4-Ethynylpyridine as a Bridging Moiety in Mixed Rh/Re Complexes

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A paramagnetic, dimeric $Rh^{III}Rh^{II}$ complex of the formula $[Rh_2(form)_4(C{\equiv}CC_5H_4N)]$ (**1**) [form = *N*,*N'*-di-*p*-tolylformamidinate; C_5H_4N = pyridyl (py)] has been synthesized and used as starting material to prepare heterotrimetallic complexes of composition $[Rh_2(form)_4(C{\equiv}Cpy)\{Re(CO)_3(bipy)\}][OS(=O)_2CF_3]$ (**2**) and $[Rh_2(form)_4(C{\equiv}Cpy)\{Re(CO)_3(t\text{bu}_2\text{bipy})\}][OS(=O)_2CF_3]$ (**3**). These complexes have been examined by vibrational spectroscopy, EPR spectroscopy, thermogravimetry and cyclic voltammetry. They are heat-stable and can be handled in air without problems. The observed interactions between the Rh_2 and the Re subunits, however, are weak, and a significant charge transfer does not seem to take place. (© Wiley-VCH Verlag GmbH & Co. KGaA, 69451 Weinheim, Germany, 2003)

Introduction

Dimeric rhodium complexes were first reported in the 1960s.[1] Since then a large number of compounds containing RhRh units have been described.[2] However, the number of Rh_2 compounds containing axial Rh−C bonds is rather limited.[3] Metal-metal units, containing axial M−C bonds in general, however, have been shown to be useful building blocks for linear organometallic oligomers and polymers.[3a,4] These oligomers and polymers may display interesting and novel optical and magnetic properties.[5] RN−RhRh as well as RN−RhRh−NR units [R = $C_5H_4NRe(bipy)(CO)_3$, $C_5H_4-C_5H_4NRe(Br)(CO)_3-NC_5H_4-C_5H_4N$, $C_5H_4C{\equiv}CC_5H_4FeC_5H_4C{\equiv}CC_5H_4N$, $C_5H_4C{\equiv}CC_5H_4FeC_5H_5$, etc.], which we used previously as building blocks for organometallic oligomers and polymers, suffer from their weaker nitrogen-rhodium interactions and are more sensitive to temperature, air, moisture and donor solvents.[6] In this work we report on an RhRh moiety with one axial 4-ethynylpyridyl ligand. This axial ligand can act as a useful linker to other transition metal complexes, as exemplified by the formation of [carbonyl(bipyridyl)-rhenium] complexes.

Results and Discussion

Synthesis and Characterization

Our aim was to synthesize compounds with the $[Rh_2(form)_4]$ (form = *N*,*N'*-di-*p*-tolylformamidinate) building block containing the two metal atoms in different oxidation states and only one axial σ-alkynyl moiety as connecting unit. To achieve this, an equimolar amount of *n*BuLi was added dropwise to a solution of 4-ethynylpyridine in dry THF at dry ice temperature. $[Rh_2(form)_4Cl]$ was added, the mixture was allowed to react for 5 h and then slowly brought to room temperature. Stirring was continued for 24 h and then the reaction mixture was exposed to air for another 24 h. The green residue formed was dissolved in CH_2Cl_2 and chromatographed to afford the paramagnetic, neutral $[Rh_2(form)_4(C{\equiv}Cpy)]$ (**1**) as a dark green solid (Scheme 1). Complex **1** displays its asymmetric C≡C vibration at 2120 cm^{-1}. The NC pyridine vibration is observed at 1590 cm^{-1}.

Under FAB-MS conditions the molecular peak $[M]^+$ is observed, as well as $[M - C{\equiv}Cpy]^+$. As in the case of the related Ru derivatives of formula $[Ru_2(form)_4(C{\equiv}Cpy)_2]$,[4d] the axial metal−carbon bond is easy to break under FAB conditions. Under TG conditions the complex starts decomposing at 373 °C by losing its C≡Cpy ligand. A second, distinct decomposition onset is observed at 435 °C when the "form" ligands start to break down. The remaining mass at 650 °C is ca. 45% of the original mass.

A solution of compound **1** and $[Re(CO)_3(L_2)(MeCN)(CF_3SO_3)]$ (L_2 = bipy, $t$bu$_2$bipy) in THF was refluxed in the dark for 3 h. The reaction mixture was then cooled to room temperature and the residue was dissolved in CH_2Cl_2 and chromatographed to yield the pale green,

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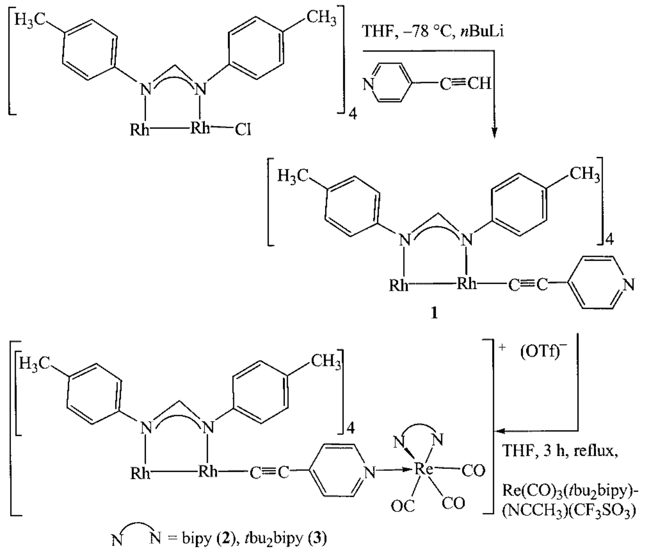

Scheme 1

paramagnetic solids [Re(CO)$_3$(bipy)Rh$_2$(form)$_4$(C≡Cpy-4)][OTf] (**2**) and [Re(CO)$_3$(*t*bu$_2$bipy)Rh$_2$(form)$_4$(C≡Cpy-4)][OTf] (**3**), respectively (Scheme 1). They display their C≡C vibration at 2108 and 2107 cm^{-1}, respectively, indicating a slightly weakened triple bond in comparison to the precursor complex **1**. The pyridine CN vibrations are observed at 1603 and 1606 cm^{-1}, shifted 13 and 16 cm^{-1}, respectively, in comparison to complex **1**, thus indicating a slight strengthening of the CN bond, possibly due to the increased electron density in the pyridine ring because of its bridging function between the RhRh and the Re units.

In the FAB mass spectrum the [M]$^+$ signals of the cations are observed with low intensities (< 5%) as well as the [M − Re(CO)$_3$(L$_2$)]$^+$ and the [M − C≡Cpy − Re(CO)$_3$(L$_2$)]$^+$ signal. The most intense peak in both mass spectra is the [Re(CO)$_3$(L$_2$)]$^+$ peak. Under TG conditions the decomposition onset of the complexes **2** and **3** is observed at 365 and 341 °C, respectively, in both cases below the onset of compound **1**, but above the decomposition onset of the Re ligands. This shows that the decomposition of the complexes **2** and **3** starts with the degradation of the Re moiety. Further clearly pronounced decomposition onsets are not observed until the end of the measurement, probably due to a simultaneous decomposition of the different organic ligands above 400 °C. Due to the coordination to the Rh$_2$(form)$_4$(C≡Cpy) building block the Re$^{\mathrm{I}}$ moiety is significantly stabilized {the first decomposition onset of the Re$^{\mathrm{I}}$ precursor, [Re(CO)$_3$(*t*bu$_2$bipy)(NCCH$_3$)] is observed at 163 °C}. Above a certain temperature level (in the temperature range of 340−370 °C), however, it starts decomposing regardless of the attached molecule. Similar observations have been made for the [Re(CO)$_3$(L$_2$)] moiety connected to other dimetallic transition metal complexes by 4-ethynylpyridine units and will be reported elsewhere.

Electrochemical Properties

Cyclic voltammetric measurements of compounds **1−3** were performed in a dichloromethane solution containing [*t*Bu$_4$N]PF$_6$ (0.2 M) as supporting electrolyte. Potentials are quoted vs. an Ag/AgCl reference electrode.

As a main feature, the cyclic voltammetric profile of the parent dinuclear complex **1**, presented in Figure 1, shows a one-electron oxidation ($E°' = +0.55$ V) and a one-electron reduction ($E°' = -0.50$ V). Both these processes are chemically and electrochemically reversible (peak current ratio at different scan rates is constantly close to 1; ΔE_p departs slightly from the theoretical value of 59 mV). Asymmetric complexes like **1** are commonly described both as an $(Rh_2)^{5+}$ or Rh$^{\mathrm{II}}$−Rh$^{\mathrm{III}}$ system.[7a] Nevertheless, it has also been suggested that, while the addition of two axial ligands does not substantially modify the Rh−Rh bonding system, asymmetric complexes such as **1** should present a large polarization toward the formally pentacoordinate rhodium atom.[7b] In spite of this, for reasons which will be discussed shortly, we adopted here the "delocalized" description. The above-mentioned processes are therefore ascribed to formal $(Rh_2)^{5+}/(Rh_2)^{6+}$ electron removal and to $(Rh_2)^{5+}/(Rh_2)^{4+}$ electron addition, respectively. The redox change $(Rh_2)^{6+}/(Rh_2)^{7+}$ is also visible at +1.3 V. This irreversible process results in the decomposition of complex **1** and generates an unknown species which gives rise to a new series of three signals at +1.38, +0.68, −0.36 V (shown in Figure 1).

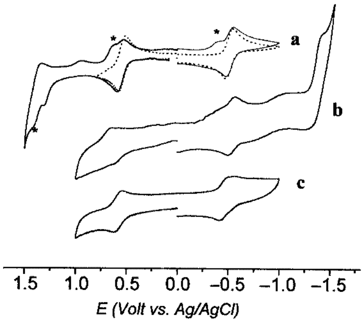

Figure 1. Cyclic voltammograms of a CH$_2$Cl$_2$ solution of [*t*Bu$_4$N]PF$_6$ (0.2 mol dm^{-3}) and the complexes (a) **1**, (b) **2**, (c) **3**; scan rate 0.2 Vs^{-1}

The main features of the cyclic voltammetric profile of the compounds **2** and **3**, also shown in Figure 1, are visible and allow some conclusions to be drawn. The main features of the redox profile of **1** appear in both complexes **2** and **3**. The more anodic irreversible processes are probably masked by the solvent discharge. In the cyclic voltammetric profile of **2** a further reduction process, possessing features of chemical quasi-reversibility, is also visible at $E°' = -1.36$ V. We ascribe this redox process to an electron addition to the bipy ligand coordinated to the rhenium atom.[7a] The equivalent redox process, expected for **3**, is not found, as it is probably cathodically shifted because of the presence of the *tert*-butyl substituents and is therefore masked by the solvent discharge. The redox potential values for the visible processes of **2** and **3** remain unaffected with respect to **1**.

The most important change is the anodic shift of 80 mV for the $(Rh_2)^{5+}/(Rh_2)^{6+}$ oxidation process of complex **2** (a minor anodic shift of 30 mV is also visible for complex **3**). This effect is probably due to the electron-withdrawing effect of the Re moiety on the central Rh_2 core. Remarkably, the $(Rh_2)^{5+}/(Rh_2)^{4+}$ reduction process, in which one electron is formally added to the axially ligated formal Rh^{III} ion, is practically unchanged in **1−3**. Therefore, it seems that such a substituent effect is mainly transmitted to the axially nonligated formal Rh^{II} ion. In this respect, it is also interesting to compare the redox behavior of complexes **1−3** with that of the parent complex $Rh_2(form)_4$, whose electrochemistry has been extensively studied by Piraino et al.[7c] In this complex the redox potential for the $(Rh_2)^{4+}/(Rh_2)^{5+}$ and $(Rh_2)^{5+}/(Rh_2)^{6+}$ changes are +0.25[7d] and +1.06 V,[7d] respectively, compared with −0.50 and +0.55 V for **1**. It is evident that the introduction of the (C≡Cpy) unit as a ligand in the axial position of the Rh−Rh core has a strong effect, inducing a significant cathodic shift on both redox changes. We interpret this behavior as evidence for the strong interaction between the two Rh ions. The formal electrode potentials of the above discussed redox changes are summarized in Table 1.

Table 1. Formal electrode potentials [V] vs. Ag/AgCl for the redox changes exhibited by complexes **1−3** in CH_2Cl_2 with $[tBu_4N]PF_6$ (0.2 M) as supporting electrolyte

Complex	$E^{\circ\prime}$ [V], (ΔE [mV])[a], i_p *ratio*[a]						
	$(Rh_2)^{6+}/(Rh_2)^{7+}$	$(Rh_2)^{5+}/(Rh_2)^{6+}$			$(Rh_2)^{5+}/(Rh_2)^{4+}$		
1	+1.30[b]	+0.55	(62)	0.98	−0.50	(72)	0.95
2	−	+0.63	−	*0.90*[c]	−0.53	(50)	*0.90*[c]
3	−	+0.58	(66)	*1.00*[c]	−0.51	(66)	*0.90*[c]

[a] Measured at 0.2 Vs^{-1}. [b] Irreversible redox process. [c] Estimated values.

EPR Spectra

The EPR spectra of the dirhodium complexes are best described by a spin-Hamiltonian of axial symmetry for one rhodium(II) ion ($4d^7$ "low-spin"). The corresponding EPR parameters are: $g_\perp = 2.110$, $g_\parallel = 1.938$ and $A_\parallel(^{103}Rh) = 28 \cdot 10^{-4}\ cm^{-1}$, for complex **1**; $g_\perp = 2.105$, $g_\parallel = 1.939$ and $A_\parallel(^{103}Rh) = 29 \cdot 10^{-4}\ cm^{-1}$ for complex **2** (N−N = bipy, Figure 2); and $g_\perp = 2.103$, $g_\parallel = 1.937$ and $A_\parallel(^{103}Rh) = 27 \cdot 10^{-4}\ cm^{-1}$ for complex **3** (N−N = tbu_2bipy). Although not absolutely symmetric, the ^{103}Rh hyperfine structure ($I = 1/2$, natural abundance 100%) was resolved or indicated for $B_o \| z$ in all spectra.

Similar EPR spectra and parameters have been reported for Rh_2 complexes in the literature,[3,7c,8] as, for example, for $[(ap)_4Rh_2(C{\equiv}CH)]$,[3b] $[(ap)_4Rh_2(C{\equiv}C)_2Si(CH_3)_3]$[3a] and $[(ap)_4Rh_2(C{\equiv}C)_2Rh_2(ap)_4]$[3a] (ap = 2-anilinopyridinate). The EPR spectra confirm for all complexes the presence of an $Rh_2^{II,III}$ unit with an electronic configuration of $(\sigma)^2(\pi)^4(\delta)^2(\pi^*)^4(\delta^*)^1$ for the Rh^{II} ion.[3b] The Rh^{III} ion of the $Rh_2^{II,III}$ unit is probably the one bound to the C≡Cpy unit since this ligand is known to be a σ-donor.

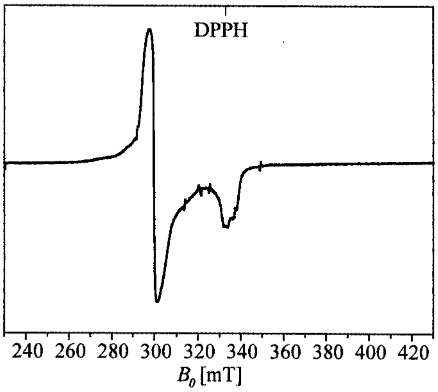

Figure 2. X-band EPR spectrum of complex **2** in a frozen solution of CH_2Cl_2; T_{rec} = 140 K (the spectrum is superimposed by small narrow lines of the standard Mn^{2+} in MgO)

Further conclusions, for example concerning partial spin density distribution to the Rh^{III} ion,[3a] are difficult to draw due to the limited resolution of the parallel features in the EPR spectra. The unequal distribution of the spin density (unpaired electron) over the two rhodium ions is underlined, however, by the observation of an additional hyperfine structure for complex **2** (Figure 2), which could be interpreted as a doublet of doublets $[A_\parallel(^{103}Rh) = 12 \cdot 10^{-4}\ cm^{-1}]$ observed in the parallel features for this particular EPR experiment.[3a] Regarding the EPR line-widths, the dirhodium unit is (magnetically) independent of the rhenium core connected via a bridging ligand.

Conclusions

Rh-based σ-alkynylpyridine complexes have been synthesized. They are stable to air, moisture and elevated temperatures (TG evidence) and can therefore be handled in air without any problems. However, the interactions along the RhRhC≡CpyRe axis do not allow significant electronic communication between the Rh_2 and the Re unit, as has been shown by CV and EPR experiments. However, the complexes are nevertheless of interest in the context of supramolecular chemistry. Work to replace the N−M bond by a C−M bond in closely related complexes is currently also under way in our laboratory. Furthermore, based on the findings presented here it should be possible to synthesize stable molecular rods based on Rh units ligated with two, instead of one, σ-alkynylpyridine ligands. This approach is also under examination in our laboratory.

Experimental Section

General: Unless stated otherwise, all reactions and manipulations were carried out in dry glassware under nitrogen or argon. Solvents were dried by standard procedures. 4-Ethynylpyridine,[9] $[Rh_2(O_2CCH_3)_4]$,[10a] $[Rh_2(O_2CCF_3)_4]$,[10b] $[Re(N{-}N)(CO)_3(MeCN)]OTf$ (N−N = bipy, tbu_2bipy; OTf = CF_3SO_3)[11] were prepared according to literature methods. $Rh_2(form)_4Cl$ was prepared according to the method described for $[Rh_2(ap)_4Cl]$ (ap = 2-anilinopyrinate), using "form" instead of "ap".[12] Elemental analyses were performed in the Mikroanalytisches Laboratorium of the TU München in Garching (Mr. M. Barth). IR (KBr pellets) and Raman spectra (powder samples) were obtained with a Bio-Rad FTS-575C spectrometer at room temperature. Mass spectra were obtained with Finnigan MAT 311 A and MAT 90 spectrometers. Cyclic voltammograms were recorded with a computer-controlled Model 173 Potentiostat/Galvanostat (EG&G Princeton Applied Research). The working electrode was platinum and the reference electrode was silver. Measurements were performed in a dichloromethane solution containing $[tBu_4N]PF_6$ as supporting electrolyte (0.2 $\textsc{m}$). Potentials are quoted vs. an Ag/AgCl reference electrode. The EPR spectra were recorded with a Jeol JES RE2X at X-band frequency ($\nu \approx 9.05$ GHz, microwave power 2 mW, modulation frequency 100 kHz).

$[Rh_2(form)_4(C{\equiv}Cpy\text{-}4)]$ (1): An equimolar amount of nBuLi was added dropwise to a solution of 4-ethynylpyridine (126.0 mg, 1.22 mmol) in 40 mL of dry THF at −78 °C under argon. $[Rh_2(form)_4Cl]$ (190 mg, 0.17 mmol) was added and the mixture was allowed to react at −78 °C for 5 h and then slowly brought to room temperature. Stirring was continued for 24 h and then the reaction mixture was exposed to air for another 24 h. The green residue was dissolved in CH_2Cl_2 and chromatographed on neutral Al_2O_3, eluting with CH_2Cl_2 to afford **1** as a dark green solid. Yield: 100 mg (50%). Dark green crystals were obtained by slow diffusion of Et_2O into a CH_2Cl_2 solution of the complex. $C_{67}H_{64}N_9Rh_2$ (1201.12): calcd. C 67.00, H 5.37, N 10.50; found C 66.55, H 5.70, N 10.36. IR (KBr): $\tilde{\nu}$ = 3019 (w), 2920 (w), 2120 (m, $\nu_{C\equiv C}$), 1590 (m), 1542 (s), 1504 (s), 1332 (m), 1219 (s), 938 (m), 821 (m), 756 (m), 710 (w), 441 (m) cm^{-1}. UV (CH_2Cl_2) = λ_{max} (ε) = 421 (10600), 591 (4200) and 905 (430 $\textsc{m}^{-1}$ cm^{-1}) nm. FAB-MS (nitrobenzyl alcohol as FAB matrix, ^{103}Rh): m/z (%) = 1201 (4) $[M]^+$, 1098 (100) $[Rh_2(form)_4]^+$, 875 (5) $[Rh_2(form)_3]^+$, 652 (9) $[Rh_2(form)_2]^+$, 429 (21) $[Rh_2(form)]^+$.

$[Re(CO)_3(bipy)Rh_2(form)_4(C{\equiv}Cpy\text{-}4)][OTf]$ (2): A solution of compound **1** (60.0 mg, 0.05 mmol) and $[Re(CO)_3(bipy)(MeCN)][CF_3SO_3]$ (31.0 mg, 0.05 mmol) in THF (20 mL) was refluxed in the dark for 3 h. The reaction mixture was then cooled to room temperature and the residue was dissolved in CH_2Cl_2 and chromatographed on neutral Al_2O_3, eluting with CH_2Cl_2/MeOH (100:1) to yield the pale green solid **2** (51.9 mg, 55%). $C_{81}H_{72}N_{11}F_3O_6ReRh_2S$ (1776.62): calcd. C 54.76, H 4.09, N 8.67; found C 55.01, H 3.99, N 8.72. IR (KBr): $\tilde{\nu}$ = 2960 (w), 2923 (w), 2860 (w), 2108 (m), 2023 (s), 1891 (s), 1590 (m), 1543 (s), 1503 (s), 1332 (m), 1260 (m), 1219 (s), 1105 (br), 1020 (m), 812 (s), 765 (m) cm^{-1}. UV (CH_2Cl_2): λ_{max} (ε) = 336 (9120), 590 (2070), 875 (460 $\textsc{m}^{-1}$ cm^{-1}) nm.

$[Re(CO)_3(tbu_2bipy)Rh_2(form)_4(C{\equiv}Cpy\text{-}4)][OTf]$ (3): A solution of compound **1** (60.0 mg, 0.05 mmol) and $[Re(CO)_3(tBu_2bipy)(MeCN)][CF_3SO_3]$ (36.5 mg, 0.05 mmol) in THF (20 mL) was refluxed in the dark for 3 h. The reaction mixture was then cooled to room temperature and the residue was dissolved in CH_2Cl_2 and chromatographed on neutral Al_2O_3, eluting with CH_2Cl_2/MeOH (200:1) to yield the pale green solid **3** (51.9 mg, 55%). $C_{89}H_{88}N_{11}F_3O_6ReRh_2S$ (1888.83): calcd. C 56.59, H 4.70, N 8.16; found C 56.72, H 4.55, N 8.22. IR (KBr): $\tilde{\nu}$ = 2961 (m), 2922 (m), 2867 (w), 2107 (m), 2027 (s), 1914 (s), 1605 (m), 1546 (s), 1503 (s), 1332 (m), 1261 (s), 1220 (s), 1096 (br), 1030 (m), 814 (s), 637 (w), 442 (w) cm^{-1}. UV (CH_2Cl_2): λ_{max} (ε) = 418 (8930, sh), 574 (1990), 885 (390 $\textsc{m}^{-1}$ cm^{-1}) nm. FAB-MS (nitrobenzyl alcohol as FAB matrix, ^{103}Rh, ^{187}Re): m/z (%) = 1738 (16) $[M]^+$, 1198 (5) $[M - Re(CO)_3(tbu_2bipy)]^+$, 1096 (8) $[M - C{\equiv}Cpy - Re(CO)_3(tbu_2bipy)]^+$, 539 (53) $[Re(CO)_3(tbu_2bipy)]^+$, 429.

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