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# Catalytic transfer hydrogenation of ketones catalyzed by orthometalated ruthenium(III) 2-(arylazo)phenolate complexes containing triphenylarsine

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**Abstract**—Air-stable, mononuclear orthometalated ruthenium(III) 2-(arylazo)phenolate complexes of the general composition $[RuX(AsPh_3)_2(L)]$ (X = Cl or Br; L = CNO donor of the 2-(arylazo)phenolate ligands) have been synthesized and characterized by IR, UV–vis, and EPR as well as by elemental analysis. One of the complexes $[RuBr(AsPh_3)_2(azo–OMe)]$ was structurally characterized by X-ray analysis and was found to be an efficient catalyst for the transfer hydrogenation of ketones with excellent conversion in the presence of isopropanol at 80 °C in 1 h.

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The intramolecular C–H activation, or cyclometalation/orthometalation reaction, which is a major achievement of organometallic chemistry, provides access to metalacyclic derivatives of the transition metals.[1] Many papers dealing with this subject have been published in the literature over the last 20 years demonstrating the enormous interest generated particularly by the cycloruthenated compounds.[2] More recently, transition metal catalyzed transfer hydrogenation reactions using isopropanol as the hydrogen source have become efficient methods in organic synthesis as illustrated by several useful applications reported in recent years.[3] Among the different metal catalyzed reactions, ruthenium based catalytic systems are effective in the transfer hydrogenation of ketones.[4] Noyori and Ohkuma discovered that ruthenium(II) complexes containing diphosphine and 1,2-diamine ligands, in the presence of a base and 2-propanol, are excellent catalysts for the hydrogenation of ketones under mild conditions.[5] Although the well known BINAP–Ru(II) complex catalysts [BINAP = 2,2′-bis-(diphenylphosphine)-1,1′-binaphthyl] have proved to be extremely efficient for the asymmetric hydrogenation of functionalized ketones, they are unable to catalyze the asymmetric hydrogenation of simple ketones because of the lack of heteroatoms to anchor the ruthenium metal.[6] Furthermore the N–N- and O–N- donors of the ligands play an important role in the catalytic reactions. Recently, Chakravarty et al.[3b] reported a ruthenium-(II)*p*-cymene system containing arylazo phenolate ligands which in the presence of base and isopropanol, proved to be a good catalysts for the transfer hydrogenation of acetophenone. In addition, large numbers of transition metal phosphine/arsine complexes have been used in catalysis due to their characteristic steric and electronic properties.[7] Although a number of cyclometalated transition metal complexes are known, to the best of our knowledge, there are no reports available on synthesis and catalytic transfer hydrogenation of orthometalated ruthenium(III) 2-(arylazo)phenolate complexes incorporating C-, N-, and O- donors and triphenylarsine. Herein, we describe a convenient synthesis of a series of new orthometalated ruthenium(III) 2-(arylazo)phenolate complexes along with a study of their catalysis of transfer hydrogenation of a variety of ketones.

The direct reaction of the ruthenium(III) precursors, $[RuCl_3(AsPh_3)_3]$ and $[RuBr_3(AsPh_3)_3]$ with 2-(arylazo)-phenol ligands[8] in dry benzene under reflux yielded a series of mononuclear orthometalated ruthenium complexes of the type $[RuX(AsPh_3)_2(L)]$ (X = Cl or Br; L = CNO donor of the ligands).[9] The choice of these molecules was due to their versatility as ligands, since they exhibit various modes of bonding to the metallic center and also because of the potential biological and

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*Keywords*: Synthesis; Ruthenium(III); Orthometalation; CNO donor; Characterization; Transfer hydrogenation.

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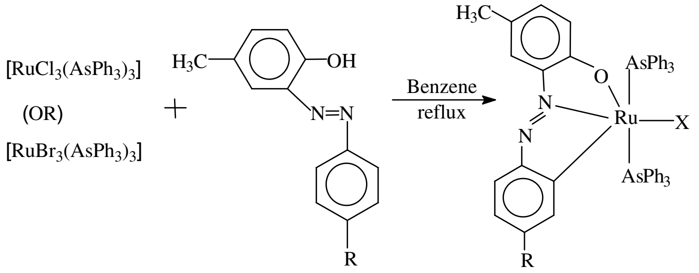


Where X=Cl (or)Br: R=H; azo-H (HL1), R=Cl; azo-Cl (HL2), R=Me; azo-Me (HL3), R=OMe; azo-OMe (HL4), R=OEt; azo-OEt (HL5)

**Figure 1.** Structures of orthometalated ruthenium(III) 2-(arylazo)phenolate complexes.

catalytic importance of their complexes. The 2-(arylazo)phenolate ligands were observed to undergo C–H activation at one *ortho* position of the phenyl ring in the arylazo fragment leading to the formation of five-membered cyclometalated complexes (Fig. 1). Elemental analyses (C, H, and N) were consistent with the composition proposed for all complexes.

The IR spectra of the complexes confirmed the coordination of the azo groups ($\nu_{N=N}$ = 1376–1388 cm$^{-1}$) and phenolic oxygens ($\nu_{C–O}$ = 1286–1310 cm$^{-1}$) to the metal atoms. In addition, these complexes showed new bands near 540, 690, 740, and 1554 cm$^{-1}$ due to the triphenylarsine ligands. The electronic spectra of the complexes in the visible region showed intense absorption at 665–630 nm ($\varepsilon$ = 708–1280 dm$^3$/mol/cm) due to d–d transitions and an absorption at 419–409 nm ($\varepsilon$ = 1668–3268 dm$^3$/mol/cm) probably due to ligand-to-metal charge transfer (LMCT) transitions in addition to the $\pi$–$\pi$* and n–$\pi$* ligand centered transitions. Room temperature magnetic susceptibility measurements showed that these complexes (1.92–1.96 BM) are one electron paramagnetic which supports the trivalent state of the ruthenium (low spin d$^5$; $S = 1/2$) in an octahedral environment. The EPR spectra of all the complexes in the solid state exhibited well-defined single isotropic features near $g_{\text{iso}} = 2$. However, the complex [RuBr(AsPh$_3$)$_2$(azo–OMe)] in dichloromethane at 77 K showed a rhombic spectrum with three distinct '*g*' values ($g_x \neq g_y \neq g_z$, $g_x = 2.212$, $g_y = 2.019$, $g_z = 1.920$) indicating rhombic distortion in these complexes.

To understand the coordination mode of the 2-(arylazo)phenolate ligands and the stereochemistry of the ruthenium(III) complexes, the X-ray crystal structure of the complex [RuBr(AsPh$_3$)$_2$(azo–OMe)] was determined and is shown in Figure 2. The 2-(arylazo)phenolate ligand is coordinated in a tridentate fashion binding the metal center at O(1), N(1), C(1) so forming two five-membered chelate rings with bite angles of 78.55(18) for N(1)–Ru(1)–O(1) and 75.5(2) for N(1)–Ru(1)–C(8). The entire tridentate ligand skeleton together with the ruthenium and bromide constitute the equatorial plane while the bromide is in the trans position with respect to the azo nitrogen. The two AsPh$_3$ ligands are mutually trans to each other, the Ru(1)–As(1) [2.472(8)] and Ru(1)–As(2) [2.472(8)] bond distances being equal from the metal center. The overall CNOAs$_2$Br coordination sphere around the ruthenium is distorted octahedral in nature, which is reflected in all the bond parameters around ruthenium.

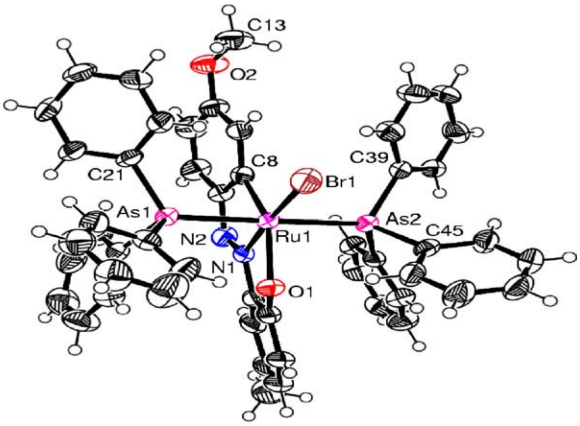
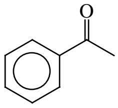
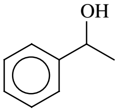
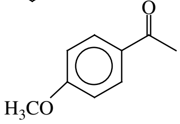
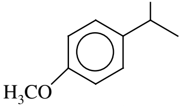
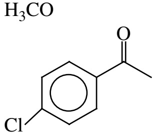
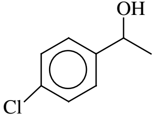
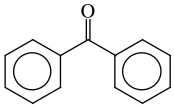
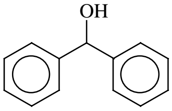
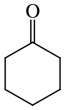
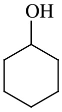
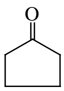
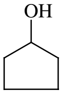
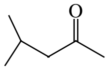
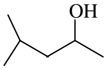
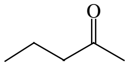
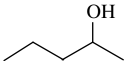
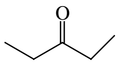
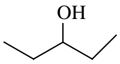


**Figure 2.** The X-ray crystal structure of the complex [RuBr(AsPh$_3$)$_2$(azo–OMe)]; selected bond lengths [Å] and bond angles [°]: Ru(1)–N(1) 2.011(5), Ru(1)–C(8) 2.038(6), Ru(1)–O(1) 2.129(4), Ru(1)–As(2) 2.4727(8), Ru(1)–As(1) 2.4727(8), Ru(1)–Br(1) 2.4882(8), N(1)–N(2) 1.265(6), N(1)–C(7) 1.413(7), N(2)–C(9) 1.391(7), O(1)–C(1) 1.312(7), N(1)–Ru(1)–C(8) 75.5(2), N(1)–Ru(1)–O(1) 78.55(18), C(8)–Ru(1)–O(1) 152.5(2), C(8)–Ru(1)–As(2) 94.46(16), O(1)–Ru(1)–As(2) 93.87(11), N(1)–Ru(1)–As(1) 92.96(13), N(1)–Ru(1)–As(2) 88.55(13), C(8)–Ru(1)–As(1) 85.37(16), O(1)–Ru(1)–As(1) 87.00(11), As(2)–Ru(1)–As(1) 178.38(3), N(1)–Ru(1)–Br(1) 176.38(13), C(8)–Ru(1)–Br(1) 107.35(16), O(1)–Ru(1)–Br(1) 98.95(12), As(2)–Ru(1)–Br(1) 89.01.

Catalytic transfer hydrogenation in which hydrogen is transferred from one organic molecule to another by ruthenium complexes is well known and this prompted us to carry out this type of reaction. The present experimental procedure for catalytic transfer hydrogenation involving a variety of aliphatic and aromatic ketones using [RuBr(AsPh$_3$)$_2$(azo–OMe)] was carried out as follows; under an inert atmosphere a mixture containing the ketone (3.75 mmol), ruthenium catalyst (0.0125 mmol) and 0.03 mmol of KOH was heated to reflux in 5 ml of isopropanol at 80 °C for the appropriate period as quoted in Table 1. The catalyst was removed from the reaction mixture by the addition of light petroleum followed by filtration and subsequent neutralization

**Table 1.** Catalytic activity in transfer hydrogenation of ketones by [RuBr$(AsPh_3)_2$(azo–OMe)]/*i*-PrOH/KOH[a]

| Entry | Substrate | Product | Time (h) | Conversion (%) | TON[b] (TOF)[c] |
|---|---|---|---|---|---|
| 1 |  |  | 1 | 97 | 291 (291) |
| 2 |  |  | 2 | 86 | 258 (129) |
| 3 |  |  | 2 | 79 | 237 (119) |
| 4 |  |  | 1 | >99 | 297 (297) |
| 5 |  |  | 1 | >99 | 297 (297) |
| 6 |  |  | 1 | >99 | 297 (297) |
| 7 |  |  | 2 | >99 | 297 (149) |
| 8 |  |  | 2 | 85 | 255 (128) |
| 9 |  |  | 2 | 98 | 294 (147) |

[a] Conditions: reactions were carried out at 80 °C using 3.75 mmol of ketone (5 ml isopropanol); catalyst/ketone/KOH ratio 1:300:2.5.

[b] Yield of product was determined using a HP 6890 series GC-FID with a DP-5 column of 30 m length, 0.32 mm diameter and 0.25 μm film thickness and by comparison with authentic samples. TON = ratio of moles of product obtained to the moles of the catalyst used.

[c] TOF (TON $h^{-1}$).

with 1 M HCl. The ether layer was filtered through a short path of silica gel. The filtrate was subjected to GC analysis and the hydrogenated product was identified by comparison with authentic samples in all cases. The catalyst performed efficiently for both aliphatic and aromatic ketones with high conversion and turnover. However, the reduction of *p*-methoxy and *p*-chloroacetophenone was slower and led to a lower yields when compared to the reduction of acetophenone. It was generally observed from the literature, that the catalytic transfer hydrogenation of aliphatic ketones was found to be difficult and takes a longer time for maximum conversion. Interestingly, the complex catalyzed efficiently the reduction of diethyl ketone, methyl propyl ketone, and isobutyl methyl ketone with a high percentage of conversion. Moreover, the complex showed good activity, >99%, for the transfer hydrogenation of both five- and six-membered cyclic ketones. In the absence of a base no transfer hydrogenation of ketones was observed. The base facilitated the formation of the ruthenium alkoxide by abstracting the proton of the alcohol and subsequently, the alkoxide underwent β-elimination to give a ruthenium hydride which is the active species in this reaction. This mechanism has been proposed by several workers on the studies of ruthenium catalyzed transfer hydrogenation reactions involving metal hydride intermediates.[10] Although several catalytic systems have been reported to support transfer hydrogenation reactions of ketones, a catalyst of this type is novel for its CNO donor, $AsPh_3$ and Cl or Br ligand environment.

In conclusion, a series of new orthometalated ruthenium(III) 2-(arylazo)phenolate complexes have been synthesized, characterized, and employed as new and efficient catalysts for transfer hydrogenation of ketones.

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9. *Synthesis of cyclometalated ruthenium(III) complexes*: the ruthenium(III) precursors [$RuX_3(AsPh_3)_3$] (X = Cl or Br) (0.15 mmol) and 2-(arylazo)phenol ligands (HL1–HL5) (0.15 mmol) were taken in 20 ml benzene. The mixture was heated under reflux, the color of the solution changed immediately and the reaction was further continued for 2 h until a deep green solution was obtained. The reactions were monitored by TLC. The solvent was then evaporated under reduced pressure and the product was purified by silica gel column chromatography with chloroform as eluent to give the green colored crystalline ruthenium complexes (yield 55–70%).
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