Facile and Successive Orthometallation in Rhenium Carbene Complex

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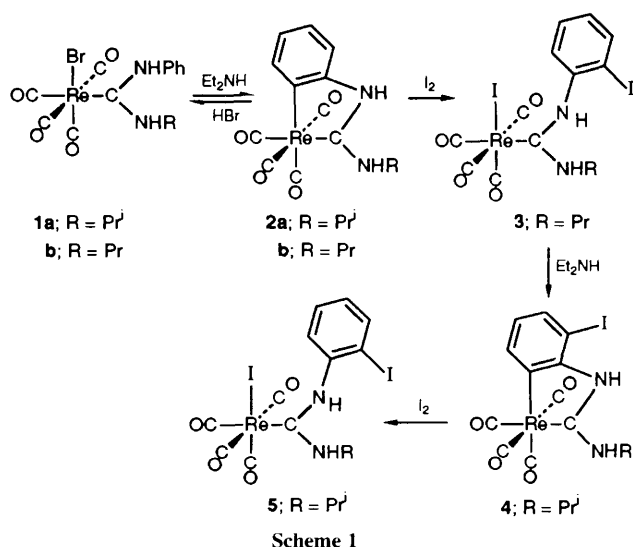
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The amidinium (carbene) complexes $ReBr(CO)_4[C(NHR)(NHPh)]$ **1** react with the secondary amine (Et_2NH) to yield the cyclometallated rhenium carbene complexes $Re(CO)_4[\mu_2-C(NHR)(NHC_6H_4)]$ **2**, which undergoes facile and successive closing and opening of the Re–C σ bond by the elimination and addition of electrophiles in rhenium carbene complexes under very mild conditions to yield the final product $ReI(CO)_4[C(NHPr^i)(NHC_6H_3I_2)]$ **5**.

An investigation of orthometallation is intriguing in view of its relevance to catalysis and organic synthesis.[1] Many metallacyclic compounds have been observed, and most of them occurred on metal complexes containing cyclometallated ligands with N and P as the donor atom.[2] In contrast, little is known about such reactions in metal carbene complexes containing cyclometallated ligands with carbon as the donor atom.[3] In the course of our attempts to evaluate the influence of isocyanide–carbonyl replacement on the reactivity of metal complexes,[4] we have reported previously the synthesis of amidinium (carbene) complexes $ReBr(CO)_4$-$[C(NHR)(NHPh)]$ **1**.[5] In this communication, we describe the unusual intramolecular activation of the C–H bond for these carbene complexes, in which an orthometallation of the carbene ligand occurs easily, and the subsequent Re–C σ bond

of the cyclometallated ring is labile and cleaved readily. A facile successive Re–C bond formation and opening have been observed under very mild conditions.

The complex $ReBr(CO)_4[C(NHPr^i)(NHPh)]$ **1a** reacts readily with Et_2NH to yield the cyclometallated carbene complex $Re(CO)_4[\mu_2-C(NHPr^i)(NHC_6H_4)]$ **2a** in 62% yield *via* an orthometallation process (Scheme 1).† The ^1H NMR spectrum of **2a** in the phenyl region is diagnostic of ortho-metallation on the phenyl group. The ^{13}C NMR spectrum showed a down field resonance peak at δ 154.53 thus providing evidence for the presence of a metal–carbon σ-bond in this type of complex.[6] Treatment of $ReBr(CO)_4[C(NHPr)$-

Scheme 1

Fig. 1 ORTEP diagram of Re(CO)₄[μ₂-C(NHPr)(NHC₆H₄)] **2b**. Selected bond distances (Å) and angles (°): Re–C(5), 2.160(8); Re–C(9), 2.187(8); N(1)–C(5), 1.340(12); N(2)–C(5), 1.328(12); N(1)–C(10), 1.412(12); C(9)–C(10), 1.411(12); C(1)–Re–C(3), 172.6(4); C(5)–Re–C(9), 76.3(3); Re–C(5)–N(1), 115.3(6); N(1)–C(5)–N(2), 117.2(7); C(2)–Re–C(9), 173.2(4); C(4)–Re–C(5), 169.4(4).

(NHPh)] **1b** with Et₂NH gives a similar cyclometallated complex Re(CO)₄[μ₂-C(NHPr)(NHC₆H₄)] **2b** in lower yield. The structure of **2b** was characterized by single-crystal X-ray diffraction analysis.‡ An ORTEP drawing of the molecule is shown in Fig. 1. Pseudooctahedral geometry is observed around the Re atom. The bond distance of Re–C(9) [2.187(8) Å] is only slightly longer than that of Re–C(5) [2.160(8) Å], suggesting delocalization throughout the five-membered metallacycle. The fused six- and five-membered rings are almost coplanar with a Re–C(9)–C(10)–C(11) dihedral angle of −178.9(9)°. The cyclometallated five-membered ring is severely distorted with ∠C(9)–Re–C(5) 76.3°. The distortion is likely to be attributed to the sp² hybridized C(9), C(10), N(1) and C(5) in the five-membered ring. In the carbene group, C(5)–N(1) and C(5)–N(2) bonds show partial double-bond character with bond distances 1.340(12) and 1.328(12) Å, respectively. The slightly longer bond length of C(9)–C(10) [1.411(12) Å] than that of other C–C bonds [av. 1.380(14) Å] of the benzene ring may be due to the involvement of the C(9)–C(10) bond in the metallopyrrole system.

The formation of complex **2** is likely attributed to the steric hindrance of the bulky amidinium ligand of the complex, which brings a proton in proximity to the bromine atom.[5] The rate of orthometallation for ReBr(CO)₄[C(NHPrⁱ)(NHPh)] **1a** with an isopropyl group is faster than that of ReBr(CO)₄-[C(NHPr)(NHPh)] **1b** with an n-propyl ligand. The orthometallation is likely to proceed via an electrophilic rather than an oxidative addition pathway. Since the rhenium atom in complex **1** is coordinatively saturated, the orthometallation involving oxidative addition is less favoured because this

would lead to an unfavourable seven-coordinated intermediate at the rhenium centre.

Reaction of **2** in CH₂Cl₂ with HBr (gas or aqueous solution) gives the amidinium complex **1** in near quantitative yield at room temp., indicating a labile cyclometallated Re–C σ bond of **2**. Treatment of complex **2a** with I₂ in CH₂Cl₂ at room temp. also leads to the opening of the Re–C σ bond to yield the amidiniumiodo complex ReI(CO)₄[C(NHPrⁱ)(NHC₆H₄I)] **3** in 72% yield.† In addition to spectroscopic characterization, complex **3** has been crystallographically defined. This reaction is believed to proceed via the electrophilic attack of iodine[7] at the cyclometallated Re–C σ bond similar to the reaction with HBr. The severe distortion of the cyclometallated ring may be responsible for the labilization of the Re–C σ bond. The IR spectrum of **3** showed terminal ν_CO stretching frequency at 2100m, 2000vs and 1932s cm⁻¹, similar to those of the carbene (amidinium) complex **1** [2104m, 2001vs and 1931s cm⁻¹].[5] The ¹H NMR spectrum showed that complex **3** exists as two isomeric forms in equilibrium in solution at room temp. The equilibrium might be due to the restricted rotation about the C–N bond[4a,8] in the amidinium ligand in solution. Three well separated multiplets centred at δ 7.96 (1 H), 7.43 (1 H) and 7.18 (2 H) correspond to four protons of the metallated C₆H₄I group, respectively.

Interestingly, intramolecular activation of the C–H bond of the iodocarbene complex **3** also proceeds readily by reacting with Et₂NH in CH₂Cl₂ at room temp. to yield the successive orthometallated complex Re(CO)₄[μ₂-C(NHPrⁱ)(NHC₆H₃I)] **4** in 48% yield.† The Re–C σ bond of the cyclometallated ring of complex **4** is also labile and is cleaved by iodine in CH₂Cl₂ at room temp. to yield ReI(CO)₄[C(NHPrⁱ)(NHC₆H₃I₂)] **5** in 38% yield.† The IR spectrum showed the same pattern in the ν_CO stretching region as that of the carbene complex **3**. The ¹H NMR spectrum also showed three characteristic proton peaks in the phenyl region. Complex **5** exists as two isomeric forms in equilibrium in solution in a 20:1 ratio, indicating that a high rotational barrier about the C–N bonds in the carbene ligand may be responsible for the equilibrium observed.[4a,8] It is noteworthy that formation of a carbene moiety containing a 2,6-diiodoaminophenyl group in complex **5** is interesting, because the preparation of the 2,6-diiodoaminophenyl group is difficult by an organic method.

‡ Crystal data for **2b**: P1̄; a = 7.7929(13), b = 10.065(3), c = 10.754(4) Å; α = 91.67(3), β = 77.617(24), γ = 110.217(22)°, V = 772.1(4) Å³, Z = 2, D_c = 1.976 g cm⁻¹. Data were collected on an Enraf-Nonius CAD4 automated diffractometer via θ/2θ scan mode and were corrected for absorption (Mo-Kα). Of the 2193 reflections collected (2θ < 49.8°), 2013 were unique, and of these 1793 that were considered observed [I > 2.0σ(I)] were used in the solution and refinement. Structure solved from a Patterson synthesis and successive Fourier maps. All non-hydrogen atoms were anisotropically refined. R = 3.0%, R_w = 3.5%.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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