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Comparative Preparations of Homoleptic Hydridic Anions of Iron and Ruthenium Using Solution-Based Organometal Hydrogenation Techniques

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A study of the preparations of the complex hydridic anions $[MH_6]^{4-}$ (M = Fe and Ru) reveals a number of distinctive features. Here a soluble homoleptic ruthenium hydride has been prepared for the first time. For example, both FeX_2 and $[Ru(\eta^4\text{-}1,5\text{-COD})X_2]$, X = Cl and Br, react with PhMgBr solutions under hydrogen to produce the title compounds. The benzene liberated in these reactions is more readily hydrogenated in the case of a homogeneous room temperature ruthenium hydride preparation to both cyclohexane and cyclohexene. The ^1H NMR spectroscopic data show that the two complex anions have hydride absorptions in the low-frequency region, δ –20.3 and –14.7, respectively. Further, ^1H spin–lattice relaxation times (T_1) for M–H are longer in the case of Ru vs Fe.

History has shown homoleptic hydridic anions such as $[FeH_6]^{4-}$ and $[ReH_9]^{2-}$ to be intriguing, if not elusive species.[1−3] Most efforts to prepare complex hydrides formulated as $[MH_6]^{4-}$ (M = Fe, Ru, and Os) have entailed the use of mixtures of active metal powders (or their hydrides), transition metal powders, and 40 bar or more of hydrogen at 480 °C for 48 h or longer.[4−7] The complexes have colors that range from red to white, depending on the countercation. The reactivity to moisture depends primarily on the transition metal with the osmium complexes combusting spontaneously in air, the ruthenium complexes reacting readily, and iron complexes requiring days to react. These complex transition hydrides have strong M−H bonds reflecting the H ligands' ability to exert a strong ligand field in the absence of any π-ligating properties.[2] Our report here compares the solution preparations of these two electron-dense (i.e., low-valent) and hydrogen-dense reagents. This represents the first report of a soluble homoleptic hydride of ruthenium.

A typical reaction to prepare $[MgX(THF)_2]_4(FeH_6)$, starting from FeX_2, results in a 30% yield. This reaction requires rigorous exclusion of moisture and air. Here the reagents THF, anhydrous FeX_2, and 6 equiv of phenylmagnesium halide are mixed in a cold reaction flask, under hydrogen, which is warmed slowly. A high vacuum line with a pressure manifold is used to add hydrogen to this stirred reactor. Gas pressure is monitored using a transducer in conjunction with an analogue output signal that is digitized and fed into a computer. Temperature is similarly monitored using a thermocouple output.

In the case of the iron reaction the uptake of hydrogen subsides rapidly. This is consistent with reaction 1 and the stoichiometry shown (THF is omitted from equations throughout). The preparation of the analogous ruthenium hexahydride complex is accomplished by reaction of the polymeric dichloro(η^4-1,5-cyclooctadiene)ruthenium(II), by utilizing similar reaction conditions. In the typical reaction, a mixture is stirred at higher temperatures (55 °C) in order to maximize the amount of hydrogen up-take. The complexes precipitate and are isolated by filtration and washing with THF. A convenient means to assay the purity of a hydride sample consists of weighing a 10−20 mg quantity of the material into a 1 dram bottle on an analytical balance in the drybox. The bottle is then sealed with septa and removed from the box. Analysis of the hydridic hydrogen is possible to deduce from volumetric measurements according to reaction 2. Data

$$FeX_2 + 6C_6H_5MgX + 6H_2 \rightarrow [FeH_6][MgX]_4 + 6C_6H_5H + 2MgX_2 \quad (1)$$

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$$[MH_6]^{4-} + 6(CH_3)_2CHOH \rightarrow M^{2+} + 6H_2 + 6(CH_3)_2CHO^- \qquad (2)$$

has been compiled wherein hydridic hydrogen content and metal analyses combine to give [hydride/metal] = 6.0 ± 0.3 (see Table 1, Supporting Information).

Both the iron and ruthenium reactions are commenced by adding the phenylmagnesium bromide reagent in THF to a pressure reactor sealed under hydrogen at −78 °C. The ruthenium organometal reaction has some distinguishing features. Hydrogen uptake commences at only −30 °C in the case of the iron and mostly at about 20 °C for the ruthenium reaction (see Figure 1). Further, reactions of the ruthenium halide complexes result in about two times more hydrogen uptake on a per mole basis (H/Ru) than in the case of the iron reactions. This higher hydrogen uptake cannot be attributed to an increased yield of complex hydride. Concomitantly the precipitates were collected and analyzed for metals and hydridic hydrogen content. Further, the organic reaction components were analyzed by gas chromatography combined with mass spectrometry. Thus, Table 1 shows compilation of data for these various reactions. The reactions of both chloro and bromo ruthenium complexes can be seen to be essentially the same. The latter was allowed to react with hydrogen longer (120 h) though the yield of hydride was essentially the same. The increased reaction time served only to yield more benzene hydrogenation (3.5 vs 1.7 mmol). Further, warming the hydrogenation reaction mixture of [Ru(η^4-1,5-COD)Cl_2] to 50 °C resulted in an earlier "endpoint" in the $\Delta P/\Delta t$ behavior.

This increased uptake in hydrogen in the case of ruthenium can be attributed to the subsequent hydrogenation of benzene and cyclooctadiene. The iron reaction shows very little benzene hydrogenation to cyclohexane (10%) in these reactions. The data show that in the case of the ruthenium hydrogenations there is a high yield of cyclooctane. This product arises from the starting diene chelate, upon this cyclic diolefin being hydrogenated off the ruthenium center. Reaction 3 summarizes the idealized reaction stoichiometry.

$$[Ru(\eta^4\text{-}C_8H_{12})X_2] + 6C_6H_5MgX + 21H_2 \rightarrow [RuH_6][MgX]_4 + C_8H_{16} + 6C_6H_{12} + 2MgX_2 \qquad (3)$$

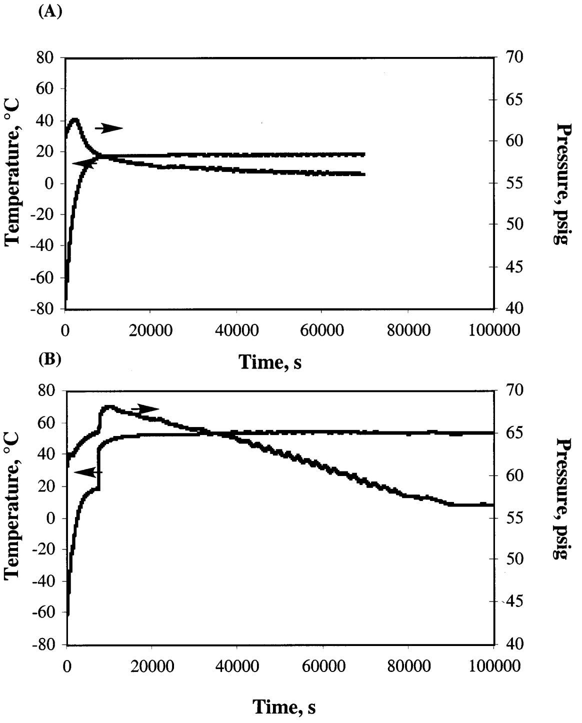
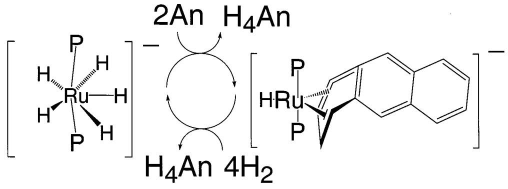


Figure 1. (A) Upper reaction profile shows reaction of $FeCl_2$ with 6 equiv of PhMgBr in THF under hydrogen pressure. (B) Lower reaction profile shows reaction of [$RuCl_2$(COD)] with 6 equiv of PhMgBr in THF under hydrogen pressure. COD = 1,5-cyclooctadiene. Conditions: A, [$FeCl_2$] = 0.12 M, [PhMgBr] = 0.71 M; B, [$RuCl_2$(COD)] = 0.060 M, [PhMgBr] = 0.36 M; the total reactor volume is 112 mL, and the solution volume is 8 mL.

Scheme 1. Arene Reactions Utilizing η^4-Olefin Complexation and Subsequent Tetrahydrogenation in a Polyhdridoruthenate Reaction with Anthracene



The catalytic activity of the polyhydridoruthium complexes in arene hydrogenation had been previously demonstrated by Halpern et al. for the polyhydrido species, K[RuH_3(PPh_3)$_3$], [RuH_4(PPh_3)$_3$], and K[RuH_5(PPh_3)$_2$].[12,13] These compounds are active in hydrogenation of anthracenes but show no reactivity toward benzene. The hexahydridoruthenate preparations have high reactivity toward benzene similar to the low-valent transition metal arylalkoxides prepared by Rothwell et al.[14] One distinct difference with the early transition metal systems is the tendency here to avoid formation of Ru−C σ bonds; on the contrary, ruthenium has a marked preference for more labile π bonds. The latter reactivity pattern is demonstrated similarly for the pentahydrido system mentioned earlier [Scheme 1, P = P(C_6H_5)$_3$].

In this case the reaction of the ruthenium pentahydrido complex and anthracene complex are in equilibrium, depending on hydrogen concentration. In the absence of hydrogen, the anthracene complex forms, and in the presence of hydrogen the pentahydrido complex forms. An outcome of Scheme 1 is that reversible hydrogenation occurs to form 1,2,3,4-tetrahydroanthracene. The complex, (η^4-1,5-cyclooctadiene)(η^6-1,3,5-cyclooctatriene)ruthenium(0), results in an analogous reaction with phenylmagnesium bromide and hydrogen. In contrast to the reaction of [Ru(η^4-C_8H_{12})Cl_2]

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this reaction is warmed to *room temperature* and results in overall quantitative formation of cyclooctane and both cyclohexane (48%) and cyclohexene (14%) formation. Finally, at elevated temperature, near complete conversion to C_6H_{12} occurs according to reaction 4.

$$[Ru(\eta^4\text{-}C_8H_{12})(\eta^6\text{-}C_8H_{10})] + 4C_6H_5MgX + 22H_2 \rightarrow [RuH_6][MgX]_4 + 2C_8H_{16} + 4C_6H_{12} \quad (4)$$

In these ruthenium organometal hydrogenation reactions a white microcystalline powder forms, which analyzes as $[MgBr(THF)_2]_4(RuH_6)$. Here also ^1H and ^2H NMR are useful methods to characterize soluble homoleptic transition metal hydrides and deuterides. Typical of covalent metal hydrides, these species all show hydride signals in the lower frequency region (negative δ). This is demonstrative of the metal d-electron anisotropy and hence the highly shielded hydridic hydrogen nuclei in these molecules. Previously this technique, though widely used in organometallic complex hydrides, has received less use in this field due to there being few soluble polyhydridometalate species. The chemical shifts for $[MgBr(THF)_2](FeH_6)$, δ −20.3 ppm, and $[MgBr(THF)_2](RuH_6)$, δ −14.6 ppm, reflect the more spatially extended d orbitals in the fifth period transition metal. Further structural information on soluble hydrides can be obtained by measuring the spin−lattice relaxation times (T_1) for the hydride signals. The T_1 measurement gives information on the distances between neighboring hydrogen nuclei, given by the equation for dipole−dipole relaxation under the "extreme narrowing condition".[15,16]

$$\frac{1}{T_1^{\mathrm{HH}}} = 1.5\gamma^4\hbar^2\sum_i r_i^{-6}\tau_c \qquad (5)$$

From eq 5 it is seen that T_1 is inversely dependent on the distances between the hydridic hydrogens, r_i, to the sixth power. The next nearest hydrogen neighbors are the distant α-CH_2 protons on the THF molecules. We can make the reasonable approximation that the neighboring hydridic hydrogens are responsible for nuclear relaxation. Further, the $[FeH_6]^{4-}$ and $[RuH_6]^{4-}$ molecules should have similar correlation times, τ_c, that are due to comparable rates of molecular tumbling. The larger molar volume of the ruthenium hydride complex would be expected to decrease T_1 by up to 30% with all else equal. Rather the T_1 for $[RuH_6]^{4-}$ is found to be twice that of $[FeH_6]^{4-}$.[17]

Another unusual feature of these transition metal polyhydridometalates concerns the cation matrix surrounding the $[MH_6]^{4-}$ complex. For example, IR data and M−H distances collected in Table 2 (Supporting Information) show that the M−H asymmetric stretching vibration is highly sensitive to the complex cation environment. Here it is observed that this frequency is somewhat lower for soluble complexes, $[MgBr(THF)_2]_4(MH_6)$, compared to their solid state counterparts. Further, a solvatochromic effect has been previously observed in the alkoxide complexes, $[MgOR(THF)_n]_4(FeH_6)$, which supports a charge transfer postulate.[18] A bonding theory of transition metal hydrides advanced by Firman and Landis has attempted to explain structures of solid state species $M_aM_bH_n$ in terms of sd^n hybrid orbitals.[19] The inactive metal p orbitals lead to the concept of M−H bonds that comprise three-center-four-electron bonds, and in some cases the postulation of charge transfer to the magnesium atom, to give formally the Mg^+ species. This would depict a "noninnocent" cation environment. The latter effect would tend to be supported by the spectroscopic evidence obtained for both the solid state and soluble molecular polyhydridometalate complexes as well.

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Supporting Information Available: Experimental details and listings of analytical (Table l) and spectroscopic data (Table 2). This information is available free of charge via the Internet at htpp://pubs.acs.org.

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(17) We thank one reviewer who pointed out that the T_1 values for Ru−H vs Fe−H are unusual and give a suspicious distance possibly due to the "noninnocent" cation matrix (vide infra).

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