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Dehydrochlorination of Complexes of Ruthenium(II), Osmium(II) and Platinum(II) by 1,8-diazabicyclo[5,4,0]undec-7-ene

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Introduction

Dehydrohalogenation is an established and effective route to d^8 and d^{10} complexes of rhodium, iridium, palladium and platinum, even to the extent that it sometimes occurs spontaneously. Such is not the case, however, for d^8 complexes of ruthenium and osmium. Dehydrochlorination of certain d^6 ruthenium and osmium complexes has been achieved but only through multistep syntheses in which the elements of hydrogen chloride are removed stepwise [1, 2]. Commercially available 1,8-diazabicyclo-[5,4,0]-undec-7-ene (DBU) enjoys an extensive chemistry including widespread use as a dehydrohalogenation reagent. It was our aim to determine whether this reagent represents a convenient means for the reduction of hydridochlorides of the group VIII metals and, in particular, whether it could be used to generate a variety of d^8 complexes of ruthenium and osmium.

Results and Discussion

As anticipated, the complexes $MHCl(CO)(PPh_3)_3$ (M = Ru, Os) react with DBU in solution under moderate pressures of carbon monoxide to give excellent yields of zerovalent $M(CO)_3(PPh_3)_2$. Considerably more forcing conditions were found necessary for reduction of the osmium complex which presumably reflects the greater kinetic stability of osmium(II). In both cases, working up the mixture before reaction was complete resulted in a mixture of $M(CO)_3(PPh_3)_2$ and $MHCl(CO)_2(PPh_3)_2$ indicating, as might be expected, that the species actually being reduced is $MHCl(CO)_2(PPh_3)_2$ rather than $MHCl(CO)(PPh_3)_3$. Although a more convenient synthesis for $Ru(CO)_3(PPh_3)_2$ has been reported [3], we believe this method to be the simplest and cleanest of the syntheses for $Os(CO)_3(PPh_3)_2$ reported to date [4].

Attempts to synthesize the known complexes, $Os(CO)(L)(PPh_3)_3$ [1, 5] (L = CO, CNR; R = p-tolyl) by dehydrochlorination of $OsHCl(CO)(L)(PPh_3)_2$ in the presence of triphenylphosphine met with failure, presumably because the conditions necessary for dehydrochlorination proved too stringent for the somewhat sensitive products. However, attempts to prepare the analogous ruthenium complexes were successful, with reduction occurring smoothly under quite mild conditions. Thus, under reflux in methanol suspension, $Ru(CO)_2(PPh_3)_3$ and $Ru(CO)(CNR)(PPh_3)_3$ can both be prepared in good yield. Both of these complexes are synthetically useful with an extensive chemistry, and in the past had to be prepared *via* less convenient, multistep syntheses [1, 2].

The potential of DBU for generating low coordination environments *in situ* was also investigated briefly by examining the reaction of DBU with $PtHCl(PPh_3)_2$. Either in benzene solution at room temperature or in methanol suspension under reflux, $PtHCl(PPh_3)_2$ reacted with DBU and diphenylacetylene to give high yields of $Pt(PH_2C_2)(PPh_3)_2$. Although this method does not represent an improvement over the published method for the synthesis of $Pt(Ph_2C_2)(PPh_3)_2$ [6], it should represent a viable alternative for the direct synthesis of complexes of type $Pt(L)(PPh_3)_2$, especially when L is a poor ligand or sensitive to the reducing agents or conditions most frequently used to generate such complexes. It should be noted here that the only by-product, DBU·HCl, is insoluble in aromatic hydrocarbons and hence can be removed by a simple filtration which greatly facilitates the isolation of products.

It would appear from this investigation that, although not a perfectly general reductant, DBU has several practical advantages as a reagent for the synthesis of certain low oxidation state complexes of the group VIII elements. It also seems obvious that this reagent will find application in many other areas of organometallic research, including ligand modification. Work in this particular area is in progress.

Experimental

All solvents were fractionated and stored over Type 4A molecular sieves before use. All solutions were degassed and reactions were carried out under an atmosphere of nitrogen. The starting materials $RuHCl(CO)(PPh_3)_3$ [7], $OsHCl(CO)(PPh_3)_3$ [8], $RuHCl(CO)(CNR)(PPh_3)_2$ [2], $RuHCl(CO)_2(PPh_3)_2$ [9] and $PtHCl(PPh_3)_2$ [10] were prepared by standard methods. DBU was used as received from Aldrich. In all cases, products were characterized by direct comparison with authentic samples prepared by published methods.

Os(CO)₃(PPh₃)₂

$OsHCl(CO)(PPh_3)_3$ (0.55 g, 0.53 mmol) and DBU (0.12 g, 0.79 mmol) in toluene (25 ml) were subjected to CO pressure (80 p.s.i.) in a Fisher-Porter glass pressure vessel. After heating in an oil bath at 150–160 °C for 5–6 hours the vessel was cooled, vented and the solvent removed under vacuum. The residue was recrystallized from dichloromethane–ethanol to give cream crystals of $Os(CO)_3(PPh_3)_2$, 0.35 g, 83%, νCO = 1890(vs) cm^{-1}, (1890 vs, lit.) [4a].

Ru(CO)₃(PPh₃)₂

In a procedure similar to that above, $RuHCl(CO)(PPh_3)_3$ (0.50 g, 0.52 mmol), DBU (0.15 g, 0.99 mmol) in benzene (25 ml) were carbonylated (20 p.s.i., 80 °C) for 3.5 hours. A similar work-up gave cream crystals of $Ru(CO)_3(PPh_3)_2$, 0.36 g, 97%, νCO = 1900(vs) cm^{-1}, (1895 vs, lit) [11].

Ru(CO)₂(PPh₃)₃

$RuHCl(CO)_2(PPh_3)_2$ (0.25 g, 0.35 mmol), DBU (0.08 g, 0.53 mmol) and triphenylphosphine (0.14 g, 0.53 mmol) were heated together under reflux in methanol suspension (20 ml) for 3 hours. The bright yellow solid was removed by filtration and washed with ethanol and hexane, 0.29 g, 88%, νCO = 1900(vs) cm^{-1}, (1905 vs, lit.) [1].

Ru(CO)(CNR)(PPh₃)₃

In a similar procedure, $RuHCl(CO)(CNR)(PPh_3)_2$ (0.30 g, 0.37 mmol), DBU (0.09 g, 0.59 mmol) and triphenylphosphine (0.15 g, 0.57 mmol) yielded (from methanol, 20 ml for 8 hours) bright orange crystals of $Ru(CO)(CNR)(PPh_3)_3$, 0.30 g, 78%, νCO = 1900(vs) cm^{-1}, νCN = 2085(vs) cm^{-1} (1901vs, 2090vs, lit) [2].

Pt(Ph₂C₂(PPh₃)₂

$PtHCl(PPh_3)_2$ (0.20 g, 0.26 mmol), DBU (0.060 g, 0.39 mmol) and diphenylacetylene (0.070 g, 0.39 mmol) were heated together under reflux in methanol suspension (15 ml) for 1 hr. The pale yellow product was removed by filtration and washed with ethanol and hexane, 0.21 g, 88%, $\nu(C\equiv C)$ = 1740(s) cm^{-1}, (1740 s lit) [6]. A yield of 82% was achieved using similar quantities in benzene at room temperature. A precipitate of DBU·HCl appeared within 5 min. Isolation was by filtration and the addition of ethanol.

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