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Syntheses of 2,9-Bis(halomethyl)-1,10-phenanthrolines: Potential Robust Ligands for Metal Oxidation Catalysts

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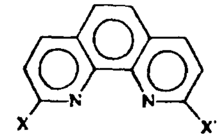
Free radical halogenation of 2,9-dimethyl-1,10-phenanthroline with *N*-bromosuccinimide and *N*-chlorosuccinimide form the known α-methyl derivatives 2,9-bis(trihalomethyl)-1,10-phenanthrolines. The compound 2,9-bis(trichloromethyl)-1,10-phenanthroline can be used for one-step syntheses of oxidatively resistant fluoro- and partially reduced chloromethyl derivatives capable of coordination to metal oxidation catalysts.

The functionalization of ligands with halogen substituents, particularily fluorine, enhance and prolong the activity of metal oxidation catalysts.[1] The *cis*-[Ru^{II}(CH$_3$CN)$_2$(1)$_2$]$^{2+}$ complex, Chart I, where 1 is 2,9-dimethyl-1,10-phenanthroline, activates dioxygen and hydrogen peroxide for hydrocarbon oxygenation including methane.[2] Methods for functionalization of the methyl substituents of 1 with halogens have been developed to incorporate the phenanthroline subunit into polydentate and macrocyclic ligands.[3] Our interest in the methyl substituents of 1, which are critical for the catalytic activity of *cis*-[Ru^{II}(CH$_3$CN)$_2$(1)$_2$]$^{2+}$,[2b] is the impact of halogenation on the activity and regioselectivity of the ruthenium and related catalysts. The syntheses of 2-5 from 1 have been accomplished previously by direct free radical halogenation or multistep syntheses.[3] We report several modified routes to 2-5, and the first preparation of fluorinated derivative 6 (Chart I).

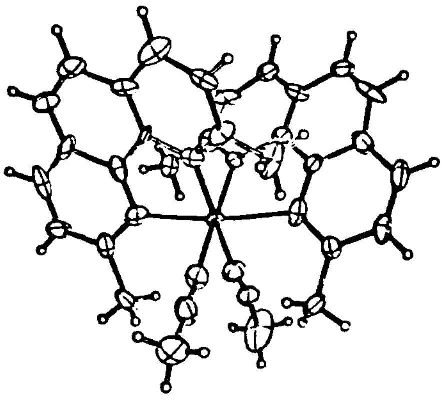
Results and Discussion

Treatment of commercially available 1 with excess *N*-bromosuccinimide (NBS) and *N*-chlorosuccinimide (NCS) afforded 2 and 3 by modification of the previous synthesis of 3.[3b] Attempts to use stoichiometric amounts of NCS or Cl$_2$ produced primarily 3 or complex mixtures of products in accord with previous reports of free radical halogenation of 1.[3a,b] Practically no reaction of [Zn(1)Cl$_2$][4] with NCS occurred under the same conditions, yielding only minor amounts of mono- and disubstituted chlorinated products 4 and 5.[3b,c] A correlation has been shown between chlorination and the electronic environment of the methyl substituent of heterocycles.[5] Though steric effects may also play a role in the suprising lack of reactivity of coordinated 1, these results suggest that the electronic effects of a metal may be used modulate reactivity of 1.

Chart I



X, X' = CH$_3$ (1), CBr$_3$ (2), CCl$_3$ (3), CH$_2$Cl (4), CH$_3$,CH$_2$Cl (5), CF$_3$ (6)



cis-[Ru^{II}(CH$_3$CN)$_2$(1)$_2$]$^{2+}$

The reported preparation of 4 and 5 from 3 utilized a multistep synthesis specific for monofunctionalized methyl derivatives.[3b,c] Reductive dehalogenation of 3 with 4 equiv of *n*-Bu$_3$SnH in benzene yielded 4 (42%) and a minor product, 5, in less but comparable amounts to the overall yield reported previously (4 steps, 68%).[3b] This synthetic route may allow more substituted derivatives of 1, i.e., *sym*-tetrachloromethyl and bromomethyl derivatives, to be prepared.

Attempts to synthesize 6 from 2 or 3 by conventional halide exchange reactions[7] with HF/*N*,*N*'-dimethylimidazolidinone or SbF$_3$ in SbCl$_5$ treated with Cl$_2$ gas failed to produce any fluorinated product.[6] A melt of excess SbF$_3$ and 3 gave 6 in low yield (18%). The physical and spectroscopic properties are consistent with the addition of a trifluoro group to the phenanthroline moiety.[6,7] The analogous reaction with 2 was unsuccessful. Space-filling

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computer models of **2**–**6** suggest that the steric bulk of the substituents on **2** and **3** preclude metal coordination, but **4**–**6** are potential ligands. We are pursuing the metal coordination chemistry and high yield synthesis of **6** and related ligands.

Experimental Section

Solvents and reagents were obtained from commercial sources and used without further purification.

2,9-Bis(trichloromethyl)-1,10-phenanthroline (3) and 2,9-Bis(tribromomethyl)-1,10-phenanthroline (2). A 3-g (13.3 mmol) portion of 1·H_2O and 15 equiv of NBS or NCS were refluxed in $CHCl_3$ for 6 h. The solution was cooled and filtered. The evaporated filtrate was washed with saturated aqueous Na_2CO_3 and extracted repeatedly with $CHCl_3$. Drying over anhydrous Na_2CO_3 and chromatography (SiO_2; 2:1 $CHCl_3$:hexanes) yielded 85–90% of pure **2** or **3**: mp(**2**) 195 °C dec, lit. mp 196–197 °C; mp(**3**) 214–6 °C as reported. Elemental analysis and ^1H NMR and mass spectral data agreed with literature values.[3a,b]

2,9-Bis(chloromethyl)-1,10-phenanthroline (4) and 2-(Chloromethyl)-9-methyl-1,10-phenanthroline (5). A 1.50-g (3.6 mmol) portion of **3** was dissolved in 20 mL of benzene (dried over Na/benzophenone ketyl) to which 3.9 mL (14.4 mmol) of n-Bu_3SnH and 50 mg of AIBN were added. The solution was refluxed under Ar for 2 h until complete (TLC, 2:1 petroleum ether:EtOAc). The reaction was quenched with aqueous Na_2CO_3 and extracted with $CHCl_3$. The combined $CHCl_3$ extracts were dried over anhydrous Na_2CO_3, evaporated, and purified by chromatography (SiO_2; 2:1 petroleum ether:EtOAc) to yield 0.42 g of **4** (42%) and 0.13 g of **5** (14%): ^1H NMR and mass spectral data agreed with literature values.[3a,b]

2,9-Bis(trifluoromethyl)-1,10-phenanthroline (6). A 0.3-g (1.25 mmol) portion of **3** (mp 214–6 °C) and 3.0 g (16.8 mmol) of SbF_3 (dec 235 °C) were ground in a mortar and pestle and then placed in a 25-mL round-bottom flask fitted with a reflux condensor under N_2. The contents of the flask were gently heated with a Bunsen burner with agitation until a melt formed. Heating and agitation were maintained for 10 min; some charring and decomposition of the SbF_3 occurred. After cooling, the solids were washed with water and neutralized with aqueous NaOH. This mixture was washed repeatedly with ethyl acetate. The washings were combined, dried over anhydrous Na_2CO_3, and evaporated. Chromatography (SiO_2; CH_2Cl_2) yielded 0.040 g of **6** (18%) as a white powder: mp 164–6 °C; MS, m/z 316 (M^+), 247 ($M^+ - CF_3$); ^1H NMR ($CDCl_3$, 300 MHz) δ 8.00 (s, H5,6, 2 H), 8.05 (d, H3,8, J = 8.5 Hz, 2 H), 8.51 (d, H4,7, J = 8.5 Hz, 2 H) vs TMS; ^{19}F NMR (d_6-DMSO, 282 MHz) δ −65.0 vs $CFCl_3$. Anal. Calcd for $C_{14}H_6N_2F_6$: C, 53.18; H, 1.61; N, 8.86. Found: C, 52.96; H, 1.51; N, 8.93.

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