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Attempts at stepwise reduction of the carbon–nitrogen triple bond of a nitrile at two metal centres: study of the reactivity of $[(CO)(PPh_3)_2Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)]$ towards tetrafluoroboric acid and dihydrogen

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Abstract

The reaction of $[(CO)(PPh_3)_2Re(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)]$ (**2**) with HBF_4–Me_2O generates $[(CO)(PPh_3)_2Re(\mu\text{-}H)_2(\mu\text{-}\eta^1,\eta^2HNCHPh)Ru(PPh_3)_2(PhCN)][BF_4]$ (**3**). Monitoring the reaction by NMR spectroscopy shows the intermediate formation of $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)][BF_4]$ (**4**). Attempted reduction of the imine ligand by a nucleophile (H^- or CN^-) failed, regenerating **2**. Under dihydrogen at 50 atm, **3** is slowly transformed into $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Ru(PPh_3)_2(PhCN)][BF_4]$ (**5**) with liberation of benzyl amine.

Key words: Rhenium; Ruthenium; Nitriles; Reduction; Dinuclear

1. Introduction

Recently we showed that $(CO)(PPh_3)_2HRe(\mu\text{-}H)_3RuH(PPh_3)_2$ (**1**) reacts easily at room temperature with benzonitrile, leading to a complex containing a bridging benzylidene imide $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)]$ (**2**) [1]. Treatment of **2** under dihydrogen at 10 atm led to traces only of amine and the regeneration of **1**. Moreover, **2** was a poor catalyst for the hydrogenation of benzonitrile.

Homogeneous hydrogenation of nitriles is not usually easy [2–5] but these are some examples of stepwise stoichiometric reduction of coordinated nitriles either on mono nuclear [6–10], dinuclear [11,12] or trinuclear [13–17] complexes. If with polynuclear complexes reduction is induced by the action of molecular hydrogen, with mononuclear compounds reduction generally cause addition of a hydride to the β-carbon atom and a proton to the nitrogen atom of the nitrile ligands.

For these reasons we have reconsidered the problem of reduction of benzonitrile on our Re–Ru bimetallic complexes, focussing on attempts at stepwise reduction using either proton + hydride or proton + hydrogen systems and we report here the results of these investigations.

2. Results and discussion

2.1. Reactivity of 2 toward tetrafluoroboric acid

A solution of **2** in dichloromethane was treated with a slight excess of tetrafluoroboric acid. Monitoring the reaction by IR spectroscopy in the $\nu(CO)$ region showed the immediate disappearance of the starting complex and the presence of a new absorption at 1873 cm^{-1} with a shoulder at 1845 cm^{-1}. The IR spectrum of the solution changed with time and the 1873 cm^{-1} band disappeared with the simultaneous increase in intensity of the band at 1845 cm^{-1}. After 2 h, only this last absorption remained. The new complex **3** was isolated by replacing the BF_4^- anion by BPh_4^-.

At 293 K, the ^1H NMR spectrum of **3** shows two resonances of equal intensity in the hydride region

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namely, a broad triplet at −9.62 ppm and a broad doublet at −10.39 ppm. In the low field region, besides the phenyl resonances, two signals of equal intensity are observed namely, a triplet at 4.95 ppm and a broad signal at 4.66 ppm, consistent with the formation of a NH=CHPh group [10,18].

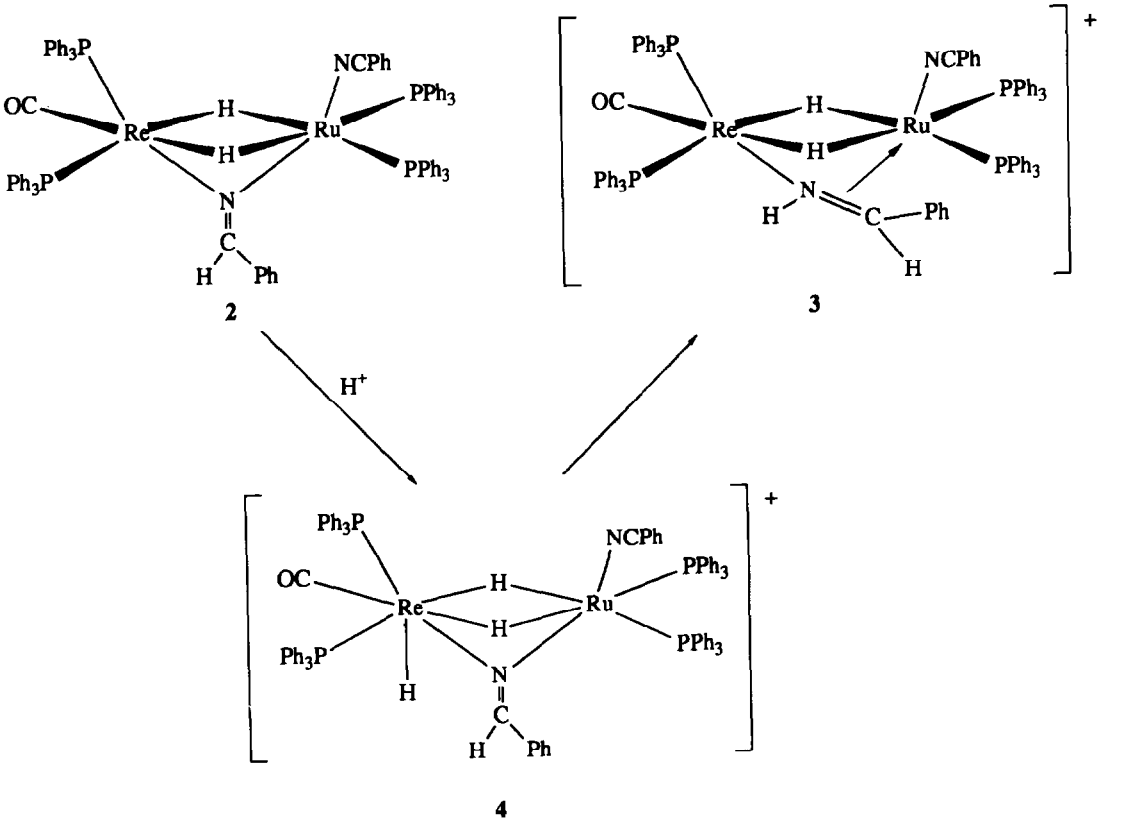
At the same temperature four resonances of equal intensity are observed in the $^{31}P\{^1H\}$ NMR spectrum namely, a doublet at 46.7 ppm, a doublet of doublets at 43.9 ppm, a doublet at 24.6 ppm and a doublet of doublets at 18 ppm. By analogy with the data of the known analogous Re–Ru polyhydride bimetallic systems [1,19], the two signals at low field are attributed to the two phosphine groups bound to ruthenium. Selective phosphorus decoupling experiments permitted the assignments of all the phosphorus–hydrogen coupling constants (see experimental section) and show that the two hydride ligands are bridging.

The presence of the imine ligand was confirmed by ^{13}C NMR spectroscopy which shows a doublet at 80.8 ppm (J_{CH} = 167 Hz). Moreover these values are consistent with π-bonding of the imine [18]. A resonance at 111 ppm characteristic of the CN group of the coordinated benzonitrile is also observed.

All these data are consistent with the formulation for **3** $[(CO)(PPh_3)_2Re(\mu\text{-}H)_2(\mu\text{-}\eta^1,\eta^2HNCHPh)Ru(PPh_3)_2(PhCN)][BPh_4]$.

Hence, tetrafluoroboric acid has protonated of the nitrogen of the benzylidene imido group of **2**. Nevertheless monitoring of the reaction by IR spectroscopy showed that the reaction occurs through an intermediate complex, and we have tried to identify this intermediate through ^1H and ^{31}P NMR experiments in an NMR tube.

Examination of the ^1H and $^{31}P\{^1H\}$ NMR spectra immediately after mixing the acid and **2** shows the complete disappearance of **2**, a small amount of **3** and a new complex **4**. This complex has three signals in a 1:1:1 ratio in the hydride region at the ^1H NMR spectrum, namely a doublet of doublets at −3.20 ppm, a complex multiplet at −8.37 ppm and a doublet at −10.13 ppm. In the $^{31}P\{^1H\}$ NMR spectrum, four signals are observed, namely at 46.9 ppm (singlet), 46.6 ppm (doublet), 34.5 ppm (doublet) and 22.5 ppm



Scheme 1.

(doublet). After 1 h at 293 K the main product in the solution is **3**.

From these experiments it is evident that the first step before the formation of **3** is the protonation of a metal and from the ^1H NMR parameters, we conclude that this has occurred on the rhenium atom (signal at -3.20 ppm) and that **4** has the formulation $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)][BF_4]$.

Scheme 1 summarizes our observations of the protonation of **2**. These results have to be contrasted with recent reports on the protonation of nitrile ligands in electron-rich rhenium complexes where protonation occurs first on the β-carbon of the nitrile, and with subsequent rearrangement leading to the metal–hydride complex [20].

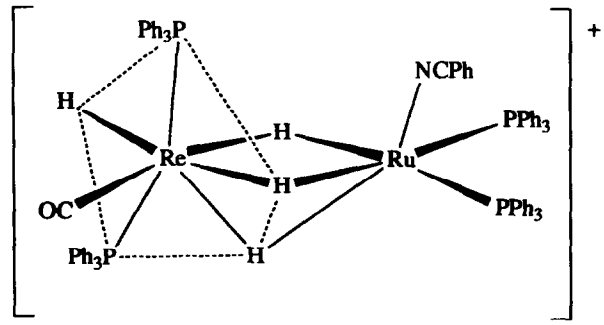


Fig. 1. Proposed structure for the cation of $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Ru(PPh_3)_2(PhCN)][BPh_4]$ (**5**).

2.2. *Attempts to reduce the conducted benzylimine to a benzylamide*

It has been demonstrated in cationic mononuclear complexes that reduction of η^1-coordinated imines is easy with nucleophiles such as H^- or CN^- [10]. In **3** the reaction should be easier owing to the η^2 mode of bonding of the imine. In fact, all the attempts with KH, $LiBEt_3H$ or KCN lead only to the deprotonation of the imine and regeneration of **2**. So we turned to the reduction by molecular hydrogen.

The action of dihydrogen needed quite forcing conditions as, for a pressure of under 50 atm at room temperature, 5 days were necessary for complete disappearance of the starting material **3** and the formation of a new complex characterized by a $\nu(CO)$ absorption at 1889 cm^{-1}.

The new complex **5** was isolated and identified by spectroscopic techniques. In the ^1H NMR spectrum in the hydride region at room temperature we observe a broad signal overlapping with a triplet centred at -4.69 ppm and a triplet at -13.20 ppm in a 3:1 ratio. At low field, only the phenyl signals are observed.

At room temperature the $^{31}P\{^1H\}$ NMR spectrum shows four broad resonances centred at 59.3, 57, 42.3 and 34.8 ppm, in an intensity ratio of 1:1:1:1. Lowering the temperature to 193 K leads to a double doublet of doublets at 56.6 ppm, a doublet at 51.7 ppm, a doublet of doublets at 39.8 ppm and a broad singlet at 33.2 ppm. At the same temperature in the ^1H NMR spectrum the hydride resonances appear as a complex multiplet at -4.17 ppm, a doublet at -4.85 ppm, a triplet at -4.96 ppm and a broad resonance at -13.22 ppm, in the ratio 1:1:1:1. In the $^{13}C\{^1H\}$ NMR spectrum at room temperature, other than the phenyl resonances, a singlet is observed at 111.2 ppm, characteristic of the CN group of a coordinated benzonitrile molecule.

From these observations it is evident that the expected amido group is not present in **5**. Nevertheless these spectroscopic data are very similar to those of the known cation $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Ru(PPh_3)_2(CH_3CN)]^+$ [1] and the structure of **5** is $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_3Ru(PPh_3)_2(PhCN)][BPh_4]$, shown in Fig. 1.

Examination of the crude reaction mixture by gas chromatography at the end of the hydrogenation showed the formation of benzylamine. This is confirmed by ^1H and ^{13}C NMR spectrometry after removal of dichloromethane under vacuum. Moreover, integration of the ^1H NMR spectrum shows that 90% of the expected quantity is present showing that the hydrogenation of the imine is stoichiometric. The following equation illustrates our observations

$$[(PPh_3)_2(CO)Re(\mu\text{-}H)_2(\mu\text{-}\eta^1,\eta^2NH{=}CHPh)Ru(PPh_3)_2(PhCN)][BPh_4] + H_2 \longrightarrow [(PPh_3)_2(CO)HRe(\mu\text{-}H)_3Ru(PPh_3)_2(PhCN)][BPh_4] + PhCH_2NH_2$$

Contrary to the reaction of binuclear rhodium polyhydride complexes with nitriles [11], no intermediate containing the benzylamido group has been trapped, and this suggests that, in contrast with rhodium, the limiting factor for efficient catalytic hydrogenation of nitriles is not the stability of the complex with the amido bridge. Our observations suggest that in our system the limiting factor is the formation of the benzylimine from the the benzylideneimido group.

To summarize, the reaction of a protonic acid and di-hydrogen with $[(CO)(PPh_3)_2HRe(\mu\text{-}H)_2(\mu\text{-}NCHPh)Ru(PPh_3)_2(PhCN)]$ (**2**) has allowed us to reduce the benzylideneimido ligand to benzylamine in a Re–Ru bimetallic complex. The intermediate formation of a complex containing $\mu\text{-}\eta^1,\eta^2$ bonded benzylimine has been indicated by the initial protonation of the rhenium and the subsequent migration of the hydride to nitrogen. Surprisingly, during all these reactions the benzonitrile coordinated to ruthenium remains unchanged.

3. Experimental section

All reactions were performed under dinitrogen with the use of standard Schlenk techniques. IR spectra were recorded on a Perkin–Elmer 225 spectrometer. NMR spectra were recorded on Bruker AC 200 (^{1}H, ^{13}C and ^{31}P) and WM 250 (^{1}H and ^{31}P) instruments. Variable-temperature and selective-decoupling experiments were carried out on the WM 250 machine. Elemental analyses for C, H and N were performed in our laboratory. [(CO)$(PPh_3)_2$HRe(μ-H)$_2$(μ-NCHPh)Ru$(PPh_3)_2$(PhCN)] (**2**) was prepared according to published procedures [1].

3.1. Synthesis of [(CO)$(PPh_3)_2$Re(μ-H)$_2$(μ-η^1,η^2NH=CHPh)Ru(PhCN)$(PPh_3)_2$][BPh_4] (3)

To 0.2 g (0.13 mmol) of **2** dissolved in 10 ml of CH_2Cl_2 was added 15 μl of HBF_4–Me_2O (0.13 mmol) at room temperature and the solution was stirred for 1 h. The solution turned red, and it was then evaporated to dryness. The metathesis of BF_4^- for BPh_4^- was done by redissolving the residue in 10 ml of acetone and adding 0.05 g of $NaBPh_4$ (0.15 mmol). After stirring for 0.5 h, the solution was evaporated to dryness and the residue was recrystallized from CH_2Cl_2–MeOH at room temperature, giving 0.22 g of red crystals of **3** (91% yield).

Anal. Found: C, 70.60; H, 4.89; N, 1.64. $C_{111}H_{94}BN_2OP_4ReRu$ calc.: C, 70.39; H, 5; N, 1.48%.

IR (CH_2Cl_2): ν(CO) 1845 cm^{-1}. ^{1}H NMR (CD_2Cl_2) except phenyl resonances: 4.98 (t, J_{HH} = 11, $J_{P(4)H}$ = 11 Hz, CHPh); 4.66 (broad, NH); −9.62 (broad t, $J_{P(1)H}$ = $J_{P(2)H}$ = 37 Hz, $J_{P(3)H}$ = 14 Hz, 1H); −10.39 (broad d, $J_{P(1)H}$ = 65.7 Hz, $J_{P(2)H}$ = 10 Hz, 1H) ppm. ^{31}P{^{1}H} NMR: 46.7 (d, $J_{P(1)P(2)}$ = 24 Hz, P(1)); 43.9 (dd, $J_{P(1)P(2)}$ = 24 Hz, $J_{P(2)P(4)}$ = 7.6 Hz, P(2)); 24.6 (d, $J_{P(3)P(4)}$ = 34 Hz, P(3)); 18 (dd, $J_{P(3)P(4)}$ = 34 Hz, $J_{P(2)P(4)}$ = 7.6 Hz, P(4)) ppm. ^{13}C NMR (CD_2Cl_2) phenyl resonances omitted: 197.7 (CO); 111 (t, J_{CH} = 9 Hz, *NC*Ph); 80.8 (d, J_{CH} = 167 Hz, CH(Ph)) ppm.

3.2. Spectroscopic characterization of [(CO)$(PPh_3)_2$HRe(μ-H)$_2$(μ-NCHPh)Ru(PhCN)$(PPh_3)_2$][BF_4] (4)

To a solution of **2** (0.1 g) dissolved in CD_2Cl_2 was added 1 equivalent of HBF_4:Me_2O. The solution was immediately investigated by IR and NMR spectroscopy.

IR (CH_2Cl_2): ν(CO) 1873 cm^{-1}. ^{1}H NMR (CD_2Cl_2) phenyl resonances omitted: 8.53 (broad, CHPh); −3.20 (dd, J_1 = 61 Hz, J_2 = 65 Hz, 1H); −8.37 (m, 1H); −10.13 (d, J = 50.8 Hz, 1H) ppm. ^{31}P{^{1}H} NMR: 46.9 (s, P(1)); 46.6 (dd, $J_{P(2)P(3)}$ = 4 Hz, $J_{P(2)P(4)}$ = 16 Hz, P(2)); 34.5 (d, $J_{P(3)P(2)}$ = 4 Hz, P(3)); 22.5 (d, $J_{P(4)P(2)}$ = 16 Hz, P(4)) ppm.

3.3. Synthesis of [(CO)$(PPh_3)_2$HRe(μ-H)$_3$Ru(PhCN)$(PPh_3)_2$][BPh_4] (5)

A solution of 0.2 g of **3** in 10 ml of dichloromethane was introduced under dinitrogen into a 100 ml stainless steel autoclave, and the solution was pressurized to 50 atm of dihydrogen. The solution was stirred for 5 days. The autoclave was then depressurized and the brown solution was recovered and evaporated to dryness. Redissolution in dichloromethane and precipitation by diethylether left 0.15 g of a brown powder (80% yield).

Anal. Found: C, 69.60; H, 4.97; N, 0.98. $C_{104}H_{89}BNOP_4ReRu$ calc.: C, 69.75; H, 5.01; N, 0.78%.

IR (CH_2Cl_2): ν(CO) 1889 cm^{-1}. ^{1}H NMR (CD_2Cl_2) phenyl resonances omitted (294 K): −4.69 (t, J = −53.3 Hz + broad resonance, 3H); −13.20 (t, J = 11 Hz, 1H) ppm. ^{1}H NMR (193 K): −4.17(m, 1H); −4.85 (t, J = 50 Hz, 1H); −4.96 (t, J = 51.7 Hz, 1H); −13.22 (broad, 1H) ppm. ^{31}P{^{1}H} NMR (294 K): 59.3 (broad, P(1)); 57 (broad, P(2)); 42.3 (broad, P(3)); 34.8 (broad, P(4)) ppm. ^{31}P{^{1}H} NMR (193 K): 56.6 (ddd, $J_{P(1)P(2)}$ = 24 Hz, $J_{P(1)P(3)}$ = 15 Hz, $J_{P(1)P(4)}$ = 5.6 Hz, P(1)); 51.7 (d, $J_{P(2)P(1)}$ = 24 Hz, P(2)); 39.8 (dd, $J_{P(3)P(1)}$ = 15 Hz, $J_{P(3)P(4)}$ = 9.6 Hz P(3)); 39.8 (broad, P(4)) ppm.

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