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A simple method of regenerating areneruthenium dichloride dimers, $[RuCl_2(\eta^6\text{-arene})]_2$, from their monomeric adducts with amines or tertiary phosphines, $RuCl_2(\eta^6\text{-arene})L$

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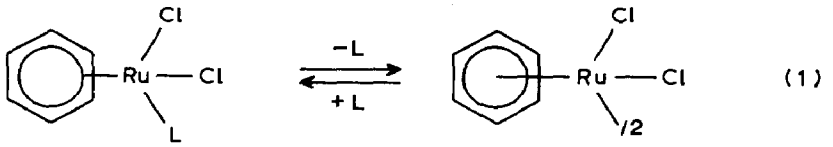
Abstract

The monomeric amine or tertiary phosphine complexes $RuCl_2(\eta^6\text{-arene})L$ (arene = benzene, *p*-cymene) can be reconverted into their dimeric precursors $[RuCl_2(\eta^6\text{-arene})]_2$ by heating with 1,5-cyclooctadiene (COD), 2-propanol, and anhydrous Na_2CO_3 and subsequent treatment of the resulting ruthenium(0) complexes $Ru(\eta^6\text{-arene})(\eta^4\text{-COD})$ with HCl; the ligand L can be recovered.

Introduction

In transition metal chemistry one often needs to remove ligands such as amines or tertiary phosphines from the coordination sphere of a metal in order to generate vacant coordination sites that determine catalytic activity [1]. Furthermore, a useful method of resolving a chiral organometallic complex involves separation of a pair of diastereomers formed by reaction with an optically active ligand [2], and then removal of the optically active ligand to complete the resolution. In our attempts to resolve chiral areneruthenium(II) complexes [3] we needed a general method for converting the monomeric amine or tertiary phosphine complexes $RuCl_2(\eta^6\text{-arene})L$ [4] into the parent dimer $[RuCl_2(\eta^6\text{-arene})]_2$ in good yield (eq. 1). The procedure we have developed is described here.



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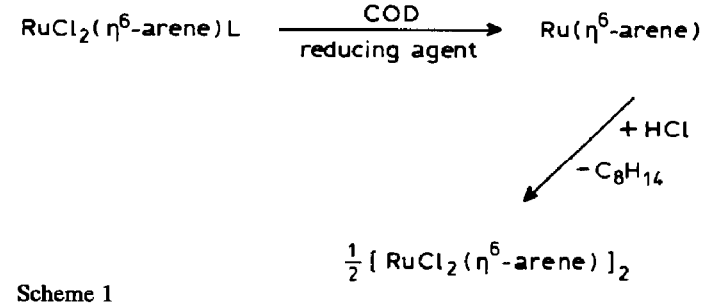
Results and discussion

The $RuCl_2(\eta^6\text{-arene})L$ complexes that we have studied contain either primary amines (sec-butylamine, 1-phenylethylamine) or tertiary phosphines (triphenylphosphine, dimethylphenylphosphine, or tri-n-butylphosphine) as the neutral ligand L, and benzene or *p*-cymene as the η^6-arene. They are easily made by reaction of L with the dimers $[RuCl_2(\eta^6\text{-arene})]_2$ [4,5]. Both the amines and the tertiary phosphines are strongly coordinated to the metal and are not removed even by prolonged treatment with hydrochloric acid. We therefore examined the possibility of removing L by reducing ruthenium(II) to ruthenium(0) in the presence of a ligand capable of stabilizing the lower oxidation state. A suitable ligand for this purpose is 1,5-cyclooctadiene (COD), since it forms stable complexes of the type $Ru(\eta^6\text{-arene})(COD)$ [6]. Moreover, the diene is readily removed from the metal in the form of cyclooctene by treatment with HCl, giving the desired $[RuCl_2(\eta^6\text{-arene})]_2$ complexes [6] (Scheme 1). The most suitable reducing agent we have found is refluxing 2-propanol in the presence of anhydrous Na_2CO_3, the presumed stoichiometry, being that shown in eq. 2.

$$RuCl_2(\eta^6\text{-arene})L + COD + (CH_3)_2CHOH + Na_2CO_3 \xrightarrow{80\,^\circ C}$$

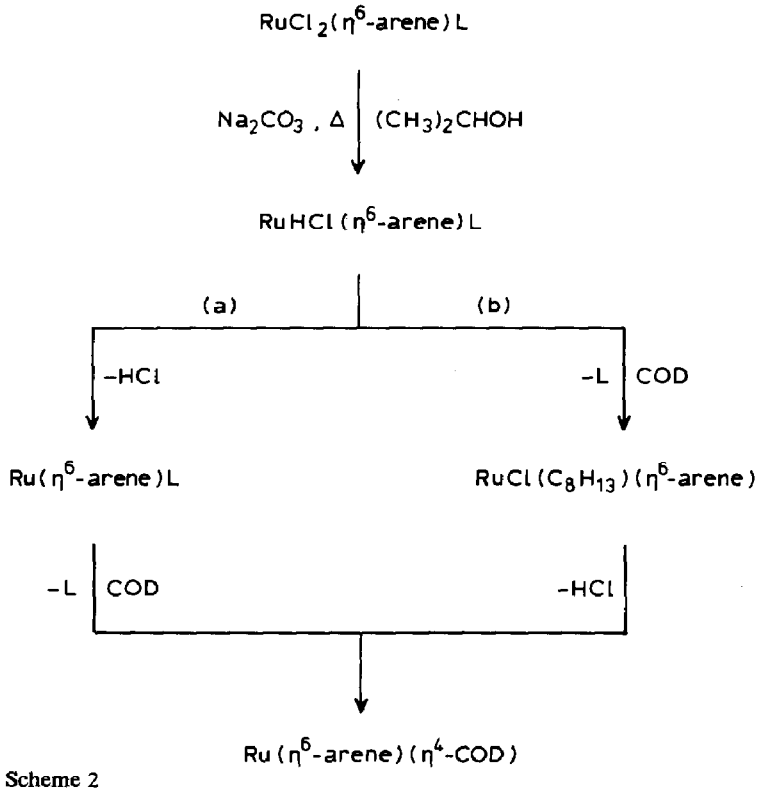
$$Ru(\eta^6\text{-arene})(\eta^4\text{-COD}) + (CH_3)_2CO + L + 2NaCl + H_2O + CO_2 \qquad (2)$$

(arene = benzene, *p*-cymene; L = triphenylphosphine, dimethylphenylphosphine, tri-n-butylphosphine, sec-butylamine, 1-phenylethylamine)



Scheme 1

The $Ru(\eta^6\text{-arene})(COD)$ complexes were isolated by extraction with pentane and chromatography on alumina, and were characterized either by elemental analysis and ^1H NMR spectroscopy (arene = *p*-cymene) or by comparison with authentic samples (arene = benzene). In general, yields of $Ru(\eta^6\text{-arene})(COD)$ were somewhat greater from the amine complexes (60–70%) than from the tertiary phosphine derivatives (40–50%); this may indicate that the "harder" nitrogen donor ligands are less firmly bound than the "softer" tertiary phosphines to the areneruthenium(II) fragment. The yields of $Ru(\eta^6\text{-arene})(COD)$ were similar for corresponding complexes of benzene and *p*-cymene. In the case of L = PPh_3, PMe_2Ph or P-n-Bu_3, the ligand could be recovered by chromatography on alumina with toluene as eluent, the $Ru(\eta^6\text{-arene})(COD)$ complex having been eluted first with pentane. This will be an important advantage when chiral phosphines that are either expensive or difficult to synthesize are used.



Scheme 2

As reducing agent zinc dust in the presence of ethanol can be also used, but the yields are lower (20–30%).

The probable mechanism of the reduction is shown in Scheme 2. In the first step, $RuCl_2(\eta^6$-arene)L reacts with 2-propanol in the presence of Na_2CO_3 to give a hydrido complex $RuHCl(\eta^6$-arene)L. Complexes of this type containing various tertiary phosphines have been isolated from this reaction in the absence of COD [5] and are probably formed by β-elimination of acetone from an unstable 2-propanoxo complex. Moreover, $[RuCl_2(\eta^6$-arene)$]_2$ complexes react with 2-propanol/Na_2CO_3 to give dinuclear ionic μ-hydrido complexes [7] and, in the presence of dienes (COD, 2,5-bicyclo[2,2,1]heptadiene, 1,3-cyclohexadiene), $Ru(\eta^6$-arene)$(\eta^4$-diene) complexes are obtained [8].

There are two routes by which $Ru(\eta^6$-arene)(COD) could be formed. The hydrido complex (Scheme 2, route a) could eliminate HCl to give a highly reactive, coordinatively unsaturated 16e-fragment $Ru(\eta^6$-arene)L which loses L in the presence of COD to give the final product. A more likely possibility (Scheme 2, route b) is that COD reacts with the hydrido complex $RuHCl(\eta^6$-arene)L, with loss of L, to give a cyclooctenyl or hydrido-diene complex $RuCl(C_8H_{13})(\eta^6$-arene) which undergoes base-promoted elimination of HCl to give $Ru(\eta^6$-arene)(COD). This type of reaction is well known in η^5-pentamethylcyclopentadienyl-rhodium(III) and -iridium(III) chemistry [9].

Preliminary attempts to remove ethylenediamine (en) from $[RuCl(\eta^6$-$C_6H_6)$en$]PF_6$

by means of 2-propanol/Na_2CO_3/COD have been unsuccessful, and in the case of complexes containing bidentate ligands other reducing systems are clearly necessary.

Experimental

All the reactions were carried out under dry oxygen-free nitrogen by conventional Schlenk-tube techniques. Solvents were purified by conventional methods, distilled, and stored under nitrogen. The phosphines and amines were used as received from commercial suppliers. 1,5-Cycloctadiene was distilled before use. The complexes $[RuCl_2(arene)]_2$ and $RuCl_2(arene)L$ (arene = benzene, *p*-cymene; L = PPh_3, PMe_2Ph, and P-n-Bu_3) were prepared as reported [4,5]. ^1H NMR spectra at 100 MHz were recorded on a Varian XL-100 spectrometer using $(CH_3)_4Si$ as internal standard (δ values). Mass spectra were measured on a Varian MAT CH7 spectrometer. Microanalyses were performed by the Laboratorio di Microanalisi, Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa.

Preparation of $RuCl_2(\eta^6$-arene)(amine) complexes

These complexes were made from $[RuCl_2(\eta^6$-arene)$]_2$ (arene = benzene, *p*-cymene), and amine (1-phenylethylamine, sec-butylamine), in methanol. Only the synthesis of $RuCl_2(\eta^6$-*p*-cymene)(1-phenylethylamine) will be described in detail, the procedure being the same for all the other $RuCl_2(\eta^6$-arene)(amine) complexes.

(η^6-p-Cymene)dichloro(1-phenylethylamine)ruthenium(II). A mixture of $[RuCl_2(\eta^6$-*p*-cymene$)]_2$ (0.25 g, 0.4 mmol) 1-phenylethylamine (0.15 ml, 1.2 mmol) and methanol (30 ml) was stirred at room temperature for 24 h. The red-brown solution was concentrated to 3 ml and ether (6 ml) was added. The red-brown precipitate, which separated at $-20\,^\circ C$ was filtered off, washed several times with ether, and dried to give 0.3 g (0.7 mmol) of the desired adduct (Found: C, 50.54; H, 5.48; Cl, 16.54; N, 3.05. $C_{18}H_{25}Cl_2NRu$ calcd.: C, 50.59; H, 5.90; Cl, 16.59; N, 3.28%). ^1H NMR ($CDCl_3$): δ 7.44 (m, 5H, C_6H_5), 5.24–4.71 (m, 4H, C_6H_4), 4.36 (m, 1H, C*H*CH_3), 3.5–3.0 (m, 2H, NH_2), 2.9 (m, 1H, C*H*$(CH_3)_2$)), 2.11 (s, 3H, C*H*$_3C_6H_4$), 1.54 (d, 3H, *J* 6.7 Hz, CHC*H*$_3$), 1.22 (d, 6H, *J* 6.9 Hz, CH(C*H*$_3)_2$).

(η^6-Benzene)dichloro(1-phenylethylamine)ruthenium(II). From $[RuCl_2(\eta^6$-benzene$)]_2$ (0.25 g, 0.5 mmol) and 1-phenylethylamine (0.19 ml, 1.5 mmol), 0.3 g (0.8 mmol) of the adduct were obtained as a red solid (Found: C, 45.2; H, 4.5; Cl, 19.05; N, 3.53. $C_{14}H_{17}Cl_2NRu$ calcd.: C, 45.29; H, 4.12; Cl, 19.5; N, 3.77%). ^1H NMR ($CDCl_3$): δ 7.48 (m, 5H, C_6H_5), 5.33 (s, 6H, C_6H_6), 4.5 (m, 1H, CH), 3.91 (m, 1H, N*H*H), 3.23 (m, 1H, NH*H*), 1.63 (d, 3H, *J* 7 Hz, CHC*H*$_3$).

(η^6-p-Cymene)dichloro(sec-butylamine)ruthenium(II). From $[RuCl_2(\eta^6$-*p*-cymene$)]_2$ (0.22 g, 0.36 mmol) and sec-butylamine (0.11 ml, 1.08 mmol), 0.22 g (0.57 mmol) of the adduct were obtained as a red-brown solid (Found: C, 44.6; H, 6.9; Cl, 18.2; N, 3.35. $C_{14}H_{25}Cl_2NRu$ calcd.: C, 44.32; H, 6.64; Cl, 18.69; N, 3.69%). ^1H NMR ($CDCl_3$): δ 5.35 (m, 4H, C_6H_4), 3.2 (m, 2H, NH_2), 3.05 (m, ^1H, C*H*NH_2), 2.9 (m, 1H, C*H*$(CH_3)_2$), 2.2 (s, 3H, C*H*$_3C_6H_4$), 1.7 (m, 2H, CH_2), 1.3 (d, 3H, *J* 7 Hz, CHC*H*$_3$), 1.25 (d, 6H, *J* 7 Hz, CH$(CH_3)_2$), 0.95 (t, 3H, *J* 7 Hz, CH_3C*H*$_3$).

(η^6-Benzene)dichloro(sec-butylamine)ruthenium(II). From $[RuCl_2(\eta^6$-benzene$)]_2$ (0.25 g, 0.5 mmol) and sec-butylamine (0.15 ml, 1.5 mmol), the adduct (0.24 g, 0.75 mmoles) was obtained as a red-brown solid (Found: C, 37.5; H, 5.1; Cl, 21.2; N, 4.05. $C_{10}H_{17}Cl_2NRu$ calcd.: C, 37.15; H, 5.3; Cl, 21.93; N, 4.33%). ^1H NMR

($CDCl_3$): δ 5.45 (s, 6H, C_6H_6), 3.15 (m, 2H, NH_2), 3.05 (m, 1H, $CHNH_2$), 1.65 (m, 2H, CH_2), 1.3 (d, 3H, J 7 Hz, $CHCH_3$), 0.95 (t, 3H, J 7 Hz, CH_2CH_3).

Reaction between $RuCl_2(\eta^6$-arene)L and 1,5-cyclooctadiene: synthesis of $Ru(\eta^6$-arene)(COD)

Only the synthesis of $Ru(\eta^6$-*p*-cymene)(COD) from $RuCl_2(\eta^6$-*p*-cymene)(PPh_3) will be described in detail, the procedure being substantially the same for all the other $RuCl_2(\eta^6$-arene)L complexes. A suspension of $RuCl_2((\eta^6$-*p*-cymene)(PPh_3) (0.33 g, 0.58 mmol) and anhydrous sodium carbonate (0.37 g, 3.5 mmol) in 1,5-cyclooctadiene (3 ml, 24.5 mmol) and 2-propanol (30 ml) was heated at reflux for 3 h. The yellow-brown solution was evaporated to dryness under reduced pressure. The residue was extracted with hexane (4 × 20 ml). The solution was concentrated to 10 ml and was chromatographed on an alumina column (20 cm, activity II-III). Hexane eluted a yellow fraction which, after evaporation of solvent, gave crystals of $Ru(\eta^6$-*p*-cymene)(COD) (0.09 g, 0.25 mmol) (Found: C, 62.7; H, 7.8; M^+, 344. $C_{18}H_{26}Ru$ calcd.: C, 62.94; H, 7.63%; M, 344). ^1H NMR (C_6D_6): δ 4.9 × 4H, C_6H_4), 3.15 (m, 4H, $CHCH_2$), 2.45 (m, 1H, $CH(CH_3)_2$), 2.25 (s, 3H, CH_3), 2.1 (m, 8H, CH_2), 1.3 (d, 6H, J 8 Hz, $CH(CH_3)_2$). Using toluene as eluent a second fraction containing triphenylphosphine (0.06 g) was obtained.

With the other $RuCl_2(\eta^6$-arene)L complexes (arene = benzene, *p*-cymene), the following yields were obtained: L = PMe_2Ph, 45%; P-n-Bu_3, 50%; sec-butylamine, 70%; 1-phenylethylamine, 60%.

Reaction of $Ru(\eta^6$-arene)(COD) with hydrochloric acid: synthesis of $[RuCl_2(\eta^6$-arene)]$_2$

This reaction was carried out as described elsewhere [6]. A solution of 36% aqueous HCl (2 ml) in acetone (4 ml) was added dropwise to a yellow solution of $Ru(\eta^6$-*p*-cymene)(COD) (0.09 g, 0.26 mmol) in acetone (5 ml). The resulting red-brown solution was concentrated to 3 ml and kept at −20 °C to give 0.07 g (90%) of $[RuCl_2(\eta^6$-*p*-cymene)$]_2$.

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