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The Conversion of Quadruply Bonded Dirhenium(III) Complexes to Mononuclear Pentakis(isocyanide) Complexes of the Type $Re(CNAr)_5X$ (Ar = 2,4,6-Tri-t-butylphenyl and X = Cl or Br)

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While homoleptic isocyanide complexes of rhenium(I) of the type $[Re(NCR)_6]^+$ and $[Re(CNAr)_6]^+$ (R = alkyl; Ar = aryl) are well known [1, 2], the corresponding pentakis(isocyanide) complexes $Re(CNR)_5X$ and $Re(CNAr)_5X$ are quite rare. Treichel and Williams described a low-yield thermal route to $Re(CN\text{-}p\text{-}tol)_5X$ (X = Cl or Br) from the reaction between $Re(CO)_5X$ and *p*-tolyl isocyanide in refluxing toluene [3], and Cameron *et al.* [4] have prepared the xylyl isocyanide complex $Re(CNxylyl)_5I$ from K_2ReI_6. More recently, we have described how the photo-induced ligand substitution of $[Re(CNxylyl)_6]^+$ with halide ions in dichloromethane yields $Re(CNxylyl)_5X$ (X = Cl, Br or I) [5]. In the present report we describe a new synthetic strategy for such derivatives, in which quadruply bonded dirhenium(III) complexes are cleaved by tri-t-butylphenyl isocyanide (TBPhNC) to give $Re(CNTBPh)_5X$ (X = Cl or Br).

The complexes $Re(CNTBPh)_5X$ (X = Cl or Br) can be synthesized through the reactions of TBPhNC with the dirhenium(III) complexes $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br), $Re_2(O_2CCH_3)_4Cl_2$, or $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ in methanol. In some instances, the homoleptic complex $[Re(CNTBPh)_6]PF_6$ could be isolated upon work-up of the reaction filtrates. While the cleavage of the Re–Re quadruple bond has been used previously as a route to alkyl and aryl isocyanide complexes of rhenium [1, 2], the formation of pentakis(isocyanide) derivatives has not previously been encountered by the use of such a method.

The identification of $Re(CNTBPh)_5X$ was based upon similarities between their spectroscopic and electrochemical properties and those of $Re(CNxylyl)_5X$ (xylyl = 2,6-dimethylphenyl; X = Cl, Br or I) [5]. The most striking similarity exists among the cyclic voltammetric (CV) data. Solutions of the TBPhNC complexes in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$ exhibit two reversible oxidations at $E_{1/2} = +0.31$ V and $E_{1/2} = +1.42$ V for $Re(CNTBPh)_5Cl$, and at $E_{1/2} = +0.36$ V and $E_{1/2} = +1.50$ V for $Re(CNTBPh)_5Br$ (all potentials versus Ag/AgCl).† The xylyl isocyanide complexes show oxidations at $E_{1/2} = +0.49$ V and $E_{p,a} = +1.44$ V for $Re(CNxylyl)_5Cl$, and at $E_{1/2} = +0.48$ V and $E_{p,a} = +1.40$ V for $Re(CNxylyl)_5Br$ [5]. The processes in the case of the xylyl complexes have been attributed to the $[Re(CNxylyl)_5X]^{+/0}$ and $[Re(CNxylyl)_5X]^{2+/+}$ couples, respectively. The fact that the processes at *c.* +1.45 V are reversible in the case of the TBPhNC complexes may reflect a greater ability of the TBPhNC ligand to more effectively stabilize the Re(II) oxidation state. The CV of $[Re(CNTBPh)_6]PF_6$ in 0.1 M $n\text{-}Bu_4NPF_6/CH_2Cl_2$ has also been recorded. This homoleptic isocyanide complex exhibits a reversible oxidation at $E_{1/2} = +1.15$ V versus Ag/AgCl which can be contrasted with that at $E_{1/2} = +1.19$ V versus SCE for $[Re(CNxylyl)_6]PF_6$ [2].

The IR spectra of $Re(CNTBPh)_5X$ (recorded as Nujol mulls) show characteristic vibrations associated with the ν(CN) modes and, for $Re(CNTBPh)_5Cl$, a mode assignable to ν(Re–Cl). The chloro complex exhibits ν(CN) modes at 2029 (s), 1931 (m) and 1915 (m) cm^{-1}; the ν(Re–Cl) mode appears at 270 cm^{-1}. The bromo derivative has ν(CN) at 2031 (s), 1934 (m) and 1917 (m) cm^{-1}; the Re–Br stretching mode occurs below 200 cm^{-1} (our instrumental limit). These values can be compared with those reported [5] for the xylyl isocyanide derivatives: 2041 (s), 2000 (m), 1950 (sh) and 1902 (m) cm^{-1} for $Re(CNxylyl)_5Cl$, and 2051 (s), 2006 (m), 1964 (m) and 1906 (m) cm^{-1} for $Re(CNxylyl)_5Br$. The homoleptic isocyanide complex displays a single, strong absorption at 2039 cm^{-1} attributable to ν(CN).

The 200 MHz ^1H NMR spectra of $CDCl_3$ and CD_2Cl_2 solutions of $Re(CNTBPh)_5Cl$ have been recorded. These show two singlets in the phenyl region (δ +7.29 and δ +7.19) with an intensity ratio of 4:1. These resonances are assigned to the phenyl ring *meta*-protons of the equatorial and axial‡ aryl isocyanide ligands, respectively. Three singlets are observed in the methyl region. A resonance at δ +1.44 corresponds to the protons of the *ortho*-t-butyl groups on the equatorial isocyanide ligands. The protons on the *ortho*-t-butyl groups of the axial ligand appear at δ +1.38. The *para*-t-butyl groups of

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†Electrochemical and spectroscopic characterizations of these complexes were carried out using procedures described previously [6]. Note that in the CV measurements the potentials are quoted relative to the ferrocenium/ferrocene couple having $E_{1/2} = +0.47$ V versus Ag/AgCl.

‡The unique axial TBPhNC ligand is defined as being *trans* to the Re–X bond in the pseudo-octahedral $Re(CNTBPh)_5X$ complexes.

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the axial and equatorial ligands resonate at δ +1.30. The corresponding 200 MHz ^1H NMR spectrum of $[Re(CNTBPh)_6]PF_6$ (in CD_2Cl_2) shows a singlet at δ +7.35 assignable to the *meta*-protons on the TBPhNC rings. The *ortho*-t-butyl protons appear at δ +1.38, and the *para*-t-butyl protons appear at δ +1.31.

Experimental

Starting Materials

The compounds $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl or Br) [7, 8], $Re_2(O_2CCH_3)_4Cl_2$ [9], and $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ [10] were prepared as described in the literature. Anhydrous ammonia was purchased from Matheson Gas Products. The compound 2,4,6-tri-t-butylnitrobenzene was obtained from Aldrich Chemical Co. and used as received. It was converted into 2,4,6-tri-t-butylaniline as described previously [11]. The isocyanide 2,4,6-tri-t-butylphenyl isocyanide (TBPhNC) was synthesized from the aniline derivative as reported by Yamamoto *et al.* [12]. This isocyanide was also prepared by the use of a procedure reported by Baldwin *et al.* [13] for the reduction of isocyanates to isocyanides. This procedure, which first requires the preparation of the isocyanate derivative 2,4,6-tri-t-butylphenyl isocyanate using the method of Habib and Rieker [14], is described below. It is an adaptation of the procedure outlined in ref. 13.

A mixture of trichlorosilane (1.21 ml, 12 mmol) and *N,N*-diisopropylethylamine (4.88 ml, 28 mmol) in dichloromethane (15 ml) was cooled to 0 °C with use of an ice–water bath. A quantity of 2,4,6-tri-t-butylphenyl isocyanate (2.57 g, 10 mmol) was added to this mixture from an L-shaped sidearm delivery tube. The reaction mixture was then stirred for 30 min, after which time anhydrous gaseous ammonia was bubbled through the resultant solution to precipitate silicon-containing species. This solid was filtered off. The filtrate was mixed with a saturated aqueous solution (*c.* 5 ml) of NaH_2PO_4. The organic phase was separated from the aqueous phase, then passed through a silica-gel plug. The volume of the organic solution was reduced under vacuum. The precipitate that formed (1.56 g) contained TBPhNC together with a small amount of unreacted isocyanate. The components of the mixture were identified by IR spectroscopy (Nujol mull): ν(CN) for TBPhNC at 2114 cm^{-1} and ν(NCO) for TBPhNCO at 2330 cm^{-1}. We found that this mixture was a good source of TBPhNC in the reactions we studied, since the isocyanate did not appear to interfere with the course of the reactions.

Reaction Procedures

Syntheses were carried out in an atmosphere of nitrogen under the pressure provided by passing the outlet nitrogen through a mineral oil bubbler. All solvents were deoxygenated prior to use.

Synthesis of $Re(CNTBPh)_5X$

(a) X = Br

A suspension of $(n\text{-}Bu_4N)_2Re_2Br_8$ (0.060 g, 0.040 mmol) and TBPhNC (0.152 g, 0.561 mmol) in methanol (20 ml) was stirred at room temperature for 20 h. The reagents reacted immediately to give a brown solution from which the green–yellow title complex precipitated. The product was filtered off and dried *in vacuo*; yield 0.038 g (29%). *Anal.* Calc. for $C_{95}H_{145}BrN_5Re$: C, 70.29; H, 9.00. Found: C, 69.25; H, 9.24%.

(b) X = Cl

(i) From $(n\text{-}Bu_4N)_2Re_2Cl_8$. A suspension of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.060 g, 0.053 mmol) and TBPhNC (0.200 g, 0.737 mmol) in methanol (20 ml) was stirred at room temperature for 20 h. The yellow product was filtered off and dried under vacuum; yield 0.037 g (22%).

(ii) From $Re_2(O_2CCH_3)_4Cl_2$. A mixture containing $Re_2(O_2CCH_3)_4Cl_2$ (0.038 g, 0.056 mmol) and TBPhNC (0.200 g, 0.737 mmol) was combined with methanol (20 ml). The suspension was refluxed for 6 days. The yellow title complex was filtered off and dried *in vacuo*; yield 0.040 g (23%).

A second compound, $[Re(CNTBPh)_6]PF_6$, was isolated from the filtrate. The filtrate was evaporated to dryness and the residue which resulted was washed with acetone. The acetone-soluble portion was collected and evaporated to dryness. This solid was treated with 3 ml of acetone saturated with KPF_6. This mixture was evaporated to dryness and then extracted into dichloromethane. Precipitation of the product from the dichloromethane soluble portion was initiated by the slow addition of petroleum ether to the extract. The pale yellow salt was recrystallized from acetone/diethyl ether; yield 0.088 g (40%). *Anal.* Calc. for $C_{114}H_{174}F_6N_6PRe$: C, 69.87; H, 8.95. Found: C, 69.99; H, 9.44%.

(iii) From $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$. The complex $Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.038 g, 0.057 mmol) and TBPhNC (0.200 g, 0.737 mmol) were combined with methanol (10 ml). The mixture was refluxed for 1 h. The yellow title complex was filtered off and dried under vacuum; yield 0.032 g (18%). The procedure described in (b) (ii) was used to isolate $[Re(CNTBPh)_6]PF_6$ from the reaction filtrate.

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