Rapid Communications

Reaction of anion radical chelates with acids: An unusual route to ruthenium azo species

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The title anion radical chelates are of type [RuII(L-)(Cl)(CO)(PPh3)] where L is azo-2,2'-bipyridine (abp), 2-(p-chlorophenylazo)pyridine (Clpap) or 2-(phenylazo)pyridine (pap) and L- is the corresponding azo anion radical. These spontaneously reduce protons in solution and secondary reactions may then follow. In this manner (the acids being HPF6, HCl and HC=CPh), the following species have been isolated and structurally characterized: [Ru(abp)(Cl)(CO)(PPh3)]PF6, [Ru(Clpap)(Cl)(CO)(PPh3)].CH2Cl2 and [Ru(pap)(Cl)(CO)(PPh3)]Cl.

Azo anion radicals characterized by the [-N=N-] function have recently been isolated in the form of metal complexes.1-3 Our synthetic method consists of homolytic M–H cleavage, (Eq.1) where L is a chelating azo ligand and L- is the corresponding azo anion radical.1-3

\[ M^+H + L \rightarrow M^L- + \frac{1}{2} H_2 \]  

(1)

The ML- species have now been found to efficiently reduce protons in solution providing synthetic access to new species. A few results for M=Ru are reported in this communication.

Experimental

Room temperature magnetic moments were measured using a PAR-155 vibrating sample magnetometer and EPR spectra were recorded on a Varian E-109C spectrometer. Electrochemistry was done with a PAR 370-4 system4 and ¹H NMR spectra were recorded on a Bruker FT 300 MHz instrument. The X-ray structures were determined using a Siemens R3m/V diffractometer (Mo-Kα radiation) and SHELXTL-Ver.5.03 software.7 Further details can be found elsewhere.8

The azo ligands (L) concerning us here are abp, Clpap and pap and their chelation modes are as shown. The relevant complexes 1-7 are listed in Chart 1. Complexes 2 and 3 were made as

1 [Ru(abp')(Cl)(CO)(PPh3)]
2 [Ru(Clpap')(Cl)(CO)(PPh3)]
3 [Ru(pap')(Cl)(CO)(PPh3)]
4 [Ru(2Clpap)(Cl)(CO)(PPh3)]
5 [Ru(2pap)(Cl)(CO)(PPh3)]
6 [Ru(2pap)(Cl)(C≡CPh)(CO)(PPh3)]
7 [Ru(2pap)(Cl)(C≡CPh)(CO)(PPh3)]

Chart 1

reported earlier.1 The new radical complex 1 (µeff 1.86 µB, EPR, g = 2.00) was prepared by heating to reflux a mixture of abp and [Ru(H)(Cl)(CO)(PPh3)](ref.9) in the molar ratio 3:1 in dry heptane for 1h.

On cooling to room temperature, the green solution afforded 1 in 82% yield. Analytical data: Found (Calcd, %): C, 64.58(64.64); H, 4.21(4.39); N, 6.31(6.42). ¹PF6- was prepared by reacting 1 with NH4PF6 in 1:1 molar ratio in wet CH2Cl2–MeCN mixture followed by chromatographic work-up on a silica gel column using toluene:acetonitrile (3:1) mixture as
eluant; yield, 60%. Analytical data: Found(Calcd, %): C, 55.35(55.43); H, 3.68(3.76); N, 5.41(5.50). 4 was synthesized by passing HCl gas through a solution of 2 in benzene for 1h under stirring followed by slow evaporation; yield, 50%. Analytical data: Found(Calcd, %): C, 52.88(52.97); H, 3.29(3.38); N, 6.12(6.18). 7 was prepared by the reaction of 3 and PhC=CH in 1:2 molar ratio in CH$_2$Cl$_2$ under stirring for 12h. The deep blue solution upon evaporation to dryness afforded the solid which was washed with hexane to remove excess PhC=CH yielding 7 in 60% yield. Analytical data: Found(Calcd, %): C, 65.06(65.12); H, 3.74(3.82); N, 5.50(5.56).

Results and discussion

Green solution of 1 (2 and 3 behave similarly) is stable in benzene even in the presence of oxygen. Addition of acids such as MeC$_2$H$_4$, however, causes a rapid colour change to red due to quantitative formation of 1$^+$, (Eq. 2). This transformation is consistent with the cyclic-voltammetric $E_{pa}$ ($-0.30$ V vs. SCE in CH$_2$Cl$_2$ solution) of 1. The salt 1$^+$PF$_6^-$ is isolated by reacting 1 with NH$_4$PF$_6$ in wet CH$_2$Cl$_2$-MeCN solution, the hydrolysis of PF$_6^-$ affording the required acid in situ.

For an acid whose conjugate base is a potent coordinating agent, further reactions may follow. Thus 2 (1 and 3 behave similarly) reacts with HCl gas in benzene transiently generating red 2$^+$ (already known as 2$^+$PF$_6^-$) which is then rapidly transformed to violet 4, (Eq. 3).

$$2^+ + \text{Cl}^- \rightarrow 4 + \text{PPh}_3$$  \hspace{1cm} (3)

The reaction of 3 (1 and 2 behave similarly) with the weak acid PhC=CH ($pK_a$ 19) in CH$_2$Cl$_2$ affords 5 (an analogue of 4) as well as the acetylide 6. The HCl required for the formation of 5 presumably originates from CH$_2$Cl$_2$. A major point of interest is that 5 and 6 cocrystallize from this reaction medium in virtually 1:1 ratio affording the solvated entity, 7.CH$_2$Cl$_2$. In solution (CDCl$_3$) the latter displays $^1$H NMR signals due to both 5 and 6. Thus the pyridyl proton para to the N atom occurs as two equally intense triplets ($J = 7.3$ Hz) at 8.04 $\delta$ (5) and 7.93 $\delta$ (6).

The X-ray structures (excluding anion/solvent) of 1$^+$PF$_6^-$, 4.CH$_2$Cl$_2$, and 7.CH$_2$Cl$_2$ are shown in Figs. 1-3 and selected bond lengths are listed in Table 1. In each case the azo ligand constitutes a planar five-

<table>
<thead>
<tr>
<th>Table 1 - Selected bond distances ($\AA$)</th>
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<tr>
<td>1$^+$PF$_6^-$</td>
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<tr>
<td>Ru-P</td>
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<tr>
<td>Ru-N(pyridine)</td>
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<tr>
<td>Ru-N(azo)</td>
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<tr>
<td>Ru-Cl</td>
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<tr>
<td>Ru-CO</td>
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<td>N-N</td>
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Fig. 1 - Molecular view and atom labeling scheme for the cation in [Ru$^{II}$ (abp)(Cl)(CO)(PPh$_3$)$_2$]PF$_6^-$, 1$^+$PF$_6^-$. 

Fig. 2 - Molecular view and atom labeling scheme for [Ru$^{II}$ (Clpap)(Cl)$_2$(CO)(PPh$_3$)$_2$]CH$_2$Cl$_2$, 4.CH$_2$Cl$_2$, (excluding CH$_2$Cl$_2$).
membered chelate ring and the N–N lengths lie in the nonradical range\(^3\) 1.28-1.29 Å. In 7 the position trans to \(\text{PPh}_3\) (position X in Fig. 3) is occupied by both \(\text{Cl}^-\) and PhC\(=\text{C}^-\) ligand (occupation factor 0.5 for each). In effect there is Cl\(^-\)/C\(=\text{C}^-\) disorder. The observed Ru–X length, 2.375(3) Å in Fig. 3 is weighted more towards Ru–Cl than Ru–C length because of the larger electron density of chlorine.

In summary the radicals 1-3 are sensitive to acids, weak or strong. The primary reaction is oxidation as in (Eq. 2) but secondary reactions can follow depending on the acid affording interesting acid-selective final products.

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References