am. Chem. Soc.* **1973**, *95*, 4194.

Results and Discussion

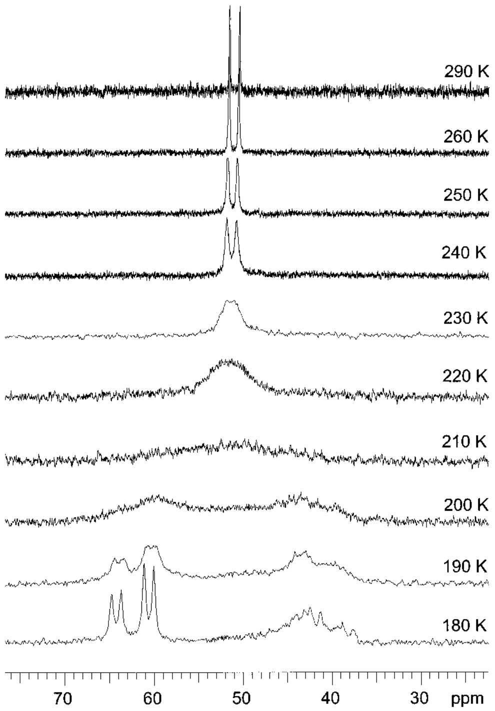


Figure 1. Variable-temperature $^{31}P\{^{1}H\}$ NMR spectra (101.25 MHz, acetone-d_6) of complex **2b**.

Table 1. Coalescence Temperatures and Free Activation Energies for the Investigated Fluxional Processes

complex		T_c (K)	$\Delta G^{\ddagger}$ (kJ/mol)[a]
2a	hydride	ca. 180	
2a	phosphorus	ca. 180	
2b	hydride	210 ± 2	37.2 ± 1
2b	phosphorus	210 ± 2	35.9 ± 1
3a	hydride	210 ± 2	34.7 ± 1
3a	phosphorus	210 ± 2	34.6 ± 1

[a] Calculated at T_c; errors are calculated using the estimated errors of T_c.

Under mild conditions, the monochelated starting complex $ClRh(P^\frown O)(P\sim O)$ ($P\sim O = \eta^1(P)$ coordination and $P^\frown O = \eta^2(P,O)$ coordination of $Cy_2PCH_2CH_2OCH_3$) oxidatively adds molecular hydrogen in a *cis* fashion to form the colorless dihydridorhodium(III) complex $ClRhH_2(P^\frown O)(P\sim O)$ (**2a**) (Scheme 1, eq a)).[6] Compound **2a** may be regarded as a coordinatively unsaturated 16-electron complex stabilized by an intramolecularly weakly bound ether oxygen atom corresponding to the postulated catalytic intermediate $ClRhH_2(PPh_3)_2$(solvent). At low temperatures ($T < 180$ K) in toluene-d_8 the ^1H and $^{31}P\{^1H\}$ NMR spectra display broad signals which are in agreement with nonequivalent hydride and phosphine ligands. As the temperature is raised, the respective resonances of the phosphorus and hydride nuclei coalesce. Finally, the typical spectra for equivalent phosphines ($^{31}P\{^1H\}$: A_2 part of an A_2X pattern) and hydrides (^1H: A_2 part of an A_2M_2X pattern) are observed. This averaging of the chemical environments on the NMR time scale indicates a rapid exchange of the two ether moieties which equilibrates the hydrides and the phosphorus nuclei (Scheme 1, eq b)). For **2a** the exchange is so fast that it was impossible to obtain spectra significantly below the coalescence temperature. Therefore, we prepared two complexes analogous to **2a**, but with a stronger metal−ether oxygen interaction: the rhodium compound **2b**, in which the ether moiety is formed by a tetrahydrofuranyl substituent, and the iridium compound **3a**, corresponding to **2a**. From previous investigations it is known that the oxygen atom of the tetrahydrofuranyl group has a higher basicity than that in open-chain ether ligands[16] and that iridium(III) is more oxophilic compared to rhodium(III).[17] With all complexes, temperature-dependent NMR investigations were performed. Figure 1 illustrates the temperature dependence of the $^{31}P\{^1H\}$ NMR spectrum of **2b**. At temperatures below the coalescence point the AB part of an ABX spin system with resonances centered at 62.7 and 39.6 ppm is observed. While the low-field pattern is attributed to the chelating ether-phosphine, the high-field signals are ascribed to the η^1-(P)-coordinated ligand.[18] The different line widths of the $^{31}P\{^1H\}$ signals of the two ether−phosphines can be explained by their different mobilities. Upon coordination of the ether oxygen to rhodium the five-membered ring generates a single environment of the phosphorus ($P^\frown O$) nucleus. This results in a sharp A part of the ABX spin system. For the nonchelating phosphine (high field) the rotation about the Rh−P axis is hindered by the two sterically demanding cyclohexyl groups and the ether−phosphine moiety. Thus, different chemical environments are possible, causing a broadening of the NMR signals at low temperature. The $^2J_{PP}$ coupling constant of 366.6 Hz confirms a *trans* arrangement of the phosphines. In the ^1H NMR spectrum below coalescence (Table 1) two signals at −19.2 and −23.4 ppm are displayed but due to line broadening no $^1J_{RhH}$, $^2J_{PH}$, or $^2J_{HH}$ coupling constants are discernible. In analogy to results of Drago et al.[19] the upfield resonances in the low-temperature ^1H NMR spectra of **2a**,**b** and **3a** are ascribed to the hydrides *trans* to chlorides. The inequivalence of the hydrides in **2b** corroborates their *cis* configuration. When the temperature is raised, the signals in the $^{31}P\{^1H\}$ and ^1H NMR spectra of **2b** become broader and finally coalesce. At ambient temperature the A_2 part of an A_2X pattern in the $^{31}P\{^1H\}$ NMR spectrum and the A_2 part of an A_2M_2X spin system in the ^1H NMR spectrum of **2b** are visible (Experimental Section). Apart from the coupling to the metal, comparable NMR spectra of the iridium(III) complex **3a** are observed throughout the temperature range (180−290 K). As for **2b**, the $^{31}P\{^1H\}$ NMR spectra of **3a** below coalescence show a broadening of the high-field signals compared to the low-field part. This effect is much less pronounced, as the ether moiety of **3a** is sterically less demanding than that of **2b**. Dissociation of the hydride or phosphine ligands during the exchange process can be excluded for **2a**,**b** and **3a** because of the couplings observed among the nuclei present in the molecules. As the molecule of **2b** contains two chiral carbon atoms (C2 of each THF ring; Scheme 1), two

---

[16] Lindner, E.; Möckel, A.; Mayer, H. A.; Kühbauch, H.; Fawzi, R.; Steimann, M. *Inorg. Chem.* **1993**, *32*, 1266.

[17] Vaska, L.; Chen, L. S.; Miller, W. V. *J. Am. Chem. Soc.* **1971**, *93*, 6671.

[18] (a) Lindner. E.; Fawzi, R.; Mayer, H. A.; Eichele, K.; Hiller, W. *Organometallics* **1992**, *11*, 1033. (b) Lindner, E.; Mayer, H. A.; Möckel, A. In *Phosphorus-31 NMR Spectral Properties in Compound Characterization and Structural Analysis*; Quin, L. D., Verkade, J. G., Eds.; VCH: New York, 1994. (c) Garrou, C. A. *Chem. Rev.* **1981**, *81*, 229.

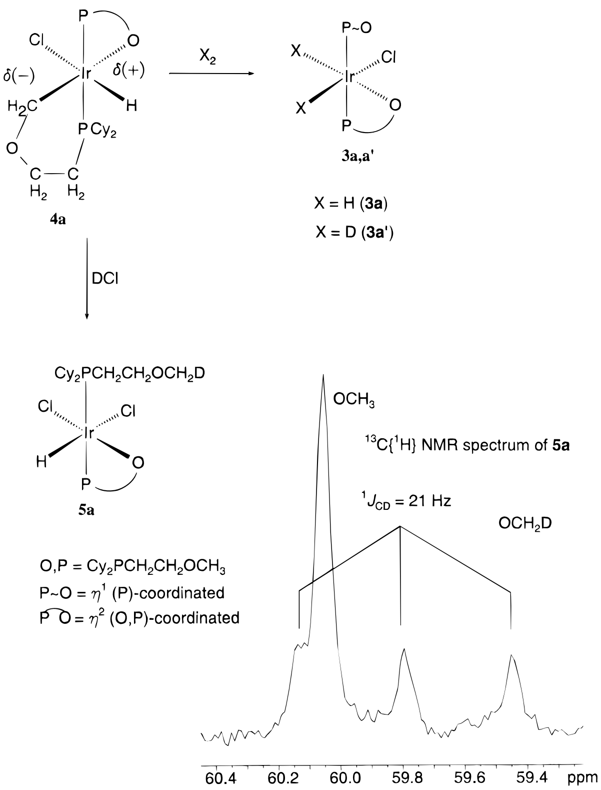
[19] Drago, R. S.; Miller, J. G.; Hoselton, M. A.; Farris, R. D.; Desmond, M. J. *J. Am. Chem. Soc.* **1983**, *105*, 444.

diastereomers, a *meso* and a racemic form, can exist in principle. However, we did not observe diastereomers in the NMR spectra of **2b**.

It was found that the rhodium complex **2b**, with a tetrahydrofuranyl substituent, and the iridium complex **3a**, with an open-chain ether moiety, show the same fluxional behavior as **2a**, but the exchange rates are much lower compared to **2a**. As it was impossible to determine reliable line widths without exchange, we did not perform a line shape analysis to determine further activation parameters.[20] The most interesting feature is that in all three complexes the hydrides exchange as quickly as the phosphine ligands (Table 1). This leads to the assumption that the hydrides exchange only when the ether oxygen atoms dissociate from the central atom and that the intermediate must have a trigonal-bipyramidal[21] coordination as depicted in Scheme 1. If a square-pyramidal structure for the intermediate[22] is taken into account, the chloride must be able to switch from one position to the other significantly faster than the "open−close" dynamic of the ether−phosphine (Scheme 1, eq c). Otherwise, the equilibration of the hydrides would take place at a higher temperature than that of the ether−phosphines. Thus, we propose the so-called "migratory mechanism" as described recently by Gusev and Berke.[23] In the catalytic cycle the presence of coordinatively unsaturated species is relevant but their availability depends on the rate constant of the dissociation of a solvent molecule. Ether−phosphine ligands are able to simulate these solvent molecules and make it possible to study species involved in catalytic cycles. Our results are in agreement with the finding that the hydride exchange in $ClRhH_2(PPh_3)_3$ is only possible when the phosphine *trans* to one hydride dissociates into the solution.[24] We can confirm the assumption of Lee and Jensen[25] that $IrXH_2(PR_3)_2$ complexes are involved in a fast exchange with the corresponding solvent complex $IrXH_2(PR_3)_2(S)$.

In the course of the synthesis of **3a** from the orthometalated complex **4a** as described by Werner et al.[7] (Scheme 2), the question was raised whether the newly formed methyl group of the ether−phosphine is completed by the hydride already present at the metal or by an incoming hydrogen. To our knowledge, this mechanistic point has not been addressed before. If dideuterium is added to **4a**, none of the methyl groups of **3a′** contain deuterium, as shown by the $^{13}C\{^1H\}$ NMR spectrum. Thus, deuterium occupies the hydride positions. By way of contrast, when **4a** is treated with DCl to form **5a**, one of the methyl groups contains a deuterium atom and the hydride remains at the metal. The $^{13}C\{^1H\}$ NMR spectrum of **5a** shows one singlet for CH_3 and a 1:1:1 triplet for the CH_2D moiety. Complex **5a** shows a fluxional behavior very similar to that of **3a**, and from its low-temperature $^{31}P\{^1H\}$ NMR spectrum a structure with *trans* phosphines is derived. For unknown reasons Werner et al. assumed a *trans* configuration of the two chlorides in a similar complex.[7] Even though FIR and Raman spectroscopic investigations did not furnish reliable data to decide this question, there are three arguments which suggest a *cis* configuration of the chlorides in **5a** (Scheme 2). (i) The low-temperature (180 K) ^1H NMR spectrum of **3a** reveals two inequivalent *cis* hydrides at −26.2 and −33.6 ppm. The latter resonance is attributed to the hydride *trans* to chloride.[17] In complex **5a** the corresponding resonance at −37.4 ppm indicates a hydride *trans* to a chloride ligand. (ii) The IR spectrum of **3a** reveals two Ir−H vibrations at 2265 and 2188 cm^{-1}. The former lies in the range of Ir−H vibrations for hydrides *trans* to chlorides as described in the literature.[26] As the Ir−H vibration of **5a** occurs at 2299 cm^{-1}, a *trans* configuration of the hydride relative to one chlorine is indicated. (iii) The ^1H NMR resonance of the hydride of **5a** does not change its shape and chemical shift in the temperature range in which the chemical exchange of the phosphines is observed. Therefore, this hydride must keep the same *trans* ligand throughout the exchange process.

Scheme 2



The different behavior of **4a** toward H_2 and HCl may be traced back to the polarity of the Ir−C bond, as the negatively charged CH_2 group is attacked by the proton of hydrochloric acid. In the case of the nonpolarized molecule H_2 a reductive elimination with re-formation of the methyl group first takes place; then, H_2 is added oxidatively.

Conclusion

In the traditional systems $ClRh(PR_3)_3$ and $ClRhH_2(PR_3)_3$ the phosphines exchange in solution[2] and their

---

(20) Binsch, G.; Kessler, H. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 411 and references cited therein.

(21) Riehl, J.-F.; Jean, Y.; Eisenstein, O.; Pélissier, M. *Organometallics* **1992**, *11*, 729.

(22) Sleigh, C. J.; Duckett, S. B.; Messerle, B. A. *J. Chem. Soc., Chem. Commun.* **1996**, 2395.

(23) Gusev, D. G.; Berke, H. *Chem. Ber.* **1996**, 129.

(24) Brown, J. M.; Evans, P. L.; Lucy, A. R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 1589.

(25) Lee, D. W.; Jensen, C. M. *J. Am. Chem. Soc.* **1996**, *118*, 8749.

(26) Weidlein, J.; Müller, U.; Dehnicke, K. *Vibrational Frequencies II*; Georg Thieme Verlag: Stuttgart, Germany, 1986.

catalytically active coordinatively unsaturated congeners $ClRh(PR_3)_2$ and $ClRhH_2(PR_3)_2$ are only present in very low concentrations.[27] The corresponding ether-phosphine species $ClRh(P\frown O)(P\sim O)$,[6] $ClRhH_2(P\frown O)(P\sim O)$ (**2a**,**b**), and $ClIrH_2(P\frown O)(P\sim O)$ (**3a**) show a fast fluxional behavior at room temperature. Hence, a free coordination site is always latently present, which can be occupied by a substrate molecule in a catalytic reaction. All these facts are reasons for the excellent activity of ether−phosphine systems in catalytic reactions, in which an empty coordination site at the metal center is decisively afforded.[3,6]

The exchange process already proposed by Werner et al.[7] for a complex analogous to **3a** has been proved, and additionally a mechanism for the formation of complexes **3a** and **5a** from the ortho-metalated complex **4a** has been found.

Acknowledgment. Support of this work by the Fonds der Chemischen Industrie, Frankfurt/Main, Germany, and by Degussa AG in the form of an $IrCl_3\cdot6H_2O$ gift is gratefully acknowledged.

OM970105J

---

[27] (a) Halpern, J.; Wong, C. S. *J. Chem. Soc., Chem. Commun.* **1973**, 629. (b) Halpern, J.; Okamoto, T.; Zakhariev, A. *J. Mol. Catal.* **1976**, *2*, 65.