Synthesis and characterization of Rh^{III} corroles: unusual reactivity patterns observed during metalation reactions†

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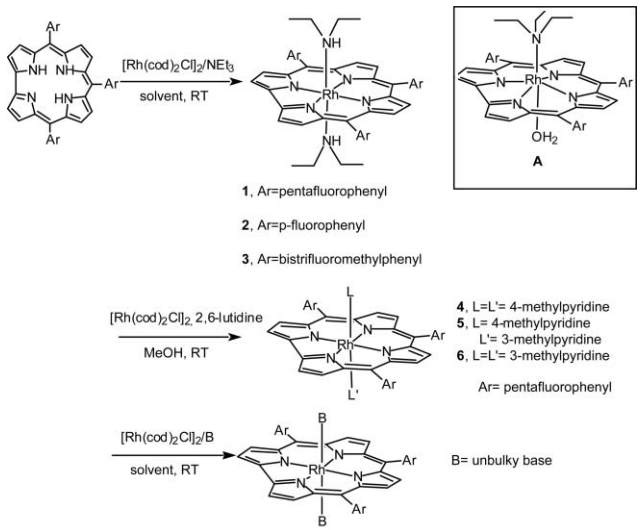
A new approach to the synthesis of Rh^{III} corrole complexes is developed and an unusual activation of C–C and C–N bonds is disclosed.

There have been dramatic developments in the field of corrole chemistry since 1999, at which time the direct synthesis of *meso*-arylcorroles was reported by two research groups.[1–3] Corroles differ from porphyrins in that the former are trianionic, have a smaller cavity and tend to stabilize higher metal oxidation states. First-row transition metal complexes of corroles have been extensively studied in recent years. In contrast, second- and third-row transition metal corroles have been only sparsely investigated. To date, there are less than ten publications related to Rh^{III} corroles.[4–12] In the search for Rh^{III} corrole complexes with labile axial ligand(s) as precursors to metal–metal bonded compounds, we have developed a facile approach to the synthesis of a series of octahedral Rh^{III} corrole complexes with nitrogen bases as the axial ligands. We have also uncovered an unusual activation of C–N and C–C bonds in bulky nitrogen bases in the presence of Rh corroles. This type of C–C and C–N bond activation has not been reported with porphyrin analogues.

meso-Tris(pentafluorophenyl)corrole (**TPFC**) reacts with $[Rh(cod)_2Cl]_2$ (cod = cyclooctadiene) in CH_2Cl_2, benzene or MeOH at room temperature, in the presence of 5–10 equivalents of an amine. The product Rh^{III} corrole is obtained in a 60–90% yield. When sterically unhindered coordinating bases such as pyridine or diethylamine ($NHEt_2$) are used, the resulting Rh^{III} corrole complex is octahedral, with the base coordinated at axial positions. When sterically hindered bases such as triethylamine (NEt_3) and 2,6-lutidine are used, the products have been identified as Rh^{III}(**TPFC**)$(NHEt_2)_2$ (**1**), and a mixture of three Rh^{III}(**TPFC**)L_2 complexes (**4–6**) in which 3 and/or 4-methylpyridine are bound at axial positions, respectively. The bulky bases are both dealkylated, and rearrangement is observed in the case of 2,6-lutidine (Scheme 1). Similar products are obtained with *meso*-tris(*p*-fluorophenyl)corrole (**TMFC**) and *meso*-tris[3,5-bis-(trifluoromethyl)phenyl]corrole (**BTFC**).

^{1}H NMR spectra of these compounds indicate they are diamagnetic, which precludes Rh=Rh double-bonded corrole dimers. The ^{1}H NMR spectral patterns of **1**, **2** [Rh^{III}(**TMFC**)$(NHEt_2)_2$] and **3** [Rh^{III}(**BTFC**)$(NHEt_2)_2$] are very similar (see ESI†). The four sets of doublets in the downfield region (8–9.5 ppm) are easily assigned to the *β*-pyrrolic protons; there are four sets of proton resonances in the upfield region (from 0 to −6.5 ppm). The triplet around −2 ppm clearly originates from methyl groups in the bound amine. The two multiplets around −3 to −4 ppm, are assigned to the protons of methylene groups of the amine; a broad peak at about −6.0 ppm, however, was puzzling. It was first assumed to be the protons of a water molecule bound to the central metal adventitiously as in structure **A**. The ^{1}H COSY NMR spectrum of compound **1** indicates weak coupling between the protons of methylene groups and the proton(s) (−6.02 ppm). The NOE spectrum of this compound also shows a close steric correlation between these protons. ^{19}F NMR spectra display two singlets for **3**, and three doublets and three triplets for **1**, suggesting that a plane of symmetry is coincident with the corrole plane. Running the reaction under dry conditions gives rise to the same compound. The ^{1}H NMR spectrum of **1** in CD_3OD indicates slow exchange (hours) between the proton(s) at −6.02 ppm with the solvent deuterium. This demonstrates that the proton is connected to a heteroatom. It appears that the NEt_3 serving as the deprotonating base in the reaction, is converted to secondary amine by losing an ethyl group. Cleavage of the C–N bond is further confirmed by the reaction between **TPFC** and $[Rh(cod)Cl]_2$ in the presence of $NHEt_2$, which generates a compound identical with **1**. The conversion of NEt_3 to $NHEt_2$ rather than to NH_2Et is revealed by the integrated ratio of the upfield resonances. In order to explore the scope of NEt_3 cleavage,



Scheme 1

† Electronic supplementary information (ESI) available: experimental details and spectroscopic data. See http://www.rsc.org/suppdata/cc/b5/b500247h/

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reaction with tributylamine was performed, which also resulted in cleaved axial ligands formed by losing one butyl group.

When a similar reaction is carried out in MeOH using 2,6-lutidine as the base, a mixture of three compounds is isolated in a yield of about 65–80%. The ^{1}H NMR spectrum of this mixture exhibits no upfield shift for the methyl groups of 2,6-lutidine, expected of protons in close proximity to the corrole ring. ^{1}H NMR spectroscopy indicates that the first fraction is bis(4-methylpyridine) Rh^{III} corrole **4**, the second fraction is a Rh^{III} corrole with 3-methylpyridine and 4-methylpyridine as the two axial ligands **5**, and the third fraction appears to be the bis(3-methylpyridine) Rh^{III} corrole **6**. The structure of **5** was confirmed using ^{1}H COSY NMR spectroscopy. The structure of **6** was confirmed by an X-ray analysis (Fig. 1).‡ It should be noted that the ratio of the three compounds varies in different runs of this reaction. It is obvious that both of the methyl groups from 2,6-lutidine have been cleaved, and one of them rearranged within the pyridine moiety at 3- or 4-positions randomly.

When $[Rh(cod)Cl]_2$ is mixed with **TPFC** in CH_2Cl_2 or MeOH in the absence of any base, no reaction is detected. When $[Rh(cod)Cl]_2$ is treated with NEt_3 in CH_2Cl_2 or 2,6-lutidine in MeOH, without any free base corrole, again, no cleavage is observed. It seems that the activation of the C–C and C–N bonds occurs after insertion of the metal into the corrole. When the reaction is carried out under anaerobic conditions in the presence of either NEt_3 or 2,6-lutidine, the color of the solution does not change from green to red (as observed for the reactions carried out in air) and a new brownish green compound is isolated. The nature of this new compound is currently under investigation. It appears that the oxidation of Rh^I to Rh^{III} is essential for the cleavage process to proceed. When $[Rh(cod)Cl]_2$ reacts with **TPFC** in CD_2Cl_2 in the presence of dry NEt_3, the ^{1}H NMR spectrum of the product does not show broadening or a decrease in the peak intensity at −6.02 ppm. These results suggest that the N–H proton of the axial $NHEt_2$ does not arise from the solvent. Alternatively, when $[Rh(cod)Cl]_2$ reacts with the deuterated corrole[13] and NEt_3 in dry CD_2Cl_2, the product also fails to exhibit a decreased and/or a broadened peak at −6.02 ppm. This indicates that the corrole NHs are also not the source of the N–H proton of the coordinated $NHEt_2$. We speculate that the dealkylation of NEt_3 may involve β-proton elimination. In order to examine this, trimethylamine (which cannot undergo β-elimination), quinuclidine (which has β-hydrogens pointing away from the active center) and *N*,*N*-dimethylbutylamine were used as base. In these examples, no cleavage is observed. It is noted, however, the absence of rearrangement with these amines is consistent with the lower steric hindrance of these ligands in addition to the changes in the β-proton availability noted. The use of 2,2,6,6-tetramethylpiperidine results in extensive decomposition. The aromatic nitrogen base, 2-picoline gives a mixture of compounds similar to those obtained with 2,6-lutidine; 2,6-difluoropyridine gives rise to decomposition, while both 2,6-dichloropyridine and 2,6-di-*tert*-butyl-4-methylpyridine do not react.

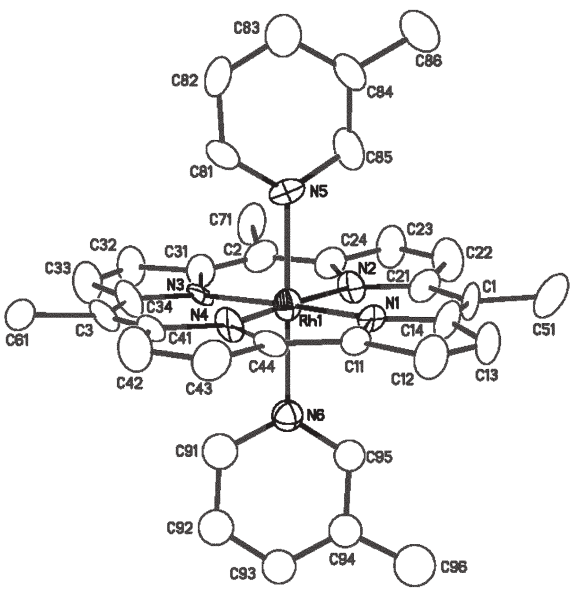

Fig. 1 The core of molecule **6** drawn with 50% probability ellipsoids. All hydrogen atoms of the disordered 3-methylpyridine groups and the C_6F_5 groups have been omitted for clarity.

The activation of C–C and C–N bonds in these axial ligands likely follows different mechanisms. It is plausible that cleavage of a C–N bond involves β-H elimination and C–C bond cleavage involves the insertion of Rh^{III} into the C–C bond as evidenced by other transition metal catalyzed C–C bond activations in homogenous systems.[14,15] We believe that steric factors play important roles in both rearrangements. As indicated above, C–C and C–N bond activation does not occur with all bulky nitrogen bases. Some bases do not react (2,6-dichloropyridine and 2,6-di-*tert*-butyl-4-methylpyridine) and some decompose (2,2,6,6-tetramethylpiperidine, 2,6-difluoropyridine). We tentatively interpret the results as follows: in the metalation process with a suitable, sterically bulky base, a five-coordinated intermediate should form. This tentative 5-coordinated Rh^{III} corrole would be a 16-electron species requiring one more axial ligand to attain a full-shell configuration; however, steric strain induced by the bulk of the base, along with the limited flexibility of the corrole macrocycle leads to dealkylation of the axial base (NEt_3 and 2,6-lutidine). Competition may exist between cleavage and degradation of the 5-coordinated intermediate. Therefore in some cases decomposition is observed (2,2,6,6-tetramethylpiperidine, 2,6-difluoropyridine). In the case of exceptionally bulky bases (2,6-dichloropyridine and 2,6-di-*tert*-butyl-4-methylpyridine), the formation of this five-coordinated intermediate may not be accessible and starting material is recovered. It is interesting to note that this reaction occurs at room temperature and that Rh^{III} corrole adducts adopt an octahedral coordination sphere with both axial bases undergoing rearrangement.

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Notes and references

‡ Crystal data for **6**: $C_{55}H_{36}F_{15}N_6Rh$, M = 1168.81, orthorhombic, space group $P2_12_12_1$. a = 8.6618(15) Å, b = 16.427(3) Å, c = 33.971(6) Å, α = 90.00°, β = 90.00°, ν = 90.00°, V = 4833.7(14) Å^3, Z = 4, μ (Mo-Kα) = 0.46 mm^{-1}, F(000) = 2352.0. The structure was solved by direct methods, and refined as a racemic twin. One of the 3-methylpyridine

groups in **6** was disordered over two positions (0.68/0.32) and modelled accordingly with distance constraints. The structure was refined to convergence in the final stage to give a Flack parameter of 0.47(5) for the twinned data set. Final *R* factors were $R_1 = 0.0586$ (observed data) and $wR_2 = 0.1072$ (all data). CCDC 260307. See http://www.rsc.org/suppdata/cc/b5/b500247h/ for crystallographic data in CIF or other electronic format.

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