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ABSTRACT ON REPRINT

98 7 08 174

93-15592
Syntheses of 2,9-Bis(halomethyl)-1,10-phenanthrolines: Potential Robust Ligands for Metal Oxidation Catalysts

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Received October 14, 1992

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(trichloromethyl)-1,10-phenanthroline. 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, particularly fluoride, enhance and prolong the activity of metal oxidation catalysts.1 The cis-[RuIII(CH3CN)2(1)] complex, Chart 1, where 1 is 2,9-dimethyl-1,10-phenanthroline, activates dioxygen and hydrogen peroxide for hydrocarbon oxidation 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-[RuIII(CH3CN)2(1)]2+, 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.4 We report several modified routes to 2–5, and the first preparation of fluorinated derivative 6 (Chart 1).

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 3.5 Attempts to use stoichiometric amounts of NCS or Cl2 produced primarily 3 or complex mixtures of products in accord with previous reports of free radical halogenation of 1.6,7 Practically no reaction of [Zn(1)-NC] with NCS occurred under the same conditions, yielding only minor amounts of mono- and disubstituted chlorinated products 4 and 5.8 A correlation has been shown between chlorination and the electronic environment of the metal substituent of heterocycles.9 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.

The reported preparation of 4 and 5 from 3 utilized a multistep synthesis specific for monofunctionalized methyl derivatives.10 Reductive dehalogenation of 3 with 4 equiv of n-Bu3SnH in benzene yielded 4 (42%) and a minor product, 5, in less but comparable amounts to the overall yield reported previously (4 steps, 68%).10 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 reactions7 with HF/N,N′-dimethylazodicinone or SbF5 in SbCl5 treated with Cl2 gas failed to produce any fluorinated product.6 A melt of excess SbF5 and 3 gave 6 in low yield (18%). The physical and spectroscopic properties are consistent with the addition of a trifluoromethyl group to the phenanthroline moiety.11 The analogous reaction with 2 was unsuccessful. Space-filling...
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). A 3-g (13.3 mmol) portion of 1,2,2′-H2O and 15 equiv of NBS or NCS were refluxed in CHCl3 for 6 h. The solution was cooled and filtered. The evaporated filtrate was washed with saturated aqueous Na2CO3 and extracted repeatedly with CHCl3. Drying over anhydrous Na2CO3 and chromatography (SiO2; 2:1 petroleum ether:EtOAc) yielded 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 SbF5 (dec 235 °C) were ground in a mortar and pestle and then placed in a 25-mL round-bottom flask fitted with a reflux condenser under N2. 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 SbF5 occurred. After cooling, the solids were washed with water and neutralized with aqueous NaOH.

Bis(tribromomethyl)-1,10-phenanthroline (2). A 3-g (13.3 mmol) portion of 1,2,2′-H2O and 15 equiv of NBS or NCS were refluxed washings were combined, dried over anhydrous Na2CO3, and evaporated. Chromatography (SiO2; CH2Cl2) yielded 0.040 g of 6 (18%) as a white powder: mp 164–6 °C; MS, m/z 316 (M+), 247 (M+ - CF3); 1H NMR (CDCl3, 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; 19F NMR (d6-DMSO, 282 MHz) δ -65.0 vs CFCl3. Anal. Calcd for C14H8N2F2: C, 53.18; H, 1.61; N, 8.86. Found: C, 52.96; H, 1.51; N, 8.93.

Acknowledgment. Funding for this research was provided by the Amoco University Methane Research Program and J.J. received support from the University of Florida Summer Research Apprenticeship Program for Minorities. We would like to thank Professor W. R. Dolbier and W.-J. Cao for helpful discussions and assistance.