Acid−Base Control of a Migratory Insertion Reaction: *p*-Aminophenyl Derivatives of Ruthenium(II) and the Crystal Structure of $Ru(\eta^2\text{-}C[O]C_6H_4NH_2\text{-}4)Cl(CO)(PPh_3)_2$

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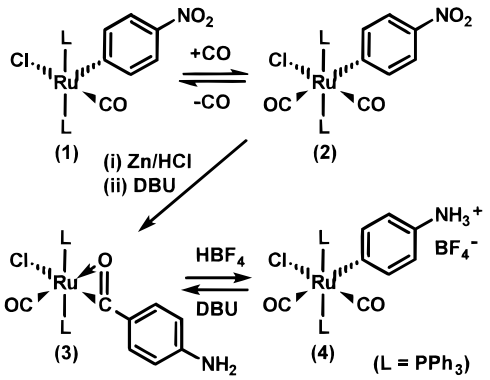
Summary: Addition of CO to $Ru(C_6H_4NO_2\text{-}4)Cl(CO)(PPh_3)_2$ (**1**) *gives* $Ru(C_6H_4NO_2\text{-}4)Cl(CO)_2(PPh_3)_2$ (**2**)*, which upon reduction with Zn/HCl followed by treatment with base produces the* η^2*-acyl complex* $Ru(\eta^2\text{-}C[O]C_6H_4NH_2\text{-}4)Cl(CO)(PPh_3)_2$ (**3**)*, the molecular structure of which has been determined. Treatment of* **3** *with* HBF_4 *protonates the amino substituent and brings about a reverse migratory insertion reaction with the formation of* $[Ru(C_6H_4NH_3\text{-}4)Cl(CO)_2(PPh_3)_2]BF_4$ (**4**)*. The process is reversible, and treatment of* **4** *with DBU returns* **3***.*

The migratory insertion reaction involving a metal-carbon σ-bond and an adjacent carbonyl ligand is a central concept of organometallic chemistry and has been extensively studied.[1ab] Finding simple ways of controlling this process is an important goal. The products of these insertion reactions may have the acyl ligand bound in either an η^1 or η^2 mode, and the factors which drive the migration reaction are both steric and electronic in nature. Bulky substituents on the migrating σ-bound group, or sterically demanding accompanying ligands, favor the acyl form,[2] while substituents which strengthen the metal-carbon bond (usually electron-withdrawing) favor the terminal carbonyl−alkyl (or aryl) form.[3ab]

The migration reactions undergone by $MRCl(CO)_2L_2$ (M = Fe, Ru, Os; L = tertiary phosphine ligand) have been studied extensively by Cardaci, and although direct comparison with iron is not possible, because of a different mechanism, the reaction rates follow the order Fe < Ru >> Os.[4] The alkyl (aryl)−acyl interconversion is clearly facile for ruthenium(II) compounds, and we have described previously the complexes Ru(*p*-tolyl)X-$(CO)_2(PPh_3)_2$ (X = Cl, Br, I), which are in equilibrium in solution with the acyl forms $Ru(\eta^2\text{-}C[O]p\text{-tolyl})X(CO)(PPh_3)_2$. In dichloromethane, X = Cl favors the terminal dicarbonyl−*p*-tolyl form and X = I favors the acyl form.[5] The structure of solid $Ru(\eta^2\text{-}C[O]p\text{-tolyl})I(CO)(PPh_3)_2$ has been confirmed by crystallography.[6] In this communication we now describe a system where this equilibrium is controlled not by steric influences but only by the electronic nature of a substituent on the phenyl group. Replacement of the *p*-tolyl group by a *p*-aminophenyl group in the above compounds produces a situation where the electron-releasing NH_2 group gives the acyl form, but protonation of this function to give the electron-withdrawing NH_3^+ brings about an immediate switch to the dicarbonyl−aryl form.

Scheme 1



We have previouly reported the synthesis of the five-coordinate complex $Ru(C_6H_4NO_2\text{-}4)Cl(CO)(PPh_3)_2$ (**1**).[7] Reaction with carbon monoxide occurs readily, forming the six-coordinate dicarbonyl complex $Ru(C_6H_4NO_2\text{-}4)Cl(CO)_2(PPh_3)_2$ (**2**) (see Scheme 1). The reaction is accompanied by a distinct color change; the five-coordinate complex is bright red, while the six-coordinate complex is a pale yellow-green, a color typical of coordinatively saturated complexes. The IR spectrum of **2** shows two bands at 1435 and 1339 cm^{-1}, which are assigned to the stretching vibrations of the nitro group.[8] The bending mode of this group is observed at 850 cm^{-1} as a weak band. The *p*-nitrophenyl ligand exerts a strong *trans* influence on the *trans* carbonyl ligand, and **2** readily loses carbon monoxide when it is under vacuum, when it is heated in air as a solid, or when a solution in toluene is heated. After **2** is heated in toluene at reflux for several hours, the formation of **1** is confirmed by IR spectroscopy through the characteristic ν(CO) band at 1937 cm^{-1}. The electron-withdrawing nature of the *p*-nitrophenyl ligand results in a strong metal−carbon bond, and a solution IR spectrum of **2**, in dichloromethane, shows that the compound exists only in the dicarbonyl form.

In a previous report we have described reduction of the nitro functionality in the complex $Ru(C_6H_4NO_2\text{-}4)(\eta^2\text{-}S_2CNMe_2)(CO)(PPh_3)_2$ with zinc and hydrochloric

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acid to form the corresponding (*p*-aminophenyl)ruthenium complex.[7] Using similar reaction conditions, excess zinc and hydrochloric acid followed by base, compound **2** also undergoes reduction to give the η^2-acyl complex Ru(η^2-C[O]$C_6H_4NH_2$-4)Cl(CO)(PPh_3)$_2$ (**3**) (see Scheme 1). The electron-donating nature of the *p*-aminophenyl ligand leads to a weakening of the metal−carbon bond, and the migratory insertion reaction then becomes favorable. The solid-state IR spectrum of **3** shows two very weak ν(CO) bands at 2035 and 1955 cm^{-1} and one strong ν(CO) band at 1910 cm^{-1}. In addition, an acyl ν(CO) band of medium intensity is observed at 1526 cm^{-1}. The solution spectrum, in dichloromethane, suggests that the ratio of the dicarbonyl complex to the acyl−monocarbonyl complex is less than 1:15. The amine protons, in the ^{1}H NMR, appear as a broad singlet at δ 3.9. This broad signal disappears upon addition of deuterium oxide. The ^{13}C NMR data supports a η^2-acyl formation. Only two downfield signals are observed, both as triplets.[8] These correspond to the metal-bound carbonyl and acyl carbons, respectively, which both couple to the phosphorus atoms of the two mutually *trans* triphenylphosphine ligands. The X-ray crystal structure determination of **3** confirms the η^2-coordination mode, and the structure is depicted in Figure 1.[9]

When compound **3** is treated with excess HBF_4, the amino group is protonated and thereby becomes electron withdrawing in nature. As a consequence, the aryl group migrates back to the metal center, forming the dicarbonyl complex **4**. The solution IR spectrum of **4** shows that only the dicarbonyl complex exists in solution. Intense ν(CO) bands at 2040 and 1972 cm^{-1} are observed. The ^{13}C NMR spectrum of **4** shows three downfield signals, each of which appears as a triplet. These arise from the the two carbonyl ligands and the metal-bound aryl carbon.[8]

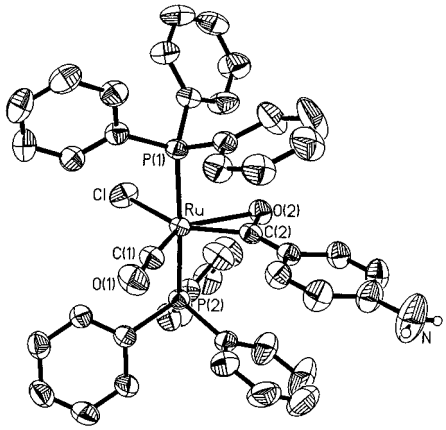

Figure 1. ORTEP diagram of compound **3** (hydrogen atoms except those on N omitted for clarity). Selected bond distances (Å) and angles (deg): Ru−C(1), 1.799(3); Ru−C(2), 1.958(3); Ru−P(2), 2.3691(9); Ru−P(1), 2.3704(9); Ru−O(2), 2.375(2); Ru−Cl, 2.4786(8); N−C(6), 1.366(5); C(2)−Ru−O(2), 31.68(9); P(2)−Ru−P(1), 177.21(3).

Deprotonation of **4** was easily achieved by treatment with the strong organic base 1,8-diazabicyclo[5.4.0]-undec-7-ene (DBU), and the acyl monocarbonyl compound **3** was recovered in excellent yield. This migratory insertion reaction, therefore, could be manipulated by simply adding acid or base (Scheme 1). In this reversible process the steric effects remain essentially constant and so it is the electronic nature of the *para* substituent which determines the migratory aptitude of the aryl ligand. Finally, we note that this facile migratory insertion is not exhibited by the corresponding osmium system, since Os($C_6H_4NH_2$-4)Cl(CO)$_2$(PPh_3)$_2$ exists exclusively in this dicarbonyl form.[10] The synthesis and further reactions of this compound will be reported subsequently.

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Supporting Information Available: A fully labeled diagram and tables of crystallographic data, data collection, and solution and refinement details, positional and thermal parameters, and bond distances and angles for **3** (10 pages). Ordering information is given on any current masthead page.

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(8) Selected spectroscopic data for **2**−**4** are as follows. **2**: IR (KBr) ν(CO) 2041 (s) and 1971 (s), ν(NO_2) 1435 (ms) and 1339 (s), δ(NO_2) 850 (w), δ(CH) 840 (w) cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 7.41−7.22 (m, PPh_3, $C_6H_4NO_2$); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 198.0 (t, ^2J(PC) = 12.1 Hz, *C*O), 193.7 (t, ^2J(PC) = 9.1 Hz, *C*O), 174.2 (t, ^2J(PC) = 12.6 Hz, *C*1), 144.7 (s, *C*4), 141.8 (s, *C*2 or *C*3), 119.6 (s, *C*2 or *C*3), 131.3 (t′[11] J(PC) = 46.3 Hz, PPh_3 *ipso-C*), 134.1 (t′, J(PC) = 10.1 Hz, PPh_3 *m-C*), 130.3 (s, PPh_3 *p-C*), 127.9 (t′, J(PC) = 9.1 Hz, PPh_3 *o-C*). **3**: IR (KBr) ν(NH_2) 3462 (w, br) and 3347 (wm, br), ν(CO) 2035 (w), 1955 (w), and 1910 (s), acyl ν(CO) 1526 (m), ν(CN) 1302 (wm) and 918 (ms), δ(CH) 837 cm^{-1}; ^{1}H NMR ($CDCl_3$, 400.1 MHz) δ 7.59−7.54, 7.36−7.23 (m, PPh_3), 6.86 (d, ^3J(HH) = 8.6 Hz, 2,6-$C_6H_4NH_2$), 6.09 (d, ^3J(HH) = 8.6 Hz, 3,5-$C_6H_4NH_2$), 3.9 (s, br, NH_2); ^{13}C NMR ($CDCl_3$, 100.6 MHz) δ 245.8 (t, ^2J(PC) = 8.0 Hz, η^2-*C*O), 211.4 (t, ^2J(PC) = 16.6 Hz, *C*O), 150.3 (s, C1), 132.8 (s, *C*2 or *C*3), 125.5 (s, *C*4), 112.8 (s, *C*2 or *C*3), 131.9 (t′, J(PC) = 45.3 Hz, PPh_3 *ipso-C*), δ 134.3 (t′, J(PC) = 11.1 Hz, PPh_3 *m-C*), 129.9, (s, PPh_3 *p-C*), 128.0 (t′, J(PC) = 10.1 Hz, PPh_3 *o-C*). **4**: IR (KBr) ν(NH_3^+) 3133 (w, br), NH_3^+ overtone 2590 (w, br), ν(CO) 2040 (s) and 1972 (s), δ(NH_3^+) 1623 (w), BF_4^- 1091 (s, br), δ(CH) 803 cm^{-1}; ^{1}H NMR (CD_3COCD_3, 400.1 MHz) δ 13.13 (s, br NH_3^+), δ 7.56−7.34 (mult, PPh_3, 2,6-$C_6H_4NH_3^+$ or 3,5-$C_6H_4NH_3^+$), 6.73 (d, ^3J(HH) = 7.5 Hz, 2,6-$C_6H_4NH_3^+$ or 3,5-$C_6H_4NH_3^+$); ^{13}C NMR (CD_3COCD_3, 100.6 MHz) δ 199.0 (t, ^2J(PC) = 12.6 Hz, *C*O), 195.1 (t, ^2J(PC) = 9.1 Hz, *C*O), 163.8 (t, ^2J(PC) = 12.6 Hz, *C*1), 143.4 (s, *C*2 or *C*3), δ 131.8 (s, *C*4), 121.97 (s, *C*2 or *C*3), 132.8 (t′, J(PC) = 46.3 Hz, PPh_3 *ipso*-C), 135.1, (t′, J(PC) = 10.1 Hz, PPh_3 *m-C*), 131.6 (s, PPh_3 *p-C*), 128.8 (t′, J(PC) = 9.1 Hz, PPh_3 *o-C*).

(9) Crystals were obtained from CH_2Cl_2/EtOH by the isopiestic method. Crystal data for **3** (from 25 reflections, 11.5° < θ < 12.7°): triclinic, space group $P\bar{1}$, a = 12.104(1) Å, b = 13.565(2) Å, c = 13.700(6) Å, α = 66.17(2)°, β = 78.85(2)°, γ = 68.450(10)°, V = 1911.2(9) Å^3; Z = 2, D_{calcd} = 1.406 g cm^{-3}, (μ(Mo Kα) = 0.602 mm^{-1}); crystal size 0.29 × 0.19 × 0.14 mm; Enraf-Nonius CAD4 diffractometer, Mo Kα radiation (0.710 69 Å), graphite monochromator, T = 295(2) K, $\omega/2\theta$ scans, maximum 2θ 54°, 8690 reflections measured, 8333 independent with R(int) = 0.0369, intensity data corrected for Lorentz and polarization effects. An empirical absorption correction (ψ scans, transmission range 0.952−0.998) was applied.[12] The structure was solved by direct methods (SHELXS-86);[13] atomic coordinates and anisotropic thermal parameters were refined by full-matrix least squares on F_o^2 (SHELXL-96).[14] Positions of all hydrogen atoms were located crystallographically and refined with isotropic thermal parameters. R = 0.0358 for $I > 2\sigma(I)$, wR2 = 0.0902. R indices (all data): R = 0.0619, wR2 = 0.1008; reflections/restraints/parameters ratio 8333/0/604; residual electron density +0.848/−0.687 e Å^{-3}. wR2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$; $w^{-1} = \sigma^2(F_o^2) + (0.0602P)^2 + 0.5257P$, where $P = (F_o^2 + 2F_c^2)/3$.

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