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A Novel Facile Synthesis of Dihalogenoruthenium(IV) Porphyrins

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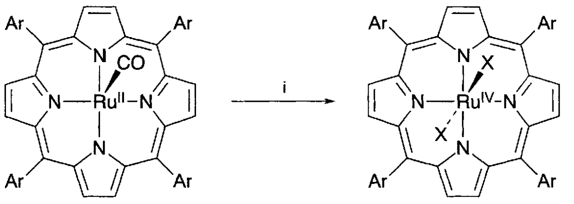
Dihalogenoruthenium(IV) porphyrins, versatile precursors to the unique organometallic chemistry of ruthenium porphyrins, are prepared directly from carbonylruthenium(II) porphyrins by reaction with CCl_4 and CBr_4 under extremely simple and mild reaction conditions.

Ongoing interest in the chemistry of ruthenium porphyrins derives from their catalytic properties for oxygenation of hydrocarbons,[1] and the rich coordination chemistry and reactivities of its various oxidation states.[2-5] Novel organo-ruthenim porphyrins can be prepared *via* two pathways, both sharing the early preparation of binuclear ruthenium(II) porphyrins $[Ru(por)]_2$.† One alternative is the reduction of $[Ru(por)]_2$ to $[Ru(por)]^{2-}$, followed by reaction with alkyl halides.[3b] In the second approach, the $[Ru(por)]_2$ complexes are first reacted with mineral acids (HX, X = Cl, Br, I) to provide the air-stable dihalogenoruthenium(IV) porphyrins, $Ru(por)X_2$.[6] Subsequent treatment with alkyl- or aryl-lithium reagents provides novel organoruthenium porphyrins. The overall reaction sequence from Ru(por)(CO), the first precursor in ruthenium porphyrin chemistry, to $Ru(por)X_2$ is summarized in Scheme 1. Since the first two steps require photochemical, high temperature, and ultra-high vacuum procedures,[7,8] simpler and shorter methods for the preparation of dihalogenoruthenium(IV) porphyrins are highly desirable. In this paper we describe an extremely simple and efficient method for the preparation of $Ru(por)X_2$ complexes directly from Ru(por)(CO) (Scheme 2).

We have decided to investigate the possibility of using CCl_4, long known to be activated by metal carbonyls,[9] for the oxidation of Ru(por)(CO) complexes. Simply heating a solution of Ru(ttp)(CO) in CCl_4 resulted in a pronounced colour change from orange to green. Spectroscopic examination of the solution by UV–VIS and ^1H NMR spectroscopy revealed that the colour change was due to the conversion of Ru(ttp)(CO) to $[Ru(ttp)X]_2O$,[10] which was complete after 2 h. This prompted us to check the same reaction with a porphyrin derivative that cannot form μ-oxo dimers. Since the commonly used Ru(tmp)(CO) complex was practically insoluble in CCl_4, we prepared the highly soluble Ru(tdmpp)(CO) derivative **1**. Heating of complex **1** in CCl_4 for 2 h resulted in a colour change from orange to red, and the ^1H NMR spectrum showed that an almost quantitative reaction to a new complex **2a** with paramagnetically shifted signals had taken place. In a similar reaction of **1** with 10 equiv. of CBr_4 in hot benzene, **2b** was formed.

$$\underset{}{Ru(tpp)(CO)} \xrightarrow{\text{i}} \underset{90\%}{Ru(tpp)(py)_2} \xrightarrow{\text{ii}} \underset{95\%}{[Ru(tpp)]_2} \xrightarrow{\text{iii}} \underset{83\text{–}95\%}{Ru(tpp)X_2}$$

Scheme 1 *Reagents and conditions*: i, *hv*, vacuum, pyridine; ii, *T* > 200 °C, 10^{-5} Torr; iii, HX



1 Ar = 2,6-dimethylphenyl

X = Cl **2a** or Br **2b**
(yield >80%)

Scheme 2 *Reagents and conditions*: i, reflux, no special precautions, CCl_4 or CBr_4–benzene

Complexes **2a**, **b** were identified as $Ru(tdmpp)Cl_2$ and $Ru(tdmpp)Br_2$, respectively‡ by MS and comparison of their ^1H NMR data to those of the related complexes $Ru(tpp)X_2$ **3** (X = Cl **a**, Br **b**, I **c**)[6] and $Ru(tmp)(OCHMe_2)_2$ **4**.[3a] In particular, the chemical shifts of the pyrrole-H of **2a** (δ −55.4) and **2b** (δ −46.0) are comparable to the values of δ −57.7, −48.0, −23.1 for **3a**, **b**, **c**, respectively ($CDCl_3$) and δ −11.95 (C_6D_6) for **4**. The high symmetry of the complexes is apparent by the observation of only one signal for both the *ortho*-CH_3 and the *meta*-H of the phenyl groups. One noteworthy difference between complexes **2** and **3** does, however, exist. Ke *et al.* have noted the alternating nature of the chemical shifts of the phenyl hydrogens in their complexes (for **3b** the chemical shifts of the *ortho*-, *meta*-, and *para*-hydrogens were at δ 5.21, 12.75 and 5.82, respectively), which shows that π-delocalization (the contact shift) dominates the paramagnetic isotropic shifts.[6] In complexes **2a** and **2b**, however, all resonances of the hydrogens on the phenyl rings (*ortho*-CH_3, *meta*-H, and *para*-H) are shifted in the same direction (downfield), consistent with a pure dipolar shift.[11] This difference between complexes **2** and **3** is readily explained as follows. The large upfield shift of the pyrrole resonance in all $Ru(por)X_2$ complexes is due to π-spin density transfer from porphyrin (3e, filled) to the metal d_π orbitals. Some of this π-spin density can 'leak' into the unsubstituted phenyl rings of $Ru(tpp)X_2$, but not to the strictly perpendicular 2,6-dimethylphenyl rings in **2**. Similar phenomena were observed in the comparison of porphyrin-oxidized Zn(tpp) and Zn(tmp) derivatives.[12]

In conclusion, we report here a one-pot preparation of dihalogenoruthenium(IV) porphyrins by an extremely easy procedure, bypassing the multi-step and experimentally demanding pathways. We trust that this will open up the opportunity for more extensive studies of the chemistry of ruthenium porphyrins. The mechanistic aspects of the reactions,§ their potential for catalytic activation of hydrocarbons, and utilizations of the primary products as precursors for new organoruthenium complexes are currently under investigation.

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Footnotes

† *Abbreviations used*: por = unspecified porphyrin dianion; tpp = 5,10,15,20-tetraphenylporphyrin dianion; ttp = 5,10,15,20-tetra-*p*-tolylporphyrin dianion; tmp = 5,10,15,20-tetrakis(2,4,6-trimethylphenyl)porphyrin dianion; tdmpp = 5,10,15,20-tetrakis(2,6-dimethylphenyl)porphyrin dianion.

‡ $[Ru(tdmpp)Cl_2]$ **2a**: MS (DCI, isobutane, negative ion), cluster around *m/z* 896.2 (M^-, 40%, correct isotopic pattern for $C_{52}H_{44}Cl_2N_4Ru$); ^1H NMR (δ, $CDCl_3$, room temperature): 12.13 (8H, d, 7.6 Hz, H_m), 8.09 (4H, t, 7.6 Hz, H_p), 4.06 (24 H, s, *o*-CH_3), −55.36 (8H, br s, pyrrole-H). $[Ru(tdmpp)Br_2]$ **2b**: MS (DCI, isobutane, negative ion), cluster around *m/z* 986.1 (M^-, 100%, correct isotopic pattern for $C_{52}H_{44}Br_2N_4Ru$); ^1H NMR (δ, $CDCl_3$, room temperature): 14.37 (8H, d, 7.5 Hz, H_m), 7.81 (4H, t, 7.5 Hz, H_p), 4.61 (12 H, s, *o*-CH_3), −45.97 (8H, br s, pyrrole-H).

§ Tetrachloroethylene was found in a GC–MS analysis of the reaction mixture, while $PhCH(Cl)CH_2CCl_3$ was identified in a reaction run in the presence of styrene (no attempts to quantify these reactions have yet been made).

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