

Inorganica Chimica Acta 269 (1998) 13-22

Inorganica Chimica Acta

Reactivity and chemical exchange processes of bis(ether-phosphine) iridium(III) complexes¹

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Received 4 March 1997; revised 9 April 1997; accepted 5 May 1997

Abstract

The orthometalated iridium(III) complex CIIrH($POCH_2$)(PO) ($POCH_2 = \eta^2(P,OCH_2)$ coordination of Cy₂PCH₂CH₂OCH₂, $PO = \eta^2(P,O)$ coordination of Cy₂PCH₂CH₂OCH₃) (1) reacts with CS₂, HCl, and H₂ under re-formation of the methoxy group to give CIIr(η^2 -CS₂)($P \sim O$)₂ (3) ($P \sim O = \eta^1(P)$ coordination of Cy₂PCH₂CH₂OCH₃), *trans*-(PO)($P \sim O$)Ir(H)Cl₂ (4a) and CIIrH₂(PO)($P \sim O$) (5), respectively. Upon the reaction of 1 with CO the orthometalation is maintained to yield the carbonyl adduct CIIrH(CO)($POCH_2$)($P \sim O$) (2). Compounds 4a and 5 represent potentially unsaturated species weakly protected by the ether moiety which acts as an intramolecular solvent. The chelated five-membered ring in 4a, *cis*-(PO)($P \sim O$)Ir(H)Cl₂ (4b) and 5 can easily be cleaved by carbon monoxide, pyridine and CS₂ whereby the complexes Cl₂IrH(CO)($P \sim O$)₂ (7), ClIrH₂(C₃H₅N)($P \sim O$)₂ (10), ClIrH₂(CO)($P \sim O$)₂ (11) and the dithioformato complex *cis*-($P \sim O$)₂Ir(H)Cl(S₂CH) (13a) are formed. In toluene 13a isomerizes to give the *trans*-product 13b. Comparative NMR studies on the fluxional behavior of the ether phosphine ligands of the five monochelated complexes 4a,b, 5, IrH₃($P \sim O$)₂(6) and Cl₃Ir(PO)($P \sim O$) (9a) were performed to determine the dependence of the exchange rates on the strength of the iridium–(ether)oxygen bond. Complex 9b, the phenyl congener of 9a, crystallizes in the orthorhombic space group *Pna*₂, with Z = 4. The cell dimensions are a = 1695.2(3), b = 1093.4(2), c = 1621.5(9) pm, $R_1 = 0.018$ and $wR_2 = 0.042$. © 1998 Elsevier Science S.A.

Keywords: Iridium complexes; Ether-phosphine complexes; Crystal structures

1. Introduction

Coordinatively unsaturated transition metal complexes represent highly reactive intermediates in catalytic processes and are able to coordinate and to activate substrate molecules [1]. The introduction of bifunctional ether-phosphines (O,P) instead of 'classical' tertiary phosphines has significantly affected the isolation and thus the examination of coordinatively unsaturated species [2]. These 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. In these 'hemilabile' ligands the ether-oxygen donor can be regarded as an intramolecular solvent molecule stabilizing the vacant coordination site by chelation and hence make these complexes much more stable than simple solvent adducts which are simulated in this way [2,3]. In the case of bis(ether-phosphine)metal complexes with only one chelating ligand exchange processes were observed. A range of (ether-phosphine)ruthenium [4], -rhodium [5] and -palladium [6] complexes shows such fluxional behavior at rates slow enough to be studied by ³¹P 'IMR spectroscopy. Valuable data on the availability of the 'free' coordination site for substrate molecules could be obtained in this way [1–4]. Passing from central atoms of the 4d series to 5d transition metals leads to an increasing oxophilicity and thus to a stronger metal–(ether)oxygen bond in osmium [7], iridium [8,9] and platinum complexes [10]. In the case of osmium and platinum a dechelation of the ether-phosphines takes place, but no exchange has been observed. Werner et al. [9] described the isopropyl congeners of the iridium compounds 1, 4a and 5 but did not investigate exchange processes.

In this paper the interest is focused on complexes of iridium(III) in order to complete the investigations on the 5d series. The availability of coordination sites occupied by the weakly bound (ether)oxygen as revealed in reactions with different donors and by chemical exchange processes

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¹ Dedicated to Professor Wolfgang Beck on the occasion of his 65th birthday.

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between chelating and non-chelating ether-phosphines was studied. Examples are pyridine, carbon monoxide and carbon disulfide which were reacted with the chelated complexes CllrH(POCH₂)(PO) (1) (POCH₂ = η^2 (P,OCH₂) coordination of Cy₂PCH₂CH₂OCH₂, $PO = \eta^2(P,O)$ coordination of $Cy_2PCH_2CH_2OCH_3$, trans-(PO)(P~O)Ir(H)Cl₂ (4a) $(\mathbf{P} \sim \mathbf{O} = \eta^{1}(\mathbf{P})$ coordination of $Cy_{2}PCH_{2}CH_{2}OCH_{3})$, $cis_{-}(PO)(P \sim O)Ir(H)Cl_2$ (4b) and $CIIrH_2(PO)(P \sim O)$ (5). In the case of the monochelated species 4a, 4b and 5 the added molecules substitute an (ether)oxygen donor and lead to non-chelating complexes. In this way, the reaction of solvent stabilized intermediates with substrates in catalytic cycles is simulated. In order to perform a comparative study on the exchange process shown by monochelated bis(etherphosphine) complexes a series of five chloro(hydrido)iridium(III) compounds were prepared: the trichloride $Cl_3Ir(\dot{P}\dot{O})(P\sim O)$ (9a), the monohydrides 4a,b, the dihydride 5 and the trihydride $IrH_3(P \sim O)_2$ (6). As three of them (4a,b and 5) exhibit fluxional behavior dynamic NMR studies were performed with the aim of correlating exchange rates with structural parameters. It has been shown that a stronger iridium-(ether)oxygen interaction results in a slower chemical exchange. This finding is also reflected by the fact that in complex 9a for which no exchange was observed the (ether)oxygen could not be substituted by other molecules. All reactions proceed under very mild conditions with high selectivities of the desired products.

2. Experimental

All manipulations were carried out under an atmosphere of argon by use of standard Schlenk techniques at ambient temperature. 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 a Perkin-Elmer model 4000 atomic absorption spectrometer. Cl and S analyses were carried out according to Schöniger [11] and analyzed as described by Dirschel and Erne [12] and Wagner [13]. ¹H and ¹³C chemical shifts were measured relative to partially deuterated solvent peaks and to deuterated solvent peaks. respectively, which are reported relative to TMS. ³¹P chemical shifts were measured relative to 85% H₃PO₄ (δ =0). Variable temperature NMR measurements were performed on a Bruker DRX 250 spectrometer. The temperature was determined with a temperature control unit (Bruker VT 100 instrument) and an external thermocouple (PT 100). The NMR probe temperature was calibrated by the method of van Geet [14] and is considered accurate ± 1 K (about 20 min was required for the temperature equilibration of the NMR sample). Calculation and estimation of exchange rates have been performed as described by Günther [15].

2.1. Reagents

The complexes 1, 4a and 5 [9] and the ligands $(C_6H_{11})_2PCH_2CH_2OCH_3$ and $(C_6H_5)_2PCH_2CH_2OCH_3$ [16] were prepared according to published procedures.

2.2. 3-Carbonyl-3-chloro-4,4-dicyclohexyl-3-[dicyclohexyl-(methoxyethyl)phosphine-P]-3-hydrido-1-oxa-3-irida-4-phosphacyclohexane (2)

A solution of 1 (75 mg, 0.1 mmol) in 2 ml of toluene was treated at room temperature for 10 min with 1 bar of carbon monoxide. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 65 mg (85%) of 2, m.p. 130°C (dec.). MS (FD, 308 K): m/z 768 [M^+]. Anal. Calc. for $C_{31}H_{58}ClIrO_3P_2$ (768.4): C, 48.46; H, 7.61; Cl, 4.61; Ir, 25.01. Found: C, 48.35; H, 7.75; Cl, 4.32; Ir, 24.70%. IR (KBr): ν (IrH) 2110, ν (CO) 1985 cm⁻¹. ¹H NMR (250.13 MHz, benzene- d_6 , 295 K): δ (ppm) 4.8 (pseudo t, 1H, ${}^{3}J_{PH}$ = 7.3, ${}^{2}J_{HH}$ = 7.3 Hz, IrCH), 4.2 (m, 1H, IrCH), -7.4 (dt, 1H, ${}^{2}J_{PH}$ = 18.0, ${}^{3}J_{HH}$ = 3.0 Hz, IrH). ${}^{13}C{}^{1}H{}$ NMR (62.90 MHz, benzene- d_6 , 295 K): δ (ppm) 178.5 (pseudo t, ${}^{2}J_{PC}$ = 5.8, ${}^{2}J_{P'C}$ = 5.8 Hz, CO), 30.0–25.0 (m, C_6H_{11}).

2.3. $(\eta^2$ -Carbon disulfide)chloro-trans-bis[dicyclohexyl-(methoxyethyl)phosphine-P; P']iridium (3)

To a solution of 1 (75 mg, 0.1 mmol) in 2 ml of toluene, 10 mg (0.13 mmol) of CS₂ were added and the solution was stirred for 10 min at room temperature. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 67 mg (82%) of 3, m.p. 150°C (dec.). MS (FD, 308 K): m/z 784 $[M^+ - S]$. Anal. Calc. for C₃₁H₅₈ClIrO₂P₂S₂ (816.5): C, 45.60; H, 7.16; Cl, 4.34; Ir, 23.54; S, 7.85. Found: C, 45.92; H, 7.31; Cl, 7.91; Ir, 23.33; S, 7.91%. IR (KBr): ν (C=S) 1262, ν (C-S) 799 cm⁻¹. ¹³C{¹H} NMR (62.90 MHz, benzene-d₆, 295 K): δ (ppm) 240.0 (t, ²J_{PC}=11.0 Hz, CS₂), 34.3 (vt, N=28 Hz² [17], PCH), 30.0–25.0 (m, C₆H₁₁), 15.3 (vt, N=20 Hz [17], PCH₂).

2.4. Dichloro-cis-bis[dicyclohexyl(methoxyethyl)phosphine-P; P',O']hydridoiridium(III) (4b)

To a solution of 5 (75 mg, 0.1 mmol) in 2 ml of toluene, 0.5 ml of a saturated solution of HCl in diethylether was added. A slight gas formation was observed. Subsequently the solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 66 mg (85%) of 4b, m.p. 121°C (dec.). MS (FD, 308 K): m/z776 [M^+ – H]. Anal. Calc. for C₃₀H₅₉Cl₂IrO₂P₂ (776.9): C, 46.38; H, 7.66; Cl, 9.13; Ir, 24.74. Found: C,

 $^{^{2}}N = |^{1}J_{PC} + ^{3}J_{PC}|$

46.20; H, 7.37; Cl, 9.52; Ir, 24.80%. IR (KBr): ν (IrH) 2223 cm⁻¹. ¹H NMR (250.13 MHz, benzene- d_6 , 295 K): δ (ppm) -21.7 (t, ² J_{PH} = 19.0 Hz, IrH).

2.5. Isomerization of 4a to 4b

A solution of 70.0 mg (0.1 mmol) 4a in 1 ml of acetoned₆ was stirred for 2 days at ambient temperature. ³¹P{¹H}, ¹³C{¹H}, ¹H NMR, and MS spectroscopy revealed the presence of ~ 30% 4b in the pale yellow solution Further stirring did not change the ratio of 4a to 4b. MS (FD, 308 K): m/z776 [M^+ – H]. IR (KBr): ν (IrH) 2223 cm⁻¹. ¹H NMR (250.13 MHz, benzene-d₆, 295 K): δ (ppm) – 21.7 (t, ²J_{PH} = 19.0 Hz, IrH).

2.6. Trans-bis[dicyclohexyl(methoxyethyl)-phosphine-P; P']trihydridoiridium(III) (6)

To a solution of 5 (75.0 mg, 0.1 mmol) in 2 ml of toluene, 10.0 mg (0.26 mmol) of NaBH₄ were added at ambient temperature. The mixture was stirred for 2 days, filtered (P4) and the solvent of the filtrate was removed in vacuo. The residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 50 mg (70%) of 6, m.p. 110°C (dec.). MS (FD, 308 K): m/z 705 [M^+ – 3H]. Anal. Calc. for C₃₀H₆₁IrO₂P₂ (708.0): C, 50.90; H, 8.68; Ir, 27.15. Found: C, 51.12; H, 8.30; Ir, 27.03%. IR (KBr): ν (IrH) 1942 cm⁻¹. ¹H NMR (250.13 MHz, benzene- d_6 , 295 K): δ (ppm) – 10.5 (t, ²J_{PH}=12.7 Hz, IrH₃). ¹³C{¹H} NMR (62.90 MHz, benzene- d_6 , 295 K): δ (ppm) 37.4 (vt, N = 29 Hz [17], PCH), 30.0–25.0 (m, C₆H₁₁).

2.7. Preparation of 6 from 4a

To a solution of 4a (78 mg, 0.1 mmol) in 2 ml of THF, 10.0 mg (0.26 mmol) of NaBH₄ were added at ambient temperature. The mixture was stirred for 2 days, filtered (P4) and the solvent of the filtrate was removed in vacuo. The residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 50 mg (70%) of 6. MS (FD, 308 K): m/z 705 [M^+ – 3H], IR (KBr): ν (IrH) 1942 cm⁻¹. ¹H NMR (250.13 MHz, benzene- d_6 , 295 K): δ (ppm) – 10.5 (t, ² J_{PH} = 12.7 Hz, IrH₃). ¹³C{¹H} NMR (62.90 MHz, benzene- d_6 , 2°5 K): δ (ppm) 37.4 (vt, N = 29 Hz [17], PCH), 30.0–25.0 (m, C₆H₁₁).

2.8. Preparation of 6 from 4b

To a solution of 4b (78 mg, 0.1 mmol) in 2 ml of THF, 10.0 mg (0.26 mmol) of NaBH₄ were added at ambient temperature. The mixture was stirred for 2 days, filtered (P4) and the solvent of the filtrate was removed in vacuo. The residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 50 mg (70%) of 6. MS (FD, 308 K): m/z 705 [M^+ - 3H], IR (KBr): ν (IrH) 1942 cm⁻¹. ¹H NMR (250.13 MHz, benzene- d_6 , 295 K): δ (ppm) - 10.5 (t, ${}^{2}J_{PH}$ = 12.7 Hz, IrH₃). ${}^{13}C{}^{1}H$ NMR (62.90 MHz, benzene- d_{6} , 295 K): δ (ppm) 37.4 (vt, N = 29 Hz [17], PCH), 30.0-25.0 (m, C₆H₁₁).

2.9. Carbonyl-cis-dichloro-trans-bis[dicyclohexyl-(methoxyethyl)phosphine-P; P']hydridoiridium(III) (7)

A solution of **4b** (77 mg, 0.1 mmol) in 2 ml of toluene was treated at ambient temperature for 10 min with 1 bar of carbon monoxide. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 73 mg (90%) of **7**, m.p. 130°C (dec.). MS (FD, 308 K): m/z 803 [$M^+ - H$]. Anal. Calc. for $C_{31}H_{59}Cl_2IrO_3P_2$ (805.0): C, 46.26; H, 7.39; Cl, 8.81; Ir, 23.88. Found: C, 46.21; H, 7.37; Cl, 8.81; Ir, 23.57%. IR (KBr): ν (IrH) 2217, ν (CO) 2013 cm⁻¹. ¹H NMR (250.13 MHz, benzene- d_6 , 295 K): δ (ppm) - 16.9 (t, $^2J_{PH} = 11.3$ Hz, IrH). $^{13}C\{^{1}H\}$ NMR (62.90 MHz, benzene- d_6 , 295 K): δ (ppm) 164.6 (t, $^2J_{PC} = 8.1$ Hz, CO), 30.0–25.0 (m, C_6H_{11}), 27.7 (vt, N = 20 Hz [17], PCH₂).

2.10. Preparation of 7 from 4a

A solution of 4a (77 mg, 0.1 mmol) in 2 ml of toluene was treated at ambient temperature for 10 min with 1 bar of carbon monoxide. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 69 mg (80%) of 7. MS (FD, 308 K): m/z 803 [M^+ – H]. IR (KBr): ν (IrH) 2217, ν (CO) 2013 cm⁻¹. ¹H NMR (250.13 MHz, bc): ene- d_6 , 295 K): δ (ppm) – 16.9 (t, ² J_{PH} =11.3 Hz, IrH). ¹³C{¹H} NMR (62.90 MHz, benzene- d_6 , 295 K): δ (ppm) 164.6 (t, ² J_{PC} = 8.1 Hz, CO), 30.0–25.0 (m, C₆H₁₁), 27.7 (vt, N= 20 Hz [17], PCH₂).

2.11. Cis-dichloro-cis-bis[dicyclohexyl(methoxyethyl)phosphine-P; P']hydrido(pyridine-N)iridium(111)(8)

To a solution of **4b** (78 mg, 0.1 mmol) in 2 ml of toluene, 10 mg (0.13 mmol) of pyridine were added and the solution was stirred for 10 min at ambient temperature. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 69 mg (80%) of **8**, m.p. 140°C (dec.). MS (FD, 308 K): m/z 777 $[M^+ - C_5H_5N]$. Anal. Calc. for $C_{35}H_{64}Cl_2IrNO_2P_2$ (856.0): C, 49.11; H, 7.54; Cl, 8.82; Ir, 22.46; N, 1.64. Found: C, 49.03; H, 7.73; Cl, 8.60; Ir, 22.25; N, 1.75%. ¹H NMR (250.13 MHz, acetone- d_6 , 295 K): δ (ppm) -22.7 (t, ² J_{PH} = 18.0 Hz, IrH). ¹³C{¹H} NMR (62.90 MHz, acetone d_6 , 295 K): δ (ppm) 158.6 (s, C2, C6 of C₅H₅N), 152.6 (s, C4 of C₅H₅N), 135.8 (s, C3, C5 of C₅H₅N), 30.0-25.0 (m, C₆H₁₁).

2.12. Mer-trichloro-cis-bis[dicyclohexyl(methoxyethyl)phosphine-P; P',O']iridium(III) (9a)

A mixture of 82 mg (0.2 mmol) of $IrCl_3 \cdot 6H_2O$, 5 ml of THF and 102 mg (0.4 mmol) of $(C_6H_{11})_2PCH_2CH_2OCH_3$ was refluxed for 3 h. After a pale yellow solution had formed it was cooled to ambient temperature and the solvent was removed in vacuo. The residue was washed with 0.5 ml of diethylether and three times with 0.5 ml of n-pentane and dried in vacuo to yield 114 mg (70%) of 9a, m.p. 180°C (dec.). MS (FD, 308 K): m/z 809 [M^+]. Anal. Calc. for $C_{30}H_{58}Cl_3IrO_2P_2$ (811.3): C, 44.41; H, 7.21; Cl, 13.14; Ir 23.80. Found: C, 44.13; H, 7.11; Cl, 12.83; Ir, 23.73%. ¹³C{¹H} NMR (62.90 MHz, acetone- d_6 , 295 K): δ (ppm) 30.0-25.0 (m, C_6H_{11}), 23.3 (d, $^{1}J_{PC}$ = 32.3 Hz, PCH₂).

2.13. Preparation of 9a from 4b

To a solution of **4b** (78 mg, 0.1 mmol) in 2 ml of THF, 1 ml of a saturated solution of HCl in diethylether was added and the mixture was stirred for 1 day at ambient temperature. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 53 mg (60%) of **9a**. MS (FD, 308 K): m/z 809 [M^+]. ¹³C{¹H} NMR (62.90 MHz, acetone- d_6 , 295 K): δ (ppm) 30.0–25.0 (m, C₆H₁₁), 23.3 (d, ¹J_{PC} = 32.3 Hz, PCH₂).

2.14. Mer-trichloro-cis-bis[diphenyl(methoxyethyl)phosphine-P; P',O']iridium(III) (9b)

A mixture of 82 mg (0.2 mmol) of $IrCl_3 \cdot 6H_2O_1$, 5 ml of THF and 109 mg (0.4 mmol) of $(C_6H_5)_2PCH_2CH_2OCH_3$ was refluxed for 3 h. After a pale yellow solution was formed it was cooled to ambient temperature and the solvent was removed in vacuo. The residue was washed with 0.5 ml of diethylether and three times with 0.5 ml of n-pentane and dried in vacuo to yield 110 mg (70%) of 9b, m.p. 200°C (dec.). MS (FD, 308 K): m/z 786 [M⁺]. Anal. Calc. for $C_{30}H_{34}Cl_{3}IrO_{2}P_{2}$ (787.1): C, 45.74; H, 4.35; Cl, 13.51; Ir, 24.42. Found: C, 46.06; H, 4.54; Cl, 13.42; Ir, 24.30%. 'H NMR (250.13 MHz, acetone- d_6 , 295 K): δ (ppm) 4.0 (s, 3H, OCH₃ of \overrightarrow{PO}), 3.8 (m, 2H, OCH₂ of \overrightarrow{PO}), 3.2 (m, 2H, PCH₂ of P~O), 3.1 (m, 2H, OCH₂ of P~O), 3.0 (s, **3H**, OCH₃ of P~O), 2.7 (m, 2H, PCH₂ of \overrightarrow{PO}). ¹³C{¹H} NMR (62.90 MHz, acetone-d₆, 295 K): δ (ppm) 127-131 (m, C_6H_5) , 31.9 $(d, {}^{1}J_{PC} = 36.4 \text{ Hz}, PCH_2 \text{ of } PO)$, 28.2 $(d, {}^{1}J_{PC} = 42.6 \text{ Hz}, PCH_2 \text{ of } P \sim O).$

2.15. Chloro-trans-bis[dicyclohexyl(methoxyethyl)phosphine-P; P']dihydrido(pyridine-N)iridium(111) (10)

To a solution of 5 (75 mg, 0.1 mmol) in 2 ml of toluene, 10 mg (0.13 mmol) of pyridine were added and the solution was stirred for 10 min at ambient temperature. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 66 mg (80%) of 10, m.p. 150°C (dec.). MS (FD, 308 K): m/z742 [$M^+ - C_5H_5N$]. Anal. Calc. for $C_{35}H_{65}$ ClIrNO₂P₂ (821.3): C, 51.17; H, 7.97; Cl, 4.32; Ir, 23.67; N, 1.70. Found: C, 50.79; H, 7.89; Cl, 4.34; Ir, 23.50; N, 1.75%. IR (KBr): ν (IrH) 2180, 2202 cm⁻¹. ¹H NMR (250.13 MHz, acetone- d_{6} , 295 K): δ (ppm) -23.4, -24.1 (each dt, ² J_{PH} =16.0, ² J_{HH} =7.3 Hz, IrH₂). ¹³C{¹H} NMR (62.90 MHz, acetone- d_{6} , 295 K): δ (ppm) 174.2 (s, C2, C6 of C₅H₅N), 135.1 (s, C4 of C₅H₅N), 123.3 (s, C3, C5 of C₅H₅N), 30.0–25.0 (m, C₆H₁₁), 23.8 (vt, N=28.4 Hz [17], PCH₂).

2.16. Carbonylchloro-trans-bis[dicyclohexyl-(methoxyethyl)phosphine-P; P']dihydridoiridium(III)(11)

A solution of 5 (75 mg, 0.1 mmol) in 2 ml of toluene was treated at ambient temperature for 10 min with 1 bar of carbon monoxide. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-p-ntane and dried in vacuo to yield 69 mg (90%) of 11, m.p. 120°C (dec.). MS (FD, 308 K): m/z 768 [M^+ – H]. Anal. Calc. for C₃₁H₆₀ClIrO₃P₂ (770.4): C, 48.33; H, 7.85; Cl, 4.60; Ir 24.95. Found: C, 48.71; H, 8.03; Cl, 4.59; Ir, 25.30%. IR (KBr): ν (IrH trans to Cl) 2197, ν (IrH trans to CO) 2079, ν (CO) 1965 cm⁻¹. ¹H NMR (250.13 MHz, benzene-d₆, 295 K): δ (ppm) –9.5 (dt, ²J_{PH} = 13.2, ²J_{HH} = 5.0 Hz, IrH trans to Cl). ¹³C{¹H} NMR (62.90 MHz, benzene-d₆, 295 K): δ (ppm) 180.1 (t, ²J_{PC} = 6.7 Hz, CO), 30.0–25.0 (m, C₆H₁₁), 24.6 (vt, N = 30.0 Hz [17], PCH₂).

2.17. Chloro-cis-bis/dicyclohexyl(methoxyethyl)phosphine-P,O; P',O' |hydridoiridium(III)tetrafluoroborate (12)

To a solution of 5 (75 mg, 0.1 mmol) in 2 ml of THF, 33 mg (0.1 mmol) of [CPh₃][BF₄] were added and the solution was stirred for 24 h at ambient temperature. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-hexane and dried in vacuo to yield 66 mg (80%) of 12, m.p. 110°C (dec.). MS (FD, 308 K): m/z 741 [M^+]. Anal. Calc. for C₃₀H₅₉BClF₄IrO₂P₂ (828.2): C, 43.51; H, 7.18; Cl, 4.28; F, 9.18; Ir, 23.21. Found: C, 43.32; H, 7.52; Cl, 4.31; F, 9.24; Ir, 23.20%. ¹H NMR (250.13 MHz, acetone-d₆, 295 K): δ (ppm) -32.8 (t, ²J_{PH} = 14.6 Hz, IrH). ¹³C{¹H} NMR (62.90 MHz, acetone-d₆, 295 K): δ (ppm) 30.0-25.0 (m, C₆H₁₁), 22.5 (vt, N = 33 Hz [17], PCH₂).

2.18. Chloro(dithioformato-S,S')-cis-bis[dicyclohexyl-(methoxyethyl)phosphine-P,P']hydridoiridium(III)(13a)

To a solution of 5 (75 mg, 0.1 mmol) in 2 ml of toluene, 10 mg (0.13 mmol) of CS_2 were added and the solution was stirred for 10 min at ambient temperature. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 72 mg (88%)

Table 1

of **13a**, m.p. 110°C (dec.). MS (FD, 308 K): m/z 818 [M^+]. Anal. Calc. for C₃₁H₆₀ClIrO₂P₂S₂ (818.7): C, 45.49; H, 7.39; Cl, 4.33; Ir, 23.48; S, 7.83. Found: C, 45.30; H, 7.18; Cl, 4.30; Ir, 23.30; S, 7.90%. ¹H NMR (250.13 MHz, benzene d_6 , 295 K): δ (ppm) 12.3 (t, 1H, ${}^{4}J_{PH}$ =7.9 Hz, S₂CH), -21.7 (t, 1H, ${}^{2}J_{PH}$ =16.5 Hz, IrH). ${}^{13}C{}^{1}H$ NMR (62.90 MHz, benzene- d_6 , 295 K): δ (ppm) 236.1 (t, ${}^{3}J_{PC}$ =5.0 Hz, HCS₂), 36.7 and 35.8 (each d, ${}^{1}J_{PC}$ =31.4 Hz, PCH), 30.0–25.0 (m, C₆H₁₁), 21.5 (d, ${}^{1}J_{PC}$ =30.4 Hz, PCH₂).

2.19. Chloro(dithioformato-S,S')-trans-bis[dicyclohexyl-(methoxyethyl)phosphine-P,P']hydridoiridium(III)(13b)

A solution of **13a** (82 mg, 0.1 mmol) in 2 ml of toluene was stirred for 1 day at ambient temperature. The solvent was removed in vacuo, the residue was washed three times with 0.5 ml of n-pentane and dried in vacuo to yield 80 mg (97%) of **13b**, m.p. 130°C (dec.). MS (FD, 308 K):m/z818 [M^+]. *Anal.* Calc. for C₃₁H₆₀ClIrO₂P₂S₂ (818.7): C, 45.49; H, 7.39; Cl, 4.33; Ir, 23.48; S, 7.83. Found: C, 45.20; H, 7.11; Cl, 4.40; Ir, 23.62; S, 7.90%. IR (KBr): ν_{as} (CS₂) 1006 cm⁻¹. ¹H NMR (250.13 MHz, benzene- d_6 , 295 K): δ (ppm) 11.9 (broad s, S₂CH), -23.0 (t, ${}^{2}J_{PH}$ = 14.7 Hz, IrH). ${}^{13}C{}^{1}H$ NMR (62.90 MHz, benzene- d_6 , 295 K): δ (ppm) 227.7 (t, ${}^{3}J_{PC}$ = 5.0 Hz, HCS₂), 34.8 and 31.8 (each vt, N = 29 Hz [17], PCH), 30.0–25.0 (m, C₆H₁₁), 18.3 (vt, N = 29 Hz [17], PCH₂).

2.20. X-ray structural determination of mer-trichloro-cisbis[diphenyl(methoxyethyl)phosphine-P; P',O']iridium(III) (**9b**)

Single crystals of 9b were grown from a toluene solution at ambient temperature. A crystal with the approximate dimensions $0.2 \times 0.2 \times 0.3$ mm was mounted on a glass fiber and transferred to a P4 Siemens diffractometer. Rotation photographs were taken and a photo search was performed to find a suitable reduced cell (graphite-monochromated Mo K α radiation). The lattice constants were determined with 25 precisely centered high-angle reflections and refined by least-squares methods. Two check reflections were monitored every 58 intensity measurements. An absorption correction was applied (ψ -scan maximal and minimal transmission 0.362 and 0.234). The structure was solved by Patterson methods [18]. All non-hydrogen atoms were refined anisotropically (based on F^2). Hydrogen atoms were placed in calculated positions (riding model). Maximum and minimum peaks in the final difference synthesis were 0.353 and -0.305 e Å⁻³. The final cell parameters and specific data collection parameters for 9b are summarized in Table 1. The final atomic positional data are listed in Table 2. See also Section 5.

Summary of crystallographic data and parameters for data collection and refinement of 9b

Formula	
Formula weight	$C_{30}H_{34}Cl_{3}IrO_{2}P_{2}$
Formula weight	/87.06
Crystal system	orthorhombic
Space group	Pna2 ₁
<i>a</i> (pm)	1695.2(3)
<i>b</i> (pm)	1093.4(2)
<i>c</i> (pm)	1621.5(3)
V (pm ³ ×10 ⁶)	3005.5(9)
Ζ	4
$\mu(Mo K\alpha) (mm^{-1})$	4.842
Calc. density (g cm ⁻³)	1.739
Temperature (K)	173
<i>F</i> (000)	1552
2θ scan limits (°)	4-40
Scan type	ω
Scan speed (° min ⁻¹)	variable, 8-30
Scan range (°)	0.8
Data collected: h, k, l	$\pm 16, \pm 10, \pm 15$
No. reflections collected	10508
No. unique reflections $F \ge 4\sigma(F)$	2573
No. parameters refined	344
GOF	1.53
R ₁ ^a	0.018
wR ₂ ^b	0.042

 $|{}^{a}R_{1} = \sum ||F_{0}| - |F_{c}|| / \sum |F_{0}|.$

^b $wR_2 = \left[\sum \left[w(F_o^2 - F_c^2)^2 \right] / \left[\sum \left[w(F_o^2)^2 \right] \right]^{0.5} \right]$

3. Results and discussion

3.1. Reaction of the orthometalated complex 1 with carbon monoxide, carbon disulfide, hydrogen chloride and dihydrogen

When the iridium complex 1 is treated with CO, the orthometalation is maintained and only the (ether)oxygen is substituted by a carbonyl ligand to give ClIrH(CO)- $(POCH_2)(P \sim O)$ (2) (Scheme 1). Carbon monoxide cannot add oxidatively to iridium and therefore the methoxy group is not rebuilt in this way. The structure of 2 was derived from the following findings: as in complex 1 the protons at the IrCH₂ moiety are inequivalent as expected for a group incorporated into a six-membered cycle. They are coupling to each other, to the two phosphorus nuclei and additionally the high-field proton is coupling to the hydride as proved by a COSY spectrum. The large ${}^{2}J_{pp}$ coupling constant of 284 Hz indicates a trans configuration of the phosphine ligands. The doublets into which the AB spin system of the ${}^{31}P{}^{1}H$ NMR spectrum is additionally split when the phosphorus nuclei are allowed to couple to the hydride indicate the presence of a single hydride at iridium. The relative low field shift of the hydride (¹H NMR: $\delta = -7.4$ ppm) [19], the low frequency of the Ir-H (IR, KBr: 2110 cm⁻¹) and the C=O (1985 cm⁻¹) vibrations indicate the structure depicted in Scheme 1 with the hydride trans to the carbonyl ligand [20].

In contrast to this behavior, the orthometalated species 1 reacts with CS_2 , HCl and H_2 [9] under re-formation of

Table 2 Atomic coordinates $[\times 10^4]$ and equivalent isotropic displacement coefficients $(pm^2 \times 10^{-1})$ of 9b

Atom	х.	у	2	Ueq
lr(1)	- 76(1)	1674(1)	0(1)	20(1)
CI (1)	2110(1)	-2122(1)	-70(1)	27(1)
Cl(2)	1158(1)	1891(1)	-135(1)	30(1)
Cl(3)	2194(1)	187(2)	-1371(1)	33(1)
P(1)	922(1)	- 164(1)	1174(1)	21(1)
C(1)	542(4)	2182(6)	1768(4)	31(2)
C(2)	634(5)	3163(6)	2289(4)	32(2)
C(3)	1163(5)	3106(6)	2936(5)	36(2)
C(4)	1577(4)	2050(7)	3077(5)	34(2)
C(5)	1483(4)	1043(6)	2564(4)	26(2)
C(6)	969(4)	1118(5)	1894(4)	20(2)
C(7)	278(4)	-1322(6)	2531(5)	37(2)
C(8)	127(5)	-2257(7)	3074(5)	41(2)
C(9)	514(5)	-3353(7)	2986(4)	38(2)
C(10)	1054(4)	-3505(6)	2351(5)	38(2)
C(11)	1203(4)	- 2560(6)	1798(4)	28(2)
C(12)	825(4)	- 1443(6)	1887(4)	27(2)
P(2)	2823(1)	581(2)	533(1)	23(1)
C(13)	3209(4)	2743(6)	-232(4)	35(2)
C(14)	3219(4)	4019(7)	-325(5)	41(2)
C(15)	2938(4)	4757(7)	280(5)	38(2)
C(16)	2648(4)	4253(6)	1005(5)	40(2)
C(17)	2628(4)	2992(6)	1104(5)	38(2)
C(18)	2913(4)	2237(6)	492(4)	26(2)
C(19)	3432(4)	845(6)	2166(5)	34(2)
C(20)	3613(5)	391(7)	2941(5)	37(2)
C(21)	3443(4)	- 787(7)	3134(5)	35(2)
C(22)	3102(4)	- 1543(6)	2571(4)	33(2)
C(23)	2914(4)	-1101(6)	1793(4)	29(2)
C(24)	3063(4)	114(5)	1580(4)	23(2)
C(25)	-63(4)	- 146(6)	701(4)	30(2)
C(26)	- 62(3)	-1056(5)	-2(6)	31(1)
0(1)	548(3)	=720(4)	- 574(3)	30(1)
C(27)	546(5)	- 1529(7)	-1280(5)	44(2)
C(28)	3659(4)	- 50(5)	- 54(8)	28(2)
C(29)	4452(4)	280(7)	305(4)	37(2)
O(2)	5019(3)	- 336(4)	- 160(3)	34(2)
C (30)	5785(4)	180(5)	155(6)	37(2)

the methoxy group to yield the complexes $ClIr(\eta^2-CS_2)(P \sim O)_2$ (3), *cis*-Cl₂IrH(PO)($P \sim O$) (4a) and *cis*-H₂IrCl(PO)($P \sim O$) (5) (Scheme 1). In complex 3 both phosphorus atoms are equivalent and no hydride is present. CS_2 is η^2 bound as shown by the IR spectrum in which both typical bands are visible (1262 and 799 cm⁻¹ for the C=S and C-S vibrations) [21]. The mechanism of the reaction with HCl and H₂ is described elsewhere [22]. Compounds 4a and 5 formed in this way show only one resonance in the ³¹P(¹H) NMR spectrum at room temperature, but cooling of both samples reveals the structures depicted in Scheme 1 with a chelating and an $\eta^1(P)$ coordinated ether-phosphine *trans* to each other as proved by the strong ²J_{PP} coupling (see later and Table 3). The *cis*-hydrides of 5 also decoalesce [22].

When 4a is reacted with NaBH₄ two chlorides are substituted quantitatively by hydrides to give the trihydridoiridium complex $H_3Ir(P \sim O)_2$ (6). If this slow reaction is monitored



³¹P{¹H} and ¹H NMR spectroscopically the resonances of the dihydride 5 along with those of the starting compound 4a and the product 6 are observed. Obviously 5 is an intermediate. Even at 170 K the resulting trihydride 6 reveals two equivalent phosphine ligands. The analogy to 4a and 5 suggests a monochelated structure for complex 6 but the exchange can not be monitored by NMR methods and the IR spectrum indicates two non-chelating ether-phosphines (Table 3). Compound 6 is also obtained directly from 5 and NaBH₄ (Scheme 1).

From the results described above it is concluded that the iridium complex 1 is reacting under retention of the orthometalation when no oxidative addition is possible as in the case of CO and under re-formation of the methoxy group when an iridium(III) species can be formed.

3.2. Formation and reactivity of $cis - (PO)(P \sim O)Ir(H)Cl_2$ (4b)

In solution at ambient temperature the *trans*-complex 4a is slowly but incompletely transformed into the *cis*-bis(etherphosphine) isomer 4b (Scheme 2). The same product is also obtained when 5 is treated with hydrogen chloride. Thus 4b is considered to be the thermodynamically stable product. The small ${}^{2}J_{PP}$ coupling constant and the doublet of doublets in the high field region of the ¹H NMR spectrum of 4b caused by the similar ${}^{2}J_{PH}$ couplings (Table 3) are in favor of the structure depicted in Scheme 2. Off resonance decoupling in

Table 3						
31P{'H},	¹³ C{ ¹ H} and I	IR (KBr)	data of	complexes	1-13 at	298 K

Complex	δ ³¹ Ρ (ppm) *	² J _{PP} (Hz)	δ ¹³ C (ppm) ^a CH ₂ O	δ ¹³ C (ppm) * OCH ₃	IR (cm ⁻¹) $\nu_{as}(C_2O)$
1	20.3(d)	348.0	74.4	62.3	1114
	-2.5(d)		67.9	67.9	1057
2	6.3(d)	284.0	75.6	59.5	1114
	-5.6(d)		70.1		1076
3	2.8(s)	-	68.8	58.4	1107
4a	11.2(s)	-	71.4	60.9	1107
					1046
4b	21.3(d)	12.0	73.5	61.9	1104
	-4.2(d)		68.1	58.7	1042
5	32.2(s)	-	73.5	60.8	1110
-	(-)			00.0	1052
6	17.2(s)	_	72.6	58 4	11032
7	3 Q(s)	_	68.0	57.7	1102
8 b	- 12 2(d)	14.0	68.5	58.3	1108
ů.	22.9(d)	14.0	00.0	56.5	1108
Qg h		11.1	73.0	60.2	1103
24	-286(d)	11.1	68.2	59 7	1005
QD b	-318(d)	15.1	73.3	36.7 60.0	1003
70	-14.6(d)	13.1	67.0	500.9 50 0	100
10 b	- 14.0(u)		07. <u>2</u> 70.4	36.U 59.D	1055
10	10.9(8)	-	70.4	38.2 59.6	1107
11	14.1(S) 26.4(J)	-	70.7	58.0	1108
12."	26.4(d)	12.1	80.0	65.3	1058
	11.2(d)		68.5	60.6	
13a	1.3(s)	-	68.3	56.9	1107
13b	-12.5(s)	-	68.0	57.4	1107

^a In benzene-d₆ at 298 K.

"NMR measurements in acetone-do at 298 K.

a ³¹P{¹H} NMR experiment allowed to determine that indeed only one hydride ligand is present in 4b. Like its trans-isomer **4a.b** reacts with NaBH₄ to give the trihydridoiridium complex 6. In compound 4b the ether-phosphines are involved in a chemical exchange process as proved by variable temperature ³¹P{¹H} NMR and EXSY spectra (see Section 3.4). Already under very mild conditions the chelating etheroxygen atom is replaced by other ligands such as carbon monoxide or pyridine to give the trans- and cis-diphosphine complexes $Cl_2IrH(CO)(P \sim O)_2$ (7) and $Cl_2IrH(C_5H_5N)$ - $(P \sim O)_2$ (8), respectively. In both complexes the hydride occupies a *cis*-position to both phosphine ligands as proved by the triplets in the ¹H NMR spectra. 7 can also be prepared by reaction of 4a with carbon monoxide. The relatively high frequency of the Ir-H vibration of 4b and 7 is consistent with a trans arrangement of the HIrCl moiety [20]. On the basis of ³¹P{¹H} and ¹H NMR spectra (Table 3 and Section 2) the pyridine complex 8 is provided with two inequivalent cisphosphines and one hydride ligand cis to both phosphines (Scheme 2).

With an excess of hydrogen chloride **4b** reacts slowly under formation of the monochelated *mer*-trichloroiridium complex $Cl_3Ir(PO)(P\sim O)$ (**9a**). This product is identical with that of the reaction between $IrCl_3 \cdot 6H_2O$ and two equivalents of $Cy_2PCH_2CH_2OCH_3$. Complex **9a** is a stable, nonfluxional species in which the (ether)oxygen moiety cannot



be replaced by other ligands. The latter was evidenced in the case of the examples carbon monoxide, pyridine, acetonitrile and THF. Treatment of **9a** with NaBH₄, NaH₂, or LiAlH₄ did not lead to a substitution of chlorides by hydrides as observed for **4a,b** and **5** (Schemes 1 and 2).



Table 4

Selected interatomic distances (Å)	and angles	(°)) fo r 9b
----------------------------------	----	------------	-----	------------------

Bond lengths			
Ir(1) - P(1)	2.294(2)	lr(1)-Cl(1)	2.359(1)
lr(1)-P(2)	2.248(2)	lr(1)-Cl(2)	2.332(2)
lr(1)-O(1)	2.237(4)	lr(1)-Cl(3)	2.408(2)
Bond angles			
P(1) - Ir(1) - P(2)	100.13(7)	P(1)-lr(1)-Cl(1)	100.04(6)
P(1)=lr(1)=O(1)	81.80(1)	P(1) = Ir(1) = CI(2)	84.71(6)
P(1)=lr(1)=Cl(3)	167.05(6)	O(1)=Ir(1)=P(2)	178.04(1)
O(1)=lr(1)=Cl(3)	88.05(1)	O(1)-lr(1)-Cl(2)	86.05(1)
O(1)=lr(1)=Cl(1)	87.09(1)	Cl(1)-lr(1)-P(2)	93,79(6)
Cl(1)-lr(1)-Cl(2)	171.02(8)	Cl(1)=lr(1)=Cl(3)	87.39(7)
Cl(2)=lr(1)=Cl(3)	86.59(6)		

The geometrical features of 9a were corroborated by an X-ray structural analysis of the analogous compound 9b with Ph₂PCH₂CH₂OCH₁ ligands³. The structural identity between 9a and 9b was proved by NMR, MS and IR spectroscopy. An ORTEP plot of the molecular structure of 9b is depicted in Fig. 1. Table 4 contains selected bond distances and angles. As expected from other characterization methods the central atom is octahedrally coordinated by two cisarranged phosphines, three chloride ligands positioned meridionally and by the chelated (ether) oxygen atom trans to P2. As this oxygen donor O1 occupies a *trans* position to the non-chelating phosphine, the same configuration for compound 4b is assumed. The five-membered chelate ring in 9b has an envelope conformation wherein the angle between the planes which are formed by the atoms P1, Ir1, O1, C26 and P1, C25, C26 is 131.1°.

3.3. Reactivity of $ClirH_2(PO)(P \sim O)(5)$

The weak (ether)oxygen-iridium bond in 5 is easily cleaved by the reaction of this compound with pyridine, car-



bon monoxide and carbon disulfide (Scheme 3). While the first two ligands mentioned simply replace the (ether)oxygen atom to give complexes $ClIrH_2(C_5H_5N)(P \sim O)_2$ (10) and $ClIrH_2(CO)(P \sim O)_2$ (11), in the case of carbon disulfide additionally an insertion into the Ir–H bond to form the dithio-formatoiridium(III) complex 13a takes place. In the case of 10 and 11 the *trans* configuration of the phosphines is maintained as proved by the presence of virtual triplets of the PCH₂ groups in the ¹³C{¹H} NMR spectra (A part of an AXX' spin system) indicating a relatively strong ²J_{PP} coupling [24]. The *cis* position of the hydrides results from their inequivalence and their weak ²J_{IHH} coupling (see Section 2).

From complex 5 a chloride ligand is removed by $[CPh_3][BF_4]$ to give the bis(chelated) cationic species $[CIIrH(PO)_2][BF_4]$ (12) with non-equivalent *cis*-phosphines and a hydride *cis* to both of the phosphines as demonstrated by NMR and IR spectra (Table 3 and Section 2).

In toluene an isomerization of the cis-bis(ether-phosphine)dithioformatoiridium(III) complex 13a to the trans product 13b is observed. An absorption at 1107 cm⁻¹ in the IR spectra of 13a and 13b which is assigned to the antisymmetric C₂O vibration is indicative for only non-chelating ether-phosphines. Off resonance decoupling of ¹H in the ³¹P{¹H} NMR spectra revcals in both complexes the presence of only one hydride. In the low field region of the 'H NMR spectra of 13a and 13b the resonances of the HCS₂ proton are found. The doublets for the PCH and PCH₂ groups in the ¹³C{¹H} NMR spectrum of **13a** resulting from the ${}^{1}J_{PC}$ coupling point to a cis arrangement of the phosphines [24]. As in the case of complexes 10 and 11 the trans configuration of the phosphines in 13b is derived from the ${}^{13}C{}^{1}H$ NMR spectrum (vide supra). As the phosphines of compound 13a are equivalent and *cis* to each other and the hydride is *cis* to the phosphines only the structure depicted in Scheme 3 is possible.

³ Complex 9b has been mentioned before, but was prepared in a different way [23].

3.4. Chemical exchange

The $(\eta^1 - P)(\eta^2 - PO)$ iridium (III) complexes **4a,b**, **5**, **6** and 9a are typical examples in which a fluxional behavior is expected. Suitable methods to investigate such exchange processes are variable temperature ³¹P{¹H} NMR and ³¹P exchange spectroscopy. Taking into account that the oxygen donor of the chelating ether-phosphine is only weakly coordinated to the iridium it can easily be replaced by the other (ether)oxygen atom as summarized in Scheme 4 for transand cis-phosphine complexes. For such an exchange the rupture of the Ir-O bond is required. Thus, a stronger interaction should lead to a higher activation energy for the process described and consequently to a slower exchange. (Ether)oxygen donors are known to be hard bases in terms of Pearson's [25] concept and hence should coordinate more strongly to hard central atoms. The hardness of the coordination center itself depends on the other ligands in the molecule. Thus chloro(hydrido)metal complexes of this type should exchange at rates depending strongly on the number of chloride and hydride ligands. More hydrides are expected to lead to a softer central atom and therefore to a faster exchange. More chlorides induce a harder central atom and give rise to a slower exchange.

In order to confirm this prediction the above-mentioned series of five iridium complexes were examined. The results obtained are represented in Scheme 5. For the trichloride **9a** no exchange is detected, a finding that corroborates the chemical stability of the Ir-O bond, as reported in Section 3.2. The trihydride **6** shows no decoalescence of the phosphines



Scheme 4

X = H, Cl

or of the hydrides even at 170 K. Taking into account that in the complexes 1, 4a,b, 5, 9a and 12 with a latently free coordination site this position is occupied by an (ether)oxygen atom, complex 6 could also possess a chelating etherphosphine. Complexes 4a,b and 5 hold positions in between these two extremes (9a and 6).

As expected, the dihydridoiridium(III) complex 5 is exchanging faster than the two monohydrido species 4a,b. The rate constant of *trans*-4a is significantly higher than that of its *cis* isomer 4b. This finding is in agreement with the different *trans* partners of the chelating (ether)oxygen atoms resulting in different Ir-O bond strengths.

The solubility of the five iridium(III) complexes 4a,b, 5, 6 and 9a follows the same trend: 9a and 4a,b are more soluble in polar solvents whereas 5 and 6 dissolve in rather non-polar media.

4. Conclusions

The investigations presented allow an insight into the reactivity and chemical exchange processes of several iridium(III) complexes provided with ether-phosphine ligands. In the case of compounds with a chelating and a non-chelating ether-phosphine the availability of the coordination site protected by the weakly coordinated (ether) oxygen was studied chemically by substitution reactions with an external donor and physically by dynamic NMR measurements of the exchange process observed in these complexes. Both methods supplied the same results: as expected a hard coordination center binds strongly to the (ether)oxygen atom leading to a low rate constant of the chemical exchange process. At the same time the replacement of the oxygen donor of the chelating phosphine by other molecules is impeded. Because these complexes are simulating coordinatively unsaturated and hence unstable intermediates in catalytic processes, this knowledge is important for the understanding of catalytic cycles.

5. Supplementary material

~0 6 4a 4b 213 < 170 > 350 260 T_c (K) 6 10 > 10* 8000 ~ 0 10 k (sec⁻¹) (estimated at 298 K)

Further details of the crystal structure investigation are available on request from the Fachinformationszentrum

Scheme 5.

Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-406483, the names of the authors and the journal citation.

Acknowledgements

Support of this work by the Fonds der Chemischen Industrie, Frankfurt/Main, Germany, and by Degussa AG in the form of an $IrCl_3 \cdot 6H_2O$ gift is gratefully acknowledged.

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