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Note

Reactivity of the binuclear ruthenium 'Pincer' complex $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)]$ towards N-donor ligands. The X-ray crystal structure of $[RuCl_2(\eta^3\text{-}NN'N)(NCPh)]$ ($NN'N$ = 2,6-bis[(dimethylamino)methyl]pyridine)

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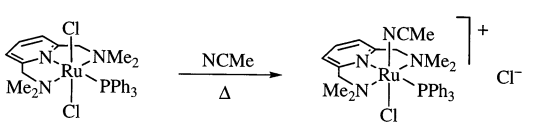
Abstract

Treatment of the binuclear, dinitrogen-bridged complex $[\{RuCl_2(\eta^3\text{-}NN'N)\}_2(\mu\text{-}N_2)]$ (**3**, $NN'N$ = 2,6-bis[(dimethylamino)methyl]pyridine) with two equivalents of acetonitrile gives the mononuclear derivative *mer*,*trans*-$[RuCl_2(\eta^3\text{-}NN'N)(NCMe)]$ (**4**), while the use of an excess of this ligand leads to the formation of the monocationic isomers *mer*,*trans*-$[RuCl(\eta^3\text{-}NN'N)(NCMe)_2]Cl$ (**5**) and *mer*,*cis*-$[RuCl(\eta^3\text{-}NN'N)(NCMe)_2]Cl$ (**6**). In contrast, when **3** is treated with an excess of benzonitrile or pyridine, the only products formed are *mer*,*trans*-$[RuCl_2(\eta^3\text{-}NN'N)(NCPh)]$ (**7**) and *mer*,*trans*-$[RuCl_2(\eta^3\text{-}NN'N)(py)]$ (**8**; py = pyridine), respectively. The X-ray structures of **7** and related reactions with other N-donor ligands are reported.

Keywords: Ruthenium complexes; Pincer complexes; N-donor ligands; X-ray crystal structure

1. Introduction

In a recent publication, the synthesis and structural characterization of the Ru(II) 'pincer' complex *mer*,*trans*-$[RuCl_2(\eta^3\text{-}NN'N)(PPh_3)]$ (**1**) Scheme 1; $NN'N$ = 2,6-bis[(dimethylamino)methyl]pyridine) has been reported [1]. This compound and a series of its cationic derivatives have been proven to have potent catalytic activity in the synthesis of piperidines and piperazines via the (cyclo)alkylation reaction of aromatic amines with alcohols [2]. Complex **1** can easily lose chloride anions in acetonitrile solution to form the monocationic derivative *mer*-$[RuCl(\eta^3\text{-}NN'N)(PPh_3)(NCMe)]Cl$ (**2**) (Scheme 1). This latter complex was shown to have an enhanced catalytic activity when compared to its neutral parent compound. The ease with which the dissociation of one of the two axial-positioned chloride ligands takes place in **1**, prompted us to propose this process as the first step in the catalytic cycle when



1 **2**

Scheme 1.

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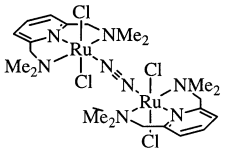


3

Fig. 1.

this species is used as catalyst precursor for this (cyclo)alkylation reaction. The loss of a chloride ligand in **1** would result in the formation of an unsaturated species which upon coordination of a substrate molecule would initiate the catalytic process.

In addition to this, a key step in the catalytic (cyclo)-alkylation reaction of amines with alcohols is the reaction of the active Ru center with the amine substrate. Although this process has been proposed to occur prior to the rate determining step of the catalytic cycle [2,3], well-defined species arising from the reaction of the Ru center with the reacting amine have not been isolated and their nature remains obscure. In order to obtain a better knowledge about this type of complexes, the reactivity of the related Ru(II) dinitrogen-bridged binuclear complex [{$RuCl_2(\eta^3$-*NN′N*)}$_2$(μ-N_2)] (**3**) (Fig. 1) towards N-donor ligands has been studied. The work reported herein shows that **3** readily reacts with N-donor ligands such as nitriles or pyridine to yield the corresponding mononuclear neutral or cationic derivatives. In contrast, treatment of **3** with primary or secondary amines leads to the formation of complex mixtures of products.

2. Results and discussion

The recently reported binuclear complex [{$RuCl_2(\eta^3$-*NN′N*)}$_2$(μ-N_2)] (**3**) can be obtained in a high yield by the simple treatment of $[RuCl_2(nbd)]_n$ (nbd = 1,5-norbornadiene) with the terdentate 'pincer' ligand under a dinitrogen atmosphere [1]. Compound **3** is very reactive under mild conditions towards a vast array of neutral donor ligands such as phosphines [4], CO [1], alkynes and alkenes [5] and sulfur containing nucleophiles [6].

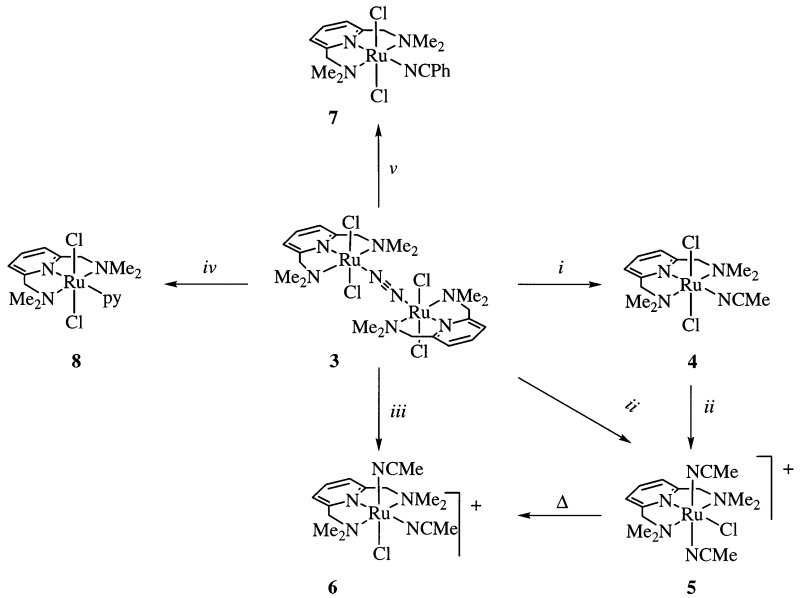
When a dichloromethane solution of **3** is treated with 2 equiv. of acetonitrile, the mononuclear derivative *mer*,*trans*-[$RuCl_2(\eta^3$-*NN′N*)(NCMe)] (**4**) (Scheme 2) is obtained in good yields. The molecular structure depicted for **4** (Scheme 2) is strongly supported by its ^{1}H NMR spectrum which shows the resonance signals corresponding to the CH_2 and NMe_2 groups of the pyridine ligand as singlets at δ 3.99 and 2.53, respectively. This strongly suggests the C_{2v} symmetry of the complex. Its $^{13}C\{^1H\}$ NMR data (see Section 3) are also in accordance with the structure proposed for **4**.

When an acetonitrile solution of **3** is stirred at r.t. for 30 min, a 2:1 mixture of the monocationic isomeric complexes *mer*,*trans*-[$RuCl(\eta^3$-*NN′N*)$(NCMe)_2$]Cl (**5**) and *mer*,*cis*-[$RuCl(\eta^3$-*NN′N*)$(NCMe)_2$]Cl (**6**) (Scheme 2) is obtained. The structure of these two compounds in solution can be determined by examination of their ^{1}H NMR spectra: complex **5** presents singlets for the benzylic protons and for the NMe_2 groups at δ 3.98 and 2.49, respectively, while the signal corresponding to the acetonitrile ligands also appears as a singlet at δ 2.29. According to the structure proposed in Scheme 2 all these data also indicate a C_{2v} symmetry for this complex in solution. Complex **5** can not be separated from this mixture and slowly isomerizes in solution at r.t. or upon heating of the reaction mixture to afford exclusively compound **6**. The asymmetry of **6** is reflected in its ^{1}H NMR spectrum, showing a simple AB pattern for the benzylic protons at δ 4.25 and 3.88 and two singlets for the NMe_2 groups at δ 2.60 and 2.53. The signals corresponding to the two asymmetric acetonitrile ligands appear as singlets at δ 2.46 and 2.39. The $^{13}C\{^1H\}$ NMR data of this complex also corroborate the structure proposed for **6**.

One can assume the coordination of the first acetonitrile ligand to take place in the position which was previously occupied by the bridging N_2 molecule to afford **4**. The second step would imply a dissociation process of one of the chloride ligands to form a 16-electron unsaturated species. This is not surprising, since related electron-deficient compounds have been isolated previously [1,5a]. Further reaction of this species with the second molecule of acetonitrile would result in the formation of **5**, which finally would undergo an isomerization reaction to afford **6**. The reason for this isomerization process may be electronic in nature, since the steric hindrance of both chloride and acetonitrile ligands is similar.

In contrast to the reaction with acetonitrile, when **3** is treated with either stoichiometric amounts or with an excess of benzonitrile, a neutral compound, i.e., *mer*,*trans*-[$RuCl_2(\eta^3$-*NN′N*)(NCPh)] (**7**) (Scheme 2) is obtained. The synthesis of **7** had been described in a previous study, and its structure in solution has been suggested on the bases of its NMR and IR data [7]. To further confirm that this structural motif is retained in the solid state, a single crystal X-ray diffraction study was carried out[3]. This study revealed that the general

[3] Crystal and refinement data for **7**·C_6H_6: orange plates, 0.6 × 0.4 × 0.2 mm; formula: $C_{18}H_{24}Cl_2N_4Ru{\cdot}C_6H_6$; MW = 546.49; a = 8.317(2), b = 27.274(4), c = 10.973(3) Å; β = 90°; V = 2489.0(9) Å^3; orthorhombic, space group *Pbcn*, Z = 4; Temperature = 173(2) K; BRUKER SMART CCD diffractometer with fine focus tube (Mo, λ = 0.71073 Å, graphite monochromator); ω-scans; 15414 measured reflections, 3496 unique reflections; 204 parameters; R_1 (F, observed reflections) = 0.0376; wR_2 (F^2, all reflections) = 0.0769; structure solution with SHELXS-97 [9a]; structure refinement with SHELXL-97 [9b]. Structure graphics and checking for higher symmetry were performed with the program PLATON [10]. Absorption correction (0.53–0.81 transmission range) has been done using SADABS [11].



Scheme 2. (i) 2 equiv. NCMe, CH_2Cl_2, r.t. (ii) Excess NCMe, r.t. (iii) Excess NCMe, reflux, 30 min. (iv) 2 equiv. pyridine, THF, r.t. (v) 2 equiv. NCPh, THF, r.t.

structure suggested in solution is also found in the solid state. A molecular plot of **7** is depicted in Fig. 2 with pertinent bond lengths and angles listed in the figure caption. The Ru atom is hexacoordinated in a distorted octahedral ligand environment with the three *N*-donor atoms positioned in a meridional configuration. In contrast to the perfect meridional geometry, **7** possesses no mirror plane, because of the non-planarity of the *NN′N* ligand. Additionally, there is an interplanar angle of 34.8(2)° of the pyridine ring to the benzyl ring of the benzonitrile ligand, which also breaks the mirror symmetry. The benzonitrile ligand is σ-coordinated via the nitrogen atom, positioned *trans* to the pyridine nitrogen atom, a situation which forces the two chloride ligands to be positioned *trans* to each other. Bond lengths and angles are typical when compared with related structures [1,4,5a,6,8]. Full structural details can be found in Section 5.

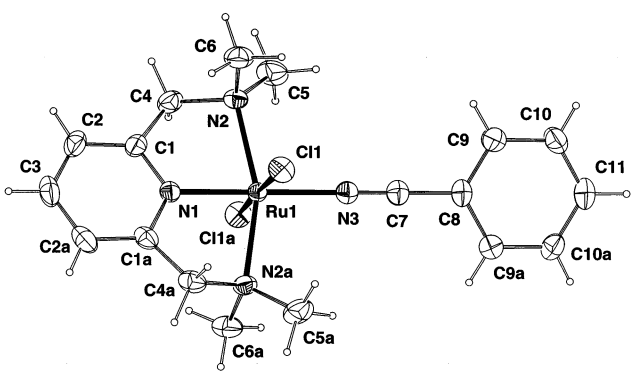


Fig. 2. Molecular structure of compound **7**. Displacement ellipsoids are drawn at the 50% probability level. Selected bond distances (Å), angles and torsion angles (°): Ru(1)–Cl(1), 2.4265(7); Ru(1)–Cl(1a), 2.4265(7); Ru(1)–N(1), 1.969(2); Ru(1)–N(2), 2.185(2); Ru(1)–N(2a), 2.185(2); Ru(1)–N(3), 2.007(3); N(3)–C(7), 1.141(4); C(7)–C(8), 1.435(4); Cl(1)–Ru(1)–Cl(1a), 177.31(3); Cl(1)–Ru(1)–N(3), 88.656(16); Cl(1a)–Ru(1)–N(3), 88.656(16); N(1)–Ru(1)–N(2), 79.92(5); N(1)–Ru(1)–N(2a), 79.92(5); N(1)–Ru(1)–N(3), 180.0; Ru(1)–N(3)–C(7), 180.0; N(3)–C(7)–C(8), 180.0; N(1)–C(1)–C(4)–N(2), −31.8(3).

Treatment of a THF solution of **3** with 2 equiv. of pyridine affords the neutral derivative *mer,trans*-$[RuCl_2(\eta^3\text{-}NN'N)(py)]$ (**8**) Scheme 2; py = pyridine). Its ^1H and $^{13}C\{^1H\}$ NMR data are listed in Section 3. These data reflect the symmetry of the complex and strongly support the structure proposed for **8** in Scheme 2. Similar treatment of **3** with other N-donor ligands such as aniline, allylamine or ammonia led to the formation of complex mixtures from which no pure compound could be isolated. Hydride-containing species were observed by ^1H NMR in the reaction mixtures.

3. Experimental

3.1. General data

Solvents were dried over sodium benzophenone ketyl (THF, hydrocarbons) or CaH_2 (CH_2Cl_2, NCMe) and distilled under a nitrogen atmosphere prior to use. All reagents were obtained from commercial sources and were used without further purification. Complexes **1** and **3** were prepared as described previously [1]. ^1H (200.133 and 300.103 MHz) and $^{13}C\{^1H\}$ (50.323 and 75.453 MHz) NMR spectra were recorded at 298 K with either a Bruker AC-200 or an AC-300 instrument, using $SiMe_4$ as internal standard (δ_H or $\delta_C = 0.00$).

Microanalyses were obtained from H. Kolbe Mikroanalytisches Laboratorium (Germany).

3.2. Synthesis of mer,trans-[$RuCl_2(\eta^3$-NN′N)(NCMe)] (4)

A solution of **3** (70 mg, 0.092 mmol) and MeCN (9.7 μl, 0.185 mmol) in CH_2Cl_2 (20 ml) was stirred at r.t. for 30 min. The colour changed from orange to red. The solvent was removed under reduced pressure and the solid residue was washed with pentane (2 × 10 ml) to give **4** as a brown solid (60 mg, 80%). *Anal*. Calc. for $C_{13}H_{22}Cl_2N_4Ru$ (406.4): C, 38.43; H, 5.46; N, 13.79. Found: C, 38.80; H, 5.67; N, 13.41%. ^{1}H NMR ($CDCl_3$): 7.40 (t, J = 7.8, 1H, Ar*H*), 7.13 (d, J = 7.8, 2H, Ar*H*), 3.99 (s, 4H, CH_2), 2.69 (s, 3H, NC*Me*), 2.53 (s, 12H, NMe_2) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): 164.8, 132.3, 118.9 (Ar*C*'s), 71.9 (*C*H_2), 54.6 (N*Me*$_2$), (*NN′N* ligand); 123.5 (CH_3CN), 5.4 (*C*H_3CN) ppm.

3.3. Synthesis of mer,trans-[$RuCl(\eta^3$-NN′N)$(NCMe)_2$]Cl (5) and mer,cis-[$RuCl(\eta^3$-NN′N)$(NCMe)_2$]Cl (6)

A solution of **3** (50 mg, 0.066 mmol) in NCMe (30 ml) was stirred at r.t. for 30 min. The colour changed from pale to dark orange. The solvent was removed under reduced pressure and the residue analyzed by ^{1}H NMR, showing a 2:1 mixture, respectively, of the isomers **5** and **6**. The residue was then redissolved in 30 ml of NCMe and heated to reflux temperature for 30 min. The solvent was then removed under reduced pressure and the residue washed with pentane (2 × 20 ml) to give **6** as a red solid (52 mg, 89%). *Anal*. Calc. for $C_{15}H_{25}Cl_2N_5Ru$ (447.4): C, 40.27; H, 5.63; N, 15.65. Found: C, 39.80; H, 5.35; N, 15.91%. ^{1}H NMR data for **5** ($CDCl_3$): 7.49 (t, J = 7.8, 1H, Ar*H*), 7.25 (d, J = 7.8, 2H, Ar*H*), 3.98 (s, 4H, CH_2), 2.49 (s, 12H, NMe_2), 2.29 (s, 6H, NC*Me*) ppm. ^{1}H NMR data for **6** (CD_3CN): 7.71 (t, J = 7.8, 1H, Ar*H*), 7.38 (d, J = 7.8, 2H, Ar*H*), 4.25 (d, J = 15.4, 2H, CH_2), 3.88 (d, J = 15.4, 2H, CH_2), 2.60 (s, 6H, NMe_2), 2.53 (s, 6H, NMe_2), 2.46 (s, 3H, NC*Me*), 2.39 (s, 3H, NC*Me*) ppm. ^{13}C{^{1}H} NMR (CD_3CN): 162.5, 135.2, 120.2 (Ar*C*'s), 72.0 (*C*H_2), 54.1 (N*Me*$_2$), 53.6 (N*Me*$_2$), (*NN′N* ligand); 129.5 (CH_3CN), 125.0 (CH_3CN), 4.8 (*C*H_3CN), 3.8 (*C*H_3CN) ppm.

3.4. Synthesis of mer,trans-[$RuCl_2(\eta^3$-NN′N)(NCPh)] (7)

A solution of **3** (150 mg, 0.2 mmol) and PhCN (40 mg, 0.4 mmol) in THF (30 ml) was stirred at r.t. for 60 min. The colour changed from orange to red. The solvent was removed under reduced pressure to approximately 5 ml; 50 ml of pentane were added and the solvent was decanted. The solid residue was dried under reduced pressure to give **7** as a brown solid (178 mg, 95%). Its analytical and spectroscopic data matched those reported in the literature [7].

3.5. Synthesis of mer,trans-[$RuCl_2(\eta^3$-NN′N)(py)] (8)

A solution of **3** (100 mg, 0.132 mmol) and pyridine (21.3 μl, 0.264 mmol) in THF (30 ml) was stirred at r.t. for 60 min. The colour changed from orange to red. The solvent was removed under reduced pressure and the solid residue was washed with pentane (2 × 10 ml) to afford **8** as a brown solid (110 mg, 94%). *Anal*. Calc. for $C_{16}H_{24}Cl_2N_4Ru$ (444.4): C, 43.24; H, 5.44; N, 12.61. Found: C, 43.99; H, 5.78; N, 12.23%. ^{1}H NMR ($CDCl_3$): 9.65 (m, 2H, *py*), 7.70 (t, J = 7.8, 1H, Ar*H*), 7.35 (m, 3H, *py*), 7.16 (d, J = 7.8, 2H, Ar*H*), 4.03 (s, 4H, C*H*$_2$), 2.28 (s, 12H, N*Me*$_2$) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): 163.2, 130.4, 118.2 (Ar*C*'s), 72.1 (*C*H_2), 53.6 (N*Me*$_2$), (*NN′N* ligand); 156.4, 133.6, 123.5 (*py* ligand) ppm.

4. Conclusions

The reactivity of the dinitrogen-bridged complex [{$RuCl_2(\eta^3$-*NN′N*)}$_2$(μ-N_2)] towards some N-donor ligands has been studied. Chloride ligand dissociation from **3** in acetonitrile solutions has been proven to be an easy process, in accordance with the data observed previously for similar complexes [2]. In contrast, treatment of **3** with an excess of benzonitrile does not lead to chloride dissociation but to the formation of the neutral derivative **7** as the only detected product. This might be due to the different electron-donating properties of both ligands, since their steric hindrances are similar. The X-ray crystal structure of **7** has been determined. The high instability of the products arising from the reaction of **3** with aniline or other primary amines may be the reason for the high catalytic activity shown by these metal fragments when they are used as precursors in the (cyclo)alkylation reactions with alcohols. Unfortunately, these species could not be isolated.

5. Supplementary material

Crystallographic data for the structure of complex **7** have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 112403. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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