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Inorganica Chimica Acta 357 (2004) 2945–2952
Inorganica Chimica Acta
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Chemical ligand non-innocence in pyridine diimine Rh complexes

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Received 16 January 2004; accepted 14 February 2004
Available online 12 March 2004

Abstract

The formation and reactivity of pyridine diimine rhodium(I) alkyl complexes without β-hydrogens (Me, Bz, CH_2SiMe_3) is described. In contrast to the corresponding cobalt complexes, the rhodium complexes could not be activated to polymerise ethene. Rh ethyl complexes could not be prepared. Examples of hydrogen transfer to and from the ligand were observed, illustrating the active role the pyridine diimine ligand can play in the reactions of its complexes. Decomposition via loss of free ligand was observed in many cases, indicating that the pyridine diimine ligand is not a very suitable one for Rh^I.

Keywords: Ligand non-innocence; Rhodium; Pyridine diimine; Alkyl

1. Introduction

For a long time, olefin polymerisation catalysis was believed to be restricted to early transition metals. The situation changed with the discovery of fairly efficient Ni and Pd catalysts bearing bulky diimine ligands [1]. Even more spectacular was the simultaneous discovery by BrookharT and Gibson [2] of Fe and Co catalysts bearing pyridine diimine (N_3) ligands. Whereas the catalysis by Ni/Pd catalysts appears to be straightforward and is understood in considerable detail, the Fe and Co systems are still shrouded in mystery. The active species remains unknown for both metals. For Fe, one generally assumes a cationic alkyl complex $LFeR^+$ to be involved, but direct evidence is lacking and Fe^{III} has also been suggested as active species [3]. Even if the active species is indeed $LFeR^+$, there is uncertainty about its spin state [4].

For Co, the situation is also unclear, but parts of the activation route have been identified. The ligand plays a prominent role here in stabilising the unusual square-planar Co^I precursors [5]. This happens through accepting an electron from the metal, i.e., the ligand is "non-innocent" in an electronic sense.

Electronic non-innocence of the pyridine diimine has been demonstrated in several cases [6] and is by now an established pattern in the chemistry of this ligand. The relevance of this form of non-innocence to catalysis is still unclear, but its stabilising role on the way to active catalysts may well be important.

Another emerging theme in the chemistry of pyridine diimine complexes is the involvement of the ligand in *chemical* transformations. Whereas with more traditional ligands (cyclopentadienyls, phosphines) reactions normally happen at the metal, complexes of the pyridine diimine ligand frequently undergo attack at the ligand, leading to alkylation [7] (at the imine carbon or the pyridine 1, 2 or 4 position) or deprotonation [8]; subsequent dimerisation of the ligand skeleton has also been observed [8b]. Fig. 1 summarises a few of the more unusual examples.

From these, it is clear that the ligand can play a role that goes beyond the normal spectator role and can really be called "chemically non-innocent". One could argue that electronic and chemical non-innocence are related, in the sense that unpaired electron density on the ligand would increase its reactivity. If that is the case, the metal should also be important, since it determines the amount of electron density transferred to the ligand and the amount of radical character involved

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doi:10.1016/j.ica.2004.02.012

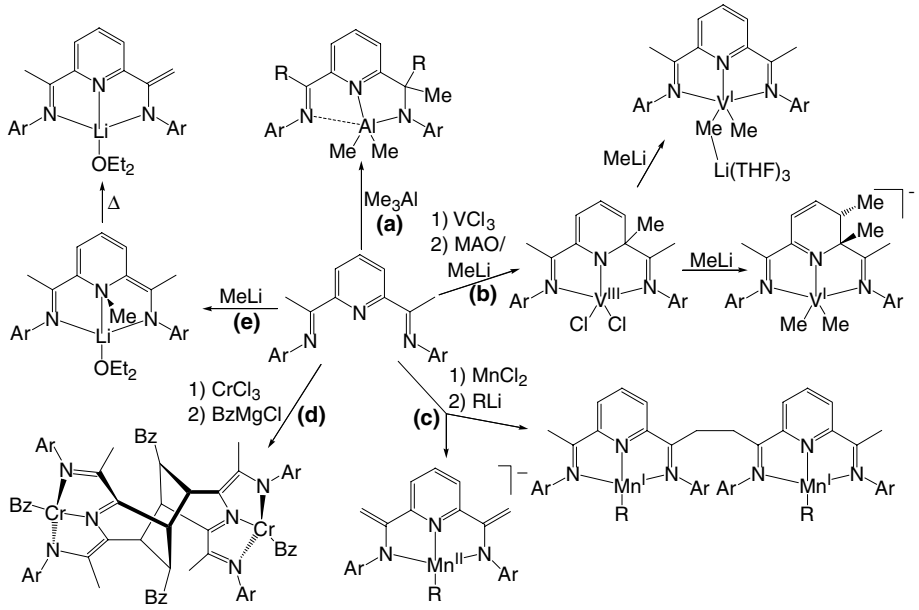

Fig. 1. Examples of ligand-centred reactivity of pyridine diimine complexes. (a) [7c]; (b) [7d]; (c) [8]; (d) [8b]; (e) [7a,7b].

[6b], both of which should influence ligand centred reactivity. The variety in reactivity and reactive sites in Fig. 1 indicates that this indeed is the case.

In the present paper, we describe a study of Rh^{I} alkyl derivatives of the pyridine diimine ligand.

Following our investigations of the Co polymerisation system [5b], we decided to study the corresponding Rh complexes, motivated by the formal analogy between square-planar LRhX and LCoX species. Several pyridine diimine Rh^{I} complexes have been reported [9] and LRhCl is easily synthesised from the ligand and $[Rh(C_2H_4)_2Cl]_2$ (Fig. 2).

Dias and his coworkers [9b] used these complexes as the starting point for studies aimed at ethene polymerisation. They were able to synthesise cationic Rh^{III} alkyl-olefin complexes by a series of substitution and oxidative-addition reactions, but were unable to induce polymerisation. We believe that the corresponding Rh^{I} alkyls would be better models for relevant Co species than the Rh^{III} alkyls studied by Dias. In any case, a comparison of the chemical behaviour of the corresponding Co^{I} and Rh^{I} alkyls (e.g., in their reactivity towards olefins) should help us understand to what extent the diimine pyridine ligand can help making Co behave like a second-row transition metal in adapting a square-planar geometry and a formal +1 oxidation state.

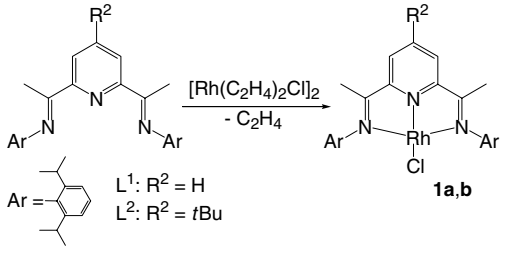

Fig. 2. Synthesis of LRhCl complexes.

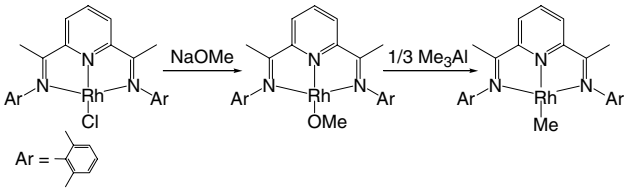

Fig. 3. Synthesis of L′RhMe [10].

Burger and his coworkers already published the synthesis of L′RhMe containing 2,6-dimethylphenyl groups at N. This complex could not be obtained via direct alkylation of the chloride derivative [10]; instead, they first synthesised the methoxy complex and converted this to the methyl complex (Fig. 3). The corresponding iridium complex L′IrMe was synthesised in the same way.

2. Experimental

All manipulations were performed under an inert atmosphere using standard Schlenk techniques or in a dry-box. Solvents were purified by distillation from an appropriate drying agent. All NMR spectra were recorded in d_6-benzene at room temperature on Bruker 200, 300 and 500 MHz or Varian Inova 400 MHz spectrometers. $[Rh(C_2H_4)_2Cl]_2$ [11], **1a** [9b], L^2 [10] were synthesised according to the literature procedures.

2.1. L^1RhMe (**2a**)

Two millilitres of toluene was added to 100 mg of **1a** (0.16 mmol) and 7.1 mg MeLi (0.32 mmol; 2 equiv.) and the mixture was stirred for 3 days. The solution was filtered and the solvent was removed in vacuo, yielding 91 mg of **2a** as a dark green solid.

^{1}H NMR (300 MHz): δ 8.19 (t, $^3J_{HH}$ 7.9 Hz, 1H, Py 4), 7.34 (d, $^3J_{HH}$ 7.7 Hz, 2H, Py 3), 7.22–7.10 (m, 6H, Ar *m*,*p*), 3.19 (sept, $^3J_{HH}$ 6.8 Hz, 4H, C*H*Me$_2$), 2.12 (d, $^2J_{RhH}$ 1.1 Hz, 3H, RhC*H*$_3$), 0.99 (m, 24H, CH*Me*$_2$), 0.73 (s, 6H, N=C*Me*).

^{13}C NMR (75 MHz): δ 166.8 (*C*=N), 155.3 (d, $^2J_{RhC}$ 2.7 Hz, Py 2), 148.3 (Ar *i*), 140.6 (Py 4), 140.4 (Ar *o*), 123.6 (Ar *m*), 123.1 (Py 3), 28.2 (*C*HMe$_2$), 23.9, 23.6 (CH*Me*$_2$), 18.9 (N=C*Me*), 1.2 (d, $^1J_{RhC}$ 21 Hz, Rh*C*H$_3$).

2.2. L^1RhBz (**3a**)

Two millilitres of toluene was added to 100 mg of **1a** (0.27 mmol) and 41 mg of Bz$_2$Mg (0.27 mmol; 2 equiv.). The mixture was stirred for 24 h, filtered and the filtrate dried in vacuo. The resulting purple powder was extracted with hexane and the solvent was removed in vacuo, giving **3a** as a purple solid.

^{1}H NMR (200 MHz): δ 7.97 (t, $^3J_{HH}$ 7.9 Hz, 1H, Py 4), 7.31–7.17 (m, 8H, Ar *m*,*p* and Py 3), 7.21 (t, $^3J_{HH}$ 7.3 Hz, 2H, Bz *m*), 6.65 (m, 1H, Bz *p*), 5.59 (d, $^3J_{HH}$ 6.9 Hz, 2H, Bz *o*), 3.69 (d, $^2J_{RhH}$ 2.6 Hz, 2H, RhC*H*$_2$C$_6$H$_5$), 3.28–3.05 (sept, $^3J_{HH}$ 8.0 Hz, 4H, C*H*Me$_2$), 1.01–0.92 (m, 30H, N=C*Me* and CH*Me*$_2$).

^{13}C NMR (75 MHz): δ 166.8 (d, $^2J_{RhC}$ 2.3 Hz, *C*=N), 156.2 (d, $^2J_{RhC}$ 2.9 Hz, Py 2), 151.9 (d, $^2J_{RhC}$ 1.7 Hz, Bz *i*), 148.4 (Ar *i*), 141.0 (Py 4), 140.6 (Ar *o*), 127.3 (Bz *o*), 127.0 (Bz *m*), 126.5 (Ar *p*), 124.2 (Ar *m*), 123.6 (Py 3), 119.6 (Bz *p*), 28.6 (*C*HMe$_2$), 24.0, 23.8 (CH*Me*$_2$), 19.5 (d, $^3J_{RhC}$ 1.7 Hz, N=C*Me*). The benzylic *C*H$_2$ signal was not observed.

2.3. $L^1RhCH_2SiMe_3$ (**4a**)

Four millilitres of toluene and 0.54 ml of 1.0 M Me$_3$SiCH$_2$Li in pentane (0.54 mmol; 2 equiv.) were added to 170 mg of **1a** (0.27 mmol). The mixture was stirred for 24 h, filtered and the filtrate was dried in vacuo, yielding a green-brown powder. Extraction with hexane and removal of the solvent resulted in a quantitative yield of **4a** as a green powder.

^{1}H NMR (300 MHz): δ 8.06 (t, $^3J_{HH}$ 7.9 Hz, 1H, Py 4), 7.24 (d, $^3J_{HH}$ 8.1 Hz, 2H, Py 3), 7.15–7.03 (m, 6H, Ar *m*,*p*), 3.26 (sept, $^3J_{HH}$ 6.8 Hz, 4H, C*H*Me$_2$), 1.87 (d, $^2J_{RhH}$ 2.2 Hz, 2H, RhC*H*$_2$), 1.28, 0.97 (d, $^3J_{HH}$ 6.6 Hz, 12H each, CH*Me*$_2$), 0.86 (s, 6H, N=C*Me*), 0.29 (s, 9H, Si*Me*$_3$).

^{13}C NMR (75 MHz): δ 165.8 (d, $^2J_{RhC}$ 0.9 Hz, *C*=N), 156.3 (d, $^2J_{RhC}$ 3.2 Hz, Py 2), 149.4 (Ar *i*), 141.1 (Py 4), 140.6 (Ar *o*), 126.7 (Ar *p*), 124.3 (Ar *m*), 123.6 (Py 3), 28.2 (*C*HMe$_2$), 24.5, 24.3 (CH*Me*$_2$), 19.9 (d, $^3J_{RhC}$ 2.0 Hz, N=C*Me*), 6.7 (d, $^1J_{RhC}$ 33 Hz, Rh*C*H$_2$SiMe$_3$), 4.0 (RhCH$_2$Si*Me*$_3$).

2.4. L^1RhX (**5a**)

In an NMR tube equipped with a septum, a few milligrams of **2a**, **3a** or **4a** were dissolved in 600 μl C$_6$D$_6$. Hydrogen (1 ml) was injected in the NMR tube and a colour change from dark green to red-brown was observed (yellow green when traces of **1a** were present in the sample).

2.5. $(L^1+4H)RhX$ (**6a**)

Two millilitres of toluene and 0.3 ml of 1.1 M Et$_2$Zn in toluene (0.33 mmol; 4 equiv.) were added to 100 mg **1a** (0.16 mmol). The mixture was stirred for 24 h and subsequently filtered. The solvent was removed in vacuo and the residue was dissolved in C$_6$D$_6$. NMR showed a mixture **6a** and free ligand. After a few days only free ligand remained.

^{1}H NMR (200 MHz): δ 7.31–6.93 (m, 6H, Ar *m*,*p*), 5.09 (t, $^3J_{HH}$ 4.0 Hz, 2H, Py′ 3), 3.56 (t, $^3J_{HH}$ 4.0 Hz, 2H, Py′ 4), 2.73 (sept, $^3J_{HH}$ 5.1 Hz, 4H, C*H*Me$_2$), 1.67 (s, 6H, N=C*Me*), 1.20, 1.00 (d, $^3J_{HH}$ 6.9 Hz, 12H each, CH*Me*$_2$).

2.6. $(L^1-H)Rh(C_2H_4)$ (**7a**)

2.6.1. With diethylzinc

Two millilitres of cyclohexane and 0.3 ml of 1.1 M Et$_2$Zn in toluene (0.33 mmol; 4 equiv.) were added to 100 mg **1a** (0.16 mmol). The mixture was stirred for 24 h and subsequently filtered. NMR showed a mixture **7a** and free ligand. After a few days only free ligand remained.

2.6.2. With hydrogen/ethene

An excess of ethene was added with a syringe to a sample of **5a** in an NMR tube equipped with a septum. The NMR tube was placed under an argon atmosphere for several hours and subsequently an NMR spectrum was recorded.

^{1}H NMR (400 MHz): δ 7.3–7.0 (br, 9H, Ar *m*,*p* and Py 3,4,5), 4.56 (s, 1H, *trans* C*H*=C–N), 4.12 (s, 1H, *cis* C*H*=C–N), 3.80 (d, 4H, $^2J_{RhH}$ 1.8 Hz, C$_2$*H*$_4$), 3.63, 2.94 (sept, $^3J_{HH}$ 7.0 Hz, 2H each, C*H*Me$_2$), 2.27 (s, 3H, N=C*Me*), 1.34, 1.27, 1.24, 0.81 (d, $^3J_{HH}$ 6.8 Hz, 6H each, CH*Me*$_2$).

2.7. L^2RhCl (**1b**)

A mixture of 1.1 g (2.0 mmol; 1 equiv.) L^2 and 0.4 g (1.0 mmol) [Rh(C$_2$H$_4$)$_2$Cl]$_2$ in 12 ml toluene was stirred

for 30 min. Removal of the solvent in vacuo gave **1b** as a dark green solid, which was used without further purification. The yield was 1.2 g (1.7 mmol; 83%).

^{1}H NMR (300 MHz): δ 7.29 (s, 2H, Py 3), 7.15–6.95 (m, 6H, Ar *m*,*p*), 3.24 (sept, $^3J_{HH}$ 6.9 Hz, 4H, C*H*Me$_2$), 1.36, 1.07 (d, $^3J_{HH}$ 6.9 Hz, 12H each, CH*Me*$_2$), 1.10 (s, 9H, C*Me*$_3$), 1.10 (s, 6H, N=C*Me*).

^{13}C NMR (75 MHz): δ 166.4 (d, $^2J_{RhC}$ 2.3 Hz, *C*=N), 156.4 (d, $^4J_{RhC}$ 3.2 Hz, Py 4), 146.6 (Py 2), 146.3 (Ar *i*), 140.5 (Ar *o*), 127.0 (Ar *p*), 123.6 (Ar *m*), 121.1 (Py 3), 37.1 (*C*Me$_3$), 29.7 (C*Me*$_3$), 29.0 (*C*HMe$_2$), 24.4, 24.3 (CH*Me*$_2$), 17.8 (d, $^3J_{RhC}$ 2.1 Hz, N=C*Me*).

2.8. L^2RhMe (**2b**)

Ten millilitres of toluene was added to 108 mg of **1b** (0.15 mmol) and 6.8 mg of MeLi (0.31 mmol; 2 equiv.). The mixture was stirred for 7 days, filtered and the filtrate dried in vacuo. The resulting dark green solid was used without further purification.

^{1}H NMR (200 MHz): δ 7.77 (s, 2H, Py 3), 7.25–7.10 (m, 6H, Ar *m*,*p*), 3.26 (sept, $^3J_{HH}$ 6.8 Hz, 4H, C*H*Me$_2$), 2.12 (d, $^2J_{RhH}$ 1.2 Hz, 3H, RhC*H*$_3$), 1.24 (s, 9H, C*Me*$_3$), 1.14, 1.08 (d, $^3J_{HH}$ 6.8 Hz, 12H each, CH*Me*$_2$), 0.86 (s, 6H, N=C*Me*).

2.9. (L^2 – H)Rh(C_2H_4) (**7b**)

2.9.1. With diethylzinc

Ten millilitres of toluene was added to 100 mg of **1b** (0.15 mmol) and 63 mg of Et$_2$Zn (0.44 mmol; 6 equiv.). The dark yellow/green mixture was stirred for 12 h, filtered and the filtrate dried in vacuo. ^{1}H NMR (C_6D_6) showed the presence of **7b** as well as several other products.

2.9.2. With hydrogen/ethene

In an NMR tube, ca. 5 mg of **2b** was dissolved in C_6D_6. Hydrogen (1 ml) was injected and a colour change from green to brown/green was observed. Next an excess of ethene was added through the septum, and subsequently an ^{1}H NMR spectrum was recorded.

2.9.3. With LDA/ethene

To a solution of 100 mg (0.15 mmol) **1b** in toluene was added an equimolar amount of an LDA solution in THF (2.5 ml) at −15 °C. The mixture was stirred vigorously under an ethene atmosphere for several minutes. The red solution was warmed to room temperature and stirred for another 20 min in which it turned yellow. Subsequently, the solvent was removed in vacuo.

^{1}H NMR (400 MHz): δ 8.11 (d, $^4J_{HH}$ 1.2 Hz, 1H, Py 3), 7.66 (d, $^4J_{HH}$ 1.2 Hz, 1H, Py 5), 7.20–7.05 (m, 6H, Ar *m*,*p*), 4.67 (s, 1H, *trans* C*H*=C–N), 4.13 (s, 1H, *cis* C*H*=C–N), 3.77 (d, J_{RhH} 2.0 Hz, 4H, C_2H_4), 3.71, 3.02 (sept, $^3J_{HH}$ 6.8 Hz, 2H each, C*H*Me$_2$), 1.38, 1.30, 1.27, 0.84 (d, $^3J_{HH}$ 6.8 Hz, 6H each, CH*Me*$_2$), 1.11 (s, 9H, C*Me*$_3$), 0.83 (s, 3H, N–C*Me*).

3. Results

3.1. Basic ligand system L^1

3.1.1. Synthesis of rhodium alkyl complexes

L^1RhCl (**1a**) was easily synthesised according to the literature procedures [9b]. In contrast to L′RhCl [10], **1a** could easily be alkylated using organolithium or organomagnesium compounds. L^1RhMe (**2a**), L^1RhBz (**3a**) and L^1RhCH$_2$SiMe$_3$ (**4a**) were obtained in good yields from the reaction of **1a** with MeLi, Bz$_2$Mg and LiCH$_2$SiMe$_3$, respectively. The two most likely side reactions in these alkylations are addition to the imine functionality or deprotonation of the ketimine methyl group. It seems probable that either or both of these caused the problems encountered by Burger. The larger isopropyl group in the ligand we used may cause just enough steric protection of the imine to prevent these reactions. When a large excess of alkylating agent was used, we obtained mixtures of various unidentified products, possibly formed via attack on the imine and/or deprotonation of the ligand. We were not able to crystallise any of the alkyl complexes due to their instability in solution. In hydrocarbons, a film or deposit of metallic rhodium was usually formed on standing. In THF the complexes reacted to a mixture of various products, while in dichloromethane **1a** was formed instantly from the methyl and benzyl complexes. Probably, dichloromethane oxidatively adds to rhodium and subsequently a chlorinated alkane is eliminated, as was reported before for related complexes [9a]. In contrast with the report by Dias [9b], even CD_2Cl_2 was found to react with **1a**, albeit very slowly: after one hour, 10% was converted to a new complex, possibly L^1RhCl$_2$(CD$_2$Cl). Oxidative addition of C–Cl bonds to rhodium(I) chloride complexes is not unusual [9a].

3.1.2. Reactivity of rhodium alkyl complexes

Because both L^1CoCl and L^1CoR polymerise ethene after activation with MAO, we tested whether the corresponding Rh complexes could be activated in the same way. After treatment with MAO under 7 bar of ethene, no polymer was formed. Because of the similarity of the complexes, this complete absence of activity was not expected.

Pyridine diimine Co^{I} alkyl complexes react with hydrogen to LCoH [12]. This hydride complex is an active catalyst for the hydrogenation of mono- and di-substituted olefins, but not for tri-substituted olefins. When L^1RhR complexes **2a**–**4a** were reacted with H_2, the NMR spectrum did not show any signals for the expected diamagnetic hydride complex. Instead, only

signals for impurities in the starting material and a very small amount of asymmetric product were visible, together with signals for RH. Most of the alkyl complex was obviously transformed into an NMR-silent paramagnetic species. This was confirmed by the presence of a very intense signal in the EPR spectrum of the product (**5a**) (Fig. 4).

The nature of complex **5a** is not clear. It most likely has the composition L^1RhX, where X is arene (solvent), N_2, H_2 or two hydrides. Burger has observed formation of $L'Rh(\mu\text{-}N_2)RhL'$ complexes [10b], but a binuclear structure would not be expected to give the type of EPR signal we observe. Assuming for the moment a composition LRhX with a neutral ligand X, the *g*-values of 2.017 and 1.978 suggest that the unpaired electron is located partly on the organic ligand and partly on the rhodium centre. This indicates that the bonding is intermediate between a true $Rh^{(0)}$ complex $L^1Rh^{(0)}$ and a complex of Rh^I with a ligand radical anion, i.e. $L^{1(\cdot-)}Rh^I$. Formation of the $L^{1(\cdot-)}$ radical anion has been observed before, e.g., in complexes with low-valent Co and Mn [5,8]. Solutions of **5a** slowly deposit a film of metallic rhodium.

A possible mechanism for the formation of **5a** is outlined in Fig. 5. The combination of oxidative addition and comproportionation leads to the formation of two molecules of a Rh^{II} complex, which eliminates methane to give the Rh^0 final product. It is not obvious how the comproportionation step occurs, since the ligands are very large and should shield the metal centre enough to hinder the close approach required for direct hydrogen transfer. It may be that a hydrogen atom is transferred via the pyridine rings of the ligands (see below).

Even though the exact formulation of complex **5a** remains unclear, hydrogenation experiments were carried out. When various olefins were added to **5a** under hydrogen, the same selective hydrogenation was observed as for L^1CoH [12] that is, mono- and di-substituted olefins were hydrogenated, but tri-substituted olefins were not. This lead us to conclude that complex **5a**, rather than Rh^0 formed by its slow decomposition, is responsible for the activity.

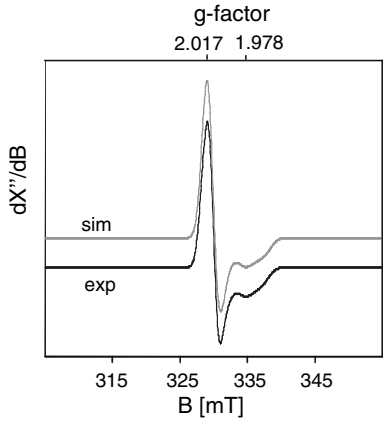

Fig. 4. EPR spectrum after reaction of L^1RhR with H_2 ($W_x = W_y = W_z = 11.00$, Mod. Ampl. = 2 G, Freq. = 9.3045, attn. = 40 dB, $T = 40$ K). Simulation: $g_x = 1.9775$, $g_y = g_z = 2.0169$, $A_z^N = 40$ MHz.

3.1.3. Attempted synthesis of L^1RhEt

L^1CoEt is easily formed from L^1CoH and ethene [12]. If the reaction of **1a** with Et_2Zn was carried out in benzene or toluene, initially broad lines were observed in the ^1H NMR spectrum, but after a few hours a diamagnetic product (**6a**) had formed; a small amount of ethene could also be seen. Product **6a** showed two triplets at 3.6 and 5.1 ppm (2H each). We believe that the only reasonable explanation is that these signals belong to a 1,4-dihydro-1-pyridyl group, formed through migration of a hydrogen atom from the metal to the 4-position of the pyridine ring. [1] The distances involved make *direct intra*molecular transfer of hydrogen to the 4-position unlikely; the hydrogen may have moved from the metal either in a stepwise fashion (i.e., via some of the other ring carbons) or via *inter*molecular hydrogen transfer.

Presumably, in **6a** an additional ligand (e.g., solvent or ethene) also coordinates to the metal (see Fig. 6). It was not possible to identify this ligand from the ^1H NMR spectrum. [2] Full characterisation of **6a** was not possible, because on standing in solution it slowly decomposed to the free ligand and metallic rhodium.

The most likely path to **6a** is initial formation of L^1RhEt followed by β-hydrogen elimination and hydride transfer to the ligand. The observed addition to the 4-position of the pyridine ring is probably the most favourable one. [3]

When the reaction of **1a** with Et_2Zn was performed in cyclohexane, the result was quite different. Instead of addition of a hydride to the ligand, a proton was removed from one of the ketimine methyl groups of the ligand and $\{L^1 - H\}Rh(C_2H_4)$ (**7a**) was formed (Fig. 7).

The complex was positively identified by ^1H NMR. The doubled set of ligand *i*Pr peaks indicates the asymmetry of the complex. The vinylic protons of the deprotonated ketimine methyl group were visible as two singlets at 3.9 and 4.5 ppm. This time the remaining ligand at Rh could be identified as ethene, observed as a

[1] *Alkyl* transfer to the 4-position of the pyridine ring has been observed in our laboratories in the reaction of L^1 with Et_3Al. The results will be published soon: Q. Knijnenburg, P.H.M. Budzelaar, submitted.

[2] ^{13}C NMR measurements were not possible because of the low solubility of the complex.

[3] It has been calculated that the 2 and 4 positions of the pyridine ring in a pyridine diimine vanadium complex are the most positively charged parts of that complex and therefore the most likely candidates to accept a hydride [7d].

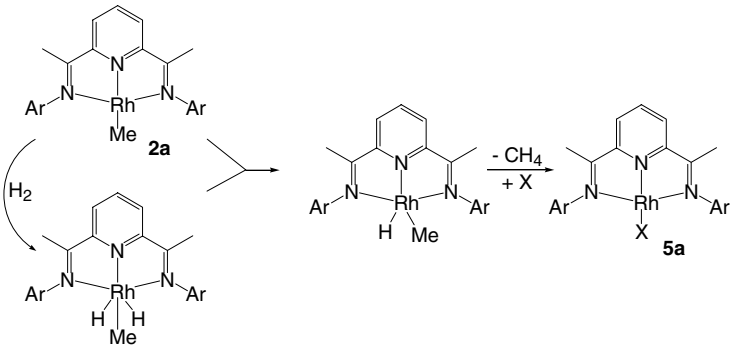

Fig. 5. Possible formation of **5a**.

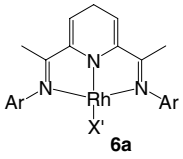

Fig. 6. Proposed structure of **6a**.

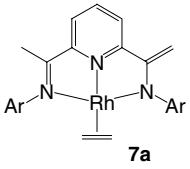

Fig. 7. Structure of **7a**.

doublet at 3.5 ppm with a small rhodium coupling of 1.8 Hz.

Complex **7a** also decomposed slowly to free ligand and metallic rhodium and had a low solubility. Therefore, no ^{13}C NMR spectrum could be obtained. Presumably, the same ethyl complex is formed initially as in toluene, but in this case, net dihydrogen elimination took place instead of hydride transfer to the ligand to give **6a**. The only difference in reaction conditions is the solvent. Therefore, it seems likely that the coordinating ability of toluene/benzene plays a role in the formation of **6a**. Surprisingly, treatment of paramagnetic complex **5a** with ethene also gave complex **7a**.

Rationalising the formation of **7a** from the presumed intermediate L^1RhEt is not easy. It is also complicated by the fact that we do not know the exact stoichiometry of the reaction, since part of the rhodium could end up as paramagnetic, NMR-silent **5a**. Formally, formation of **7a** from L^1RhEt involves loss of H_2, but it is unlikely H_2 is lost as such. Assuming that the hydrogen is lost as ethane, and that **5a** is a dihydrogen or dihydride complex (see next section), a possible reaction stoichiometry compatible with the observations is shown in Fig. 8. If this is indeed what happens, the reaction must involve several intermolecular transfers of hydrogen and/or ethene, similar to that suggested in Fig. 5. The difference

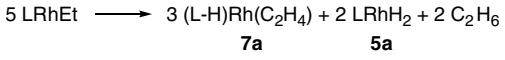

Fig. 8. Possible formation of **7a** from L^1RhEt.

between reactions carried out in benzene/toluene and cyclohexane could be that, in an arene solvent, ethene is easily lost from L^1RhEt via β-elimination and ligand displacement, whereas in the absence of such a solvent ethene can only be lost as ethane, taking a ligand hydrogen with it and producing a highly unsaturated Rh complex. Formation of **7a** from **5a** and ethene could similarly be explained via loss of hydrogens as ethane. However, in the absence of additional evidence these explanations and the reactions depicted in Figs. 5 and 8 must remain speculative.

3.1.4. L^2: blocking the pyridine 4-position

Nückel reported that substitution of pyridine H4 by a *tert*-butyl group significantly increased the solubility of pyridine diimine rhodium complexes in apolar solvents [10]. Higher solubility (and stability) of the products described in the previous sections would be desirable to obtain more complete NMR characterization of the products (^{13}C NMR); the additional aliphatic group could result in better crystallisation behaviour as well. Moreover, the *tert*-butyl group causes significant steric shielding of the pyridine 4-position and might make hydrogen transfer to the 4-position more difficult.

L^2RhMe (**2b**) was synthesised in two steps from the ligand and $[Rh(C_2H_4)_2Cl]_2$, similar to **2a**. Again, two equivalents of MeLi were used to achieve complete alkylation of the chloride complex and to prevent the formation of unwanted side products. No crystals suitable for X-ray diffraction could be obtained.

When **2b** was exposed to H_2, a colour change from green to brown was observed. In the ^1H NMR spectrum, no signals for either product or starting material were present. Therefore, it is suspected that a paramagnetic complex **5b** was formed similar to **5a**. Unfortunately, also in this case attempted isolation of the complex was unsuccessful.

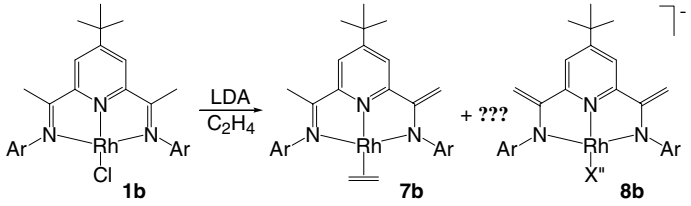

Fig. 9. Reaction of **1b** with LDA and ethene.

If **5b** is indeed a complex of $Rh^{(0)}$, it might be possible to trap it by adding strong π-acceptor ligands (CO, isocyanides). Addition of CO to a sample of **5b** produced a black precipitate; NMR of the remaining solution showed only signals for free ligand and a signal at 4.46 ppm that we attribute to H_2. H_2 was not visible in the NMR spectrum of **5b** before reaction. This suggests that the ligand X in **5a/5b** may be dihydrogen or two hydrides, which would not be strange for a complex that was formed in the presence of excess dihydrogen. When the slightly weaker π-acceptor *t*BuNC was used, again loss of ligand and liberation of H_2 was observed. In a separate experiment, addition of CO to **2b** also resulted in loss of the free ligand. Evidently, the strong π-acid CO does not stabilise LRh complexes.

Reaction of **1b** with Et_2Zn in *toluene* initially resulted in line broadening in the ^1H NMR spectrum, but after a few hours, the reaction was finished and a diamagnetic complex (**7b**) had formed. ^1H NMR showed that this was the analogue of **7a** formed from **1a** in *cyclohexane*. Two singlets of vinylic protons at 4.13 and 4.67 ppm indicated that one of the ketimine methyl groups was deprotonated. As in **7a**, an ethene molecule is coordinated to the metal. Apparently, the hydride transfer to the ligand encountered in toluene and benzene with L^1 does not proceed when the pyridine 4-position is substituted with a *t*Bu group. Another difference is that **7b** is more stable than **7a**. Even after several weeks in solution, only part of the complex had lost its ligand. This made more extensive NMR work possible. From a NOESY experiment the vinylic protons could be assigned. The *cis* proton showed a clear contact with the isopropyl group on one of the aryl rings, while the *trans* proton had a contact with one of the protons at the pyridine 3-position. Unfortunately, no ^{13}C NMR spectrum could be obtained.

In the reaction of **1b** with Et_2Zn, formation of a substantial amount of side product (**8b**) was observed (sometimes up to 40%). The typical vinylidene resonances observed for it lead us to suspect that it contains a doubly deprotonated ligand similar to the one reported by Gambarotta for Mn [8b].

Analogous to the behaviour observed for **5a**, treatment of **5b** with ethene resulted in very slow formation of **7b**. These observations demonstrate that the complexes of L^1 and L^2 behave similarly, except that hydrogen transfer to the pyridine 4-position is apparently blocked in L^2.

In order to confirm the structure of **7b**, we attempted to prepare it via the alternative route of deprotonation of **1b** in the presence of ethene. Addition of one equivalent of an LDA solution to **1b** resulted in an immediate colour change from green to red and in five minutes to yellow/green. NMR clearly showed that both **7b** and the above-mentioned side product **8b** had been formed, but attempts to separate the complexes were unsuccessful (see Fig. 9).

4. Conclusions

When the reactivity of LRhCl and LCoCl is compared, the similarity stops after the alkylation to LMR. In the case of Co, all complexes can be activated with MAO to become highly active olefin polymerisation catalysts. It is even likely that they all form the same active species. All Rh complexes are completely inactive towards ethene polymerisation, even after reaction with MAO. The hydrogenation activity of Rh and Co complexes seems similar, but while for Co the active species appears to be LCoH, for Rh the catalysis is probably caused by a paramagnetic species (**5a**). Unexpectedly, reaction of this paramagnetic species with ethene leads to a *diamagnetic* ethene complex containing a *deprotonated* ligand (**7a**). Hydrogen transfer *to* the ligand has also been observed (**6a**). Thus, the "chemically non-innocent" character of the ligand shows up quite clearly in its Rh chemistry. For Co, in contrast, we merely see "electronic non-innocence" in the stabilisation of unusually low oxidation states [5,6].

One final conclusion from the present work is that the pyridine diimine ligand, despite being a tridentate ligand, is remarkably easily lost from Rh^I. One possible reason could be steric: for large metal atoms like Rh, the ligand "fit" is not very good. But in addition, it seems likely that the combination of a ligand that easily forms radical anions with a metal that prefers closed-shell structures constitutes an unhappy marriage.

Acknowledgements

This research was sponsored by CW/STW and Basell Technology Company. We thank Dr. B. de Bruin for EPR measurements and simulations.

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