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Intramolecular dealkylation of chelating diamines with Ru(II) complexes

M. Esther Morilla,[a] Galanda Morfes,[b] M. Carmen Nicasio,[a] Tomás R. Belderrain,[a] M. Mar Díaz-Requejo,[a] Claudia Graiff,[c] Antonio Tiripicchio,[c] Roberto Sánchez-Delgado*[b] and Pedro J. Pérez*[a]

[a] *Departamento de Química y Ciencia de los Materiales, Universidad de Huelva, Carretera de Palos de la Frontera s/n, E-21819 Huelva, Spain. E-mail: perez@dqcm.uhu.es; Fax: +34 959 017414; Tel: +34 959 017411*

[b] *Instituto Venezolano de Investigaciones Científicas, Apartado 21827, Caracas 1020-A, Venezuela*

[c] *Dipartimento di Chimica Generale ed Inorganica, Chimica Analitica, Chimica Fisica, Università di Parma, Parco Area delle Scienze 17A, I-43100, Parma, Italy*

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***N*,*N*, *N′*,*N′*-Tetraethylethylenediamine undergoes simple or double intramolecular dealkylation reactions in the presence of the complexes $[RuCl_2(diene)]_n$ (diene = cod, nbd) or *trans*-$[RuCl_2(diene)(morfoline)_2]$ at 80 °C to afford chelating amine ligands which contains one or two N–H functionalities.**

Transition metal-assisted C–N bond activation of amines and N-heterocycles constitutes a crucial step in the catalytic hydrodenitrogenation[1] of crude oil, as well as in the metabolism of amines by enzymes such as cytochrome P-450.[2] In addition, processes involving C–N single bond cleavage have found important synthetic applications such as metal-catalysed synthesis of unsymmetrical amines[3] or N-heterocycles.[4] Despite the importance of these reactions in terms of their potential applications, only few reports have appeared in the literature in the past few years. Those involved the rupture of C–N single bond of aniline[5] and the ring-opening of pyridine[6] and pyrrol[7] rings by complexes containing highly reactive trivalent Group 5 metals (Nb and Ta), the cleavage of the allylic-N bond of allylamines by Ru,[8a] Ni,[8b] and Rh[8c] complexes or the C–N bond scissions of aliphatic amines by Ru and Os carbonyl clusters.[9] To the best of our knowledge, no examples appear in the literature regarding the *N*-dealkylation of tertiary chelating diamines by a transition metal complex.

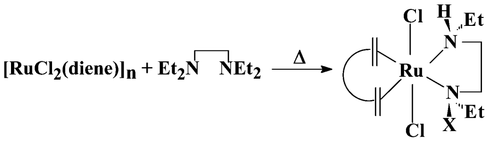
We have focused our attention in the synthesis of ruthenium complexes with chelating diamines and the study of their potential catalytic applications. During the course of these investigations, we have prepared a series of compounds of formula [RuCl$_2$(diene)(TMEDA)] (diene = 2,5-norbornadiene, nbd, **1a**; diene = 1,5-cyclooctadiene, cod, **1b**; TMEDA = *N*,*N*, *N′*,*N′*-tetramethylethylenediamine) by heating a suspension of the $[RuCl_2(diene)]_n$ in toluene in the presence of an excess of the diamine [eqn. (1)]. The complexes have been characterised by their analytical and spectroscopic data.[10]

$$[RuCl_2(diene)]_n + tmeda \xrightarrow{\Delta} [RuCl_2(diene)(tmeda)] \qquad (1)$$

1a,b

tmeda = Me_2N NMe_2
diene = nbd, 1a; cod, 1b

Upon changing the TMEDA ligand by the more sterically demanding *N*,*N*, *N′*,*N′*-tetraethylethylenediamine, TEEDA, an unexpected transformation is observed. Thus, when a toluene suspension of [RuCl$_2$(nbd)] is heated at 80 °C in the presence of a 5-fold excess of the ligand TEEDA, orange crystals of the new Ru(II) species [RuCl$_2$(diene)(Et(H)NCH$_2$CH$_2$N(X)Et)] (diene = nbd, X = Et, **2a**; diene = cod, X = H, **2b**) are obtained in moderate yield [eqn. (2)].† These transformations suppose the formal loss of one or two C_2H_4 fragments of the TEEDA ligand and the subsequent conversion of the tertiary into secondary amines. The presence of a N–H functionality in the co-ordinated diamine is supported by a sharp absorption in the IR spectrum (3220 cm^{-1} for **2a**, 3200 cm^{-1} for **2b**) and a broad resonance at δ 3.18 (1H) for **2a** and 3.61 (2H) for **2b** in the ^{1}H NMR spectrum. The proposed *trans*-geometry for both complexes is inferred from their NMR features. Complexes **2a** and **2b** could also be prepared directly and quantitatively from the commercially available diamines, Et$_2$NCH$_2$CH$_2$NHEt and EtHNCH$_2$CH$_2$NHEt, as shown in Scheme 1. It is interesting to note that, for the complex containing cod as the diene, **2b** is the only product formed upon reaction with the Et$_2$NCH$_2$CH$_2$NHEt diamine.



(2)

2a : X = Et, diene = nbd
2b : X = H, diene = cod

To unambiguously demonstrate the loss of the C_2H_4 moieties, a crystal structure determination of compound **2b** has been carried out.‡ Fig. 1 shows an ORTEP view of the structure of **2b** including the atom labelling scheme and some relevant bonding parameters. The complex has an imposed crystallographic C_2 symmetry, with the ruthenium atom lying on the two fold axis. The distorted octahedral environment of Ru1 involves the nitrogen atoms from the diamine ligand and the mid points of the C5–C6 and C5′–C6′ double bonds from the cod moiety in the equatorial positions; and two chlorine atoms at the apices. The Cl1–Ru–Cl1′ bond angle deviates significantly from linearity with value 159.19(4) °. The chlorine atoms and the ethyl groups of the diamine point away from the cod moiety.

To our knowledge, this is the first example of dealkylation of a chelating, tertiary diamine. As mentioned before, the exchange of alkyl groups between primary and/or secondary

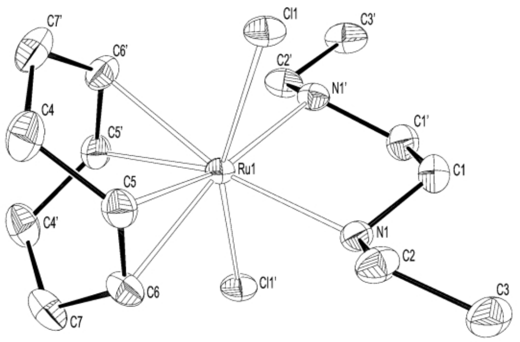


Fig. 1 View of the molecular structure of **2b** together with the atomic numbering scheme. Selected bond distances (Å) and angles (°): Ru1–N1 2195(2), Ru1–M1 2.117(2), Ru1–Cl1 2.466(1), N1–C2 1.504(3), C2–C3 1.539(4), N1–C1 1.493(3), C1–C1′ 1.530(5). N1–Ru1–N1′ 82.2(1), Cl1–Ru1–Cl1′ 159.19(4), Cl1–Ru–N1 83.37(7), Cl1–Ru1–N1′ 80.98(6), M1–Ru1–M1′ 85.42(7), M1–Ru1–Cl1 97.05(5), M1–Ru1–Cl1′ 98.019(5). M1 and M1′ are the mid points of the C5–C6 and C5′–C6′ bond distances respectively. Symmetry operations = −x + 1, y, −z + 1/2.

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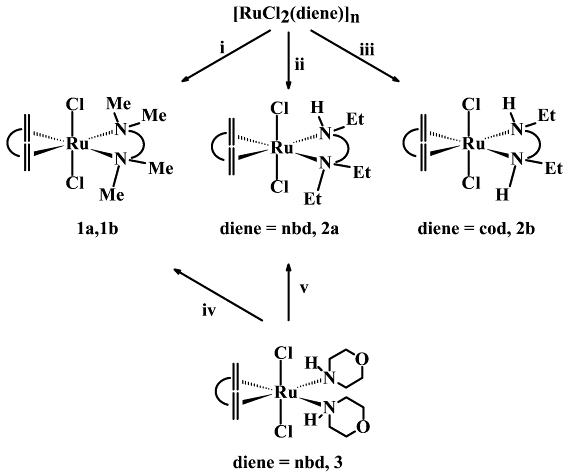

Scheme 1 Reactions conditions: (i) toluene, 80 °C, excess TMEDA; (ii) toluene, 80 °C, excess TEEDA or $Et_2NCH_2CH_2NHEt$; (iii) toluene, 80 °C, excess TEEDA, or $Et_2NCH_2CH_2NHEt$ or $EtHNCH_2CH_2NHEt$; (iv) $CDCl_3$, 1 equiv. TMEDA, 80 °C, 3 h, 70%; (v) $CDCl_3$, 1 equiv. $Et_2NCH_2CH_2NHEt$, rt, 1 h, 100%, or dichloroethane, 1 equiv. TEEDA, 80 °C, 15 h, 90%.

amines catalysed by use of the homogeneous catalyst $RuCl_2(PPh_3)_3$ is well documented.[3b,c] These transformations involve the formation of imine hydride complexes which react with nucleophiles such as additional amine to give intermediates from which the exchange of amines is produced. Since the transformations described in our system have been carried out with an excess of TEEDA, a similar pathway could in principle be invoked to account for these processes. However, such excess is not a requirement, as we have collected some mechanistic information that enforces the proposition of an intramolecular mechanism for the observed dealkylation reactions.

Given the heterogeneity of the reactions performed with the polymeric $[RuCl_2(diene)]_n$, we decided to develop an alternative synthesis of complexes **1** and **2** in the homogeneous phase. Thus, we have prepared the complex *trans*-$[RuCl_2(nbd)(morfoline)_2]$,[11] **3**, a soluble Ru(II) precursor. The addition of one equivalent of $Et_2NCH_2CH_2NHEt$ to a solution of **3** affords complex **2a** in quantitative yield upon stirring at room temperature for 1 h. NMR monitoring of the reaction shows the clean conversion of **3** into **2a**. In contrast, the reaction of **3** with 1 equiv. of TMEDA, at room temperature, proceeds quite slowly. Upon heating at 80 °C for 3 h, a 70 : 30 mixture of **1** : **3** is formed. Further heating (15 hours) does not produce any change in the reaction yield, as a clear indication of the existence of a thermodynamic equilibrium under those conditions. Addition of a slight excess of TMEDA provided quantitative conversions. Moreover, the thermal reaction of **3** with 1 equiv. of TEEDA, which is slower than with TMEDA, leads to complex **2a** in quantitative yield after 15 hours. In all cases, free morpholine is observed in the ^1H NMR of reaction mixtures.

Although mechanistic studies are still under way, some information could be gained from the available data. The conversion of **3** into **2a** using the $Et_2NCH_2CH_2NHEt$ ligand takes place almost instantaneously at room temperature. When 2 equivalents of morpholine are added to the mixture, the reaction rate decreases considerably. The fact that, at room temperature TMEDA reacts more slowly than $Et_2NCH_2CH_2NHEt$ is a good indication that coordination of the latter to the Ru(II) centre must occur initially through the NHEt-arm, which provides less steric hindrance than the NEt_2 counterpart. Attempts to isolate or detect a TEEDA adduct have failed, probably due steric reasons. We believe such an effect also accounts for the observed double *N*-dealkylation of the diamine ligand when cod is used as the diene moiety. The high steric demand of the cod ligand is manifested in the deviation of Cl1–Ru–Cl1′ angle (159.19(4)°) from lineality in **2b**. The almost quantitative yields of products observed when using one equivalent of the chelating amines unambiguously establish the intramolecular nature of this transformation, in contrast to the previously reported intermolecular alkyl group exchange catalysed by ruthenium.

In conclusion, we have demonstrated that the dealkylation of chelating amines such as $Et_2NCH_2CH_2NEt_2$ or $Et_2NCH_2CH_2NHEt$ in the coordination sphere of Ru(II) complexes proceeds by means of an intramolecular pathway. Work aimed to provide mechanistic information about the nature of the dealkylation process is currently underway in our laboratories.

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Notes and references

† General experimental procedure: To a suspension of $[RuCl_2(nbd)]_n$ (0.95 mmol) in toluene, *N*,*N*, *N′*,*N′*-tetraethylethylenediamine (1 mL) was added. The mixture was heated at 80 °C for 24 h and the resulting reddish-brown solution was evaporated to dryness. The residue was extracted in 30 mL of a 3 : 1 mixture of $Et_2O : CH_2Cl_2$, the solution was concentrated under vacuum and cooled to −20 °C. Orange crystals of **1** were obtained in 70% yield. Anal. Calcd for $C_{15}H_{28}Cl_2N_2Ru$: C, 44.12; H, 6.86; N, 6.91. Found: C, 43.80; H, 6.89; N, 7.03%. Selected NMR data for **2a**: ^1H NMR (C_6D_6, 400 MHz): (4.79 (m, 2 H, =C*H* of nbd), 4.72 (m, 2 H, =C*H* of nbd), 3.91 (sa, 2 H, C*H* of nbd), 1.28 and 1.21 (ABq, 2 H, CH_2 of nbd, J_{AB} = 8.9 Hz), 0.78 (t, 3 H, NCH_2CH_3, J_{HH} = 6.8 Hz), 0.46 (t, 3 H, NCH_2CH_3, J_{HH} = 6.9 Hz), 0.44 (t, 3 H, NCH_2CH_3, J_{HH} = 6.8 Hz).

‡ *Crystal data*: $C_{14}H_{28}Cl_2N_2Ru$, M = 396.35, a = 10.548(5), b = 15.762(5), c = 10.797(5) Å, β = 106.12(5)°, V = 1725(1) Å^3, monoclinic, space group $C2/c$, Z = 4, μ(Mo-Kα) = 1.209 mm^{-1}, T = 293(2) K, 7242 reflections measured, 2622 unique (2373 with $I > 2\sigma(I)$, R_{int} = 0.0292) which were used in all calculations. Final R values were $R1$ = 0.0321 and w$R2$ = 0.0853 (for $I > 2\sigma(I)$). $R1$ = 0.0361 and $wR2$ = 0.0887 (for all data). CCDC 186621. See http://www.rsc.org/suppdata/cc/b2/b205078a/ for crystallographic data in .cif or other electronic format.

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