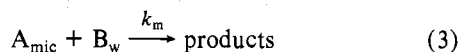
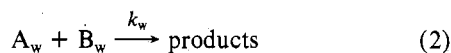
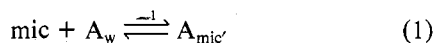


faster (by a factor of ca. 2) than that observed for  $\text{Mo}(\text{CN})_8^{4-}$ , and this behavior makes it more difficult to follow the reaction progress; values of  $2.4 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at 0.005 M SDS and  $3 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$  at 0.010 M SDS were estimated.

### Discussion

The effect of surfactants on the rate of electron-transfer reactions between ions can be represented as follows if we assume that one reactant (A) can interact with micelles while the other is in the bulk (as is the case of  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Mo}(\text{CN})_8^{4-}$ ).



On the assumption that the process (1) always equilibrated, the usual equation is derived where  $k_{\text{obsd}}$  is the observed second-order rate constant<sup>9</sup>

$$k_{\text{obsd}} = \frac{k_w + k_m K_1 [\text{mic}]}{1 + K_1 [\text{mic}]} \quad (4)$$

where  $[\text{mic}] = (C_{\text{surf}} - \text{cmc})/N$ ;  $C_{\text{surf}}$  is the concentration of surfactant and  $N$  the aggregation number. Then from the observed decrease in the rate of reaction with  $\text{Fe}(\text{CN})_6^{4-}$  and  $\text{Mo}(\text{CN})_8^{4-}$  it follows that  $K_1 [\text{mic}] \gg 1$ , hence

$$k_{\text{obsd}} = k_w K^{-1} [\text{mic}]^{-1} + k_m \quad (5)$$

Since  $k_{\text{obsd}}$  is more than 2 orders of magnitude smaller than the electron-transfer rate constant in the absence of SDS, we can safely conclude that  $K_1 [\text{mic}] \geq 2 \times 10^2$ , and since  $[\text{mic}] \approx 2 \times 10^{-5}$  to  $5 \times 10^{-4} \text{ M}$ , we get  $K_1 \geq 10^7 \text{ M}^{-1}$ . This latter value is quite reasonable for the present case where both electrostatic interactions (triply charged positive ion and a negative micelle) and hydrophobic interactions (imposed by the hydrophobic bpy ligands) are operative. The data in Table I can now be used to analyze for the location of the electron-transfer reaction, namely, a bulk reaction where  $k_w$  plays the dominant role or a micellar reaction where  $k_m$  contributes the major part of  $k_{\text{obsd}}$ . From expression 5 it is clear that the rate of the reaction should be inversely proportional to  $[\text{mic}]$  when the reaction is a bulk reaction. Although the values of the cmc and  $N$  under the present conditions cannot be exactly evaluated, it is safe to assume that by changing the surfactant concentration in the range 0.005–0.030 M,  $[\text{mic}]$  was changed by at least an order of magnitude. However, the data in the table indicate only a slight increase in  $k_{\text{obsd}}$ . We therefore conclude that the main pathway for the reaction is at the micelle–water interface. The small increase in  $k_{\text{obsd}}$  is easily explained by the increased ionic strength with increasing  $C_{\text{surf}}$  which will facilitate the approach of the negative reactants to the negative micelles.

A similar argument can rationalize the effect of  $\text{NaClO}_4$ . The decrease in the surface potential on increasing the ionic strength is expected to enhance the rate of the reaction at the micellar–water interface. In excess  $\text{Na}^+$  ions, the possibility of displacement of  $\text{Ru}(\text{bpy})_3^{3+}$  by the inert ions should however be considered. In the case of purely electrostatic interaction, the association constant for a triply charged ion can be estimated to be ca.  $10^5$  times larger than for a singly charged ion.<sup>2,9,10</sup> In the present case where hydrophobic interaction is considerable for the Ru complex this association constant should be even larger. We therefore conclude that even at the highest  $[\text{Na}^+]$  most of  $\text{Ru}(\text{bpy})_3^{3+}$  stays attached to the micelle.

Then also the enhancement of the electron-transfer rate observed with  $\text{Fe}^{2+}(\text{aq})$  can be attributed to the location of

$\text{Ru}(\text{bpy})_3^{3+}$  in a negative micelle.

In conclusion, the rates of electron transfer to  $\text{Ru}(\text{bpy})_3^{3+}$ , as well as  $\text{Ru}(\text{bpy})_3^{2+}$  and its excited state,<sup>4</sup> have been shown to be greatly altered by the presence of micelles. In view of the current interest in polyimine complexes of Ru in solar energy conversion, such effects might be useful in these systems. Further investigations are in progress aiming at the elucidation of the mechanisms controlling electron-transfer rates in micellar solutions.

Registry No.  $\text{Ru}(\text{bpy})_3^{3+}$ , 18955-01-6; SDS, 151-21-3;  $\text{Mo}(\text{CN})_8^{4-}$ , 17923-49-8;  $\text{Fe}(\text{CN})_6^{4-}$ , 13408-63-4;  $\text{Fe}^{2+}$ , 15438-31-0.

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### Arene–Transition Metal Chemistry. 2.<sup>1a</sup> Hydrogenation of Metal–Arene and Allylmetal–Arene Complexes

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In our studies of the hydrogenation of arenes catalyzed by discrete coordination or organometallic complexes, we have evidence that an  $\eta^4$ -arene binding of the aromatic hydrocarbon may be a favorable type of intermediate and that an allyl ligand and a  $d^8 = d^6$  electronic couple may be important to stereoselectivity and chemoselectivity in the catalyst, e.g., as in the  $\eta^6\text{-C}_6(\text{CH}_3)_6\text{Ru-}\eta^4\text{-C}_6(\text{CH}_3)_6$  and the unique<sup>3</sup>  $\eta^3\text{-C}_3\text{H}_5\text{Co[P(OR)}_3\text{]}_4$  catalyst precursors. We describe here the hydrogen chemistry for a range of metal–arene, allylmetal–arene, and hydridometal–arene complexes.

Two allylmetal– $\eta^6$ -arene complexes, the  $d^6$   $[\eta^3\text{-C}_3\text{H}_5\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Cl}]_2$  dimer and the  $d^8$   $\eta^3\text{-C}_3\text{H}_5\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}$  monomer, reacted with hydrogen at  $\sim 85^\circ\text{C}$  in benzene and toluene solvents, respectively, with exclusive transfer of the hydride hydrogen to the allyl ligand to irreversibly yield propylene.<sup>6</sup> There was no evidence of hydrogenation of either the arene ligand or the arene solvent. This suggests a relative resistance to direct hydrogen transfer to an  $\eta^6$ -arene ligand. Consistent with these and earlier observations, a molybdenum complex with both hydride ligands and an  $\eta^6$ -arene ligand,  $d^4$   $\text{H}_2\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , showed no evidence of hydrogen transfer to either the toluene ligand or the benzene solvent up to  $85^\circ\text{C}$  where gross decomposition occurred to

give the hydrogen and toluene molecules. A potential precursor,  $\eta^6\text{-CH}_3\text{C}_6\text{H}_5\text{Mo}[\text{P}(\text{OCH}_3)_3]_3$ , of the trimethyl phosphite analogue did not react with hydrogen at 124 °C to yield hydrogenation of either the toluene ligand or the benzene solvent.

An examination of  $d^x$  configuration effects upon the hydrogenation potential of bis( $\eta^6$ -arene)metal and ( $\eta^6$ -arene)-metal diene complexes showed no arene hydrogenation, either arene ligand or arene solvent, for the  $d^4$ ,  $d^6$ , and  $d^7$  bis( $\eta^6$ -arene)metal and also the  $d^8$  ( $\eta^6$ -arene)metal diene complexes of titanium(0)<sup>7</sup> at 20 °C, the chromium group<sup>2,8</sup> at 150 °C, cobalt(II) at 50 °C, and ruthenium(0) diene<sup>9</sup> at 20 °C. All except the chromium group complexes suffered gross decomposition at the indicated temperatures.

The titanium(II)-arene complex  $\text{CH}_3\text{C}_6\text{H}_5\text{TiAl}_2\text{Cl}_8$  was dissolved in benzene and then heated to 90 °C for 10 h in a hydrogen atmosphere. Gas chromatographic analysis of the volatile products showed only the presence of toluene and benzene. The only reaction under these conditions was arene exchange. At higher temperatures, the reaction mixture showed minor evidence of decomposition (black or brown tar); however, even at 125 °C the majority of the titanium was recovered as the benzene complex. Under these conditions, there was about a 10% conversion of benzene to cyclohexane. With deuterium at 125 °C, the recovered toluene and benzene were not enriched in deuterium but the cyclohexane showed  $d_1$  through  $d_{12}$  species to be present with the  $d_6$  through  $d_{11}$  the major ones.

The observed reluctance of the  $\eta^6$ -arene ligands in the metal complexes to undergo hydrogenation (although negative evidence) is consistent with the thesis that an  $\eta^4$ -arene binding is an important intermediate<sup>10</sup> in coordination catalysis of arene hydrogenation. An  $\eta^4$ -binding is, of course, a potential excited state for an  $\eta^6$ -arene-metal complex; the activation energy for this process in bis(hexamethylbenzene)ruthenium(0) is low,  $\sim 16$  kcal/mol, and this process may be facilitated by the presence of alanes<sup>11</sup> as shown for the ruthenium complex and implicated for the titanium(II) complex (arene) $\text{TiAl}_2\text{Cl}_8$ .<sup>12</sup>

## Experimental Section

**Reagents and Procedure.** Solvents were vacuum distilled from lithium aluminum hydride prior to use. Prepurified (99.5%) Matheson and Co. hydrogen was used in the hydrogenation reactions. All the arene-metal complexes were prepared by literature procedures<sup>13</sup> except the titanium(0) species which is described below. All manipulations were effected by high vacuum or Schlenk techniques or with a Vacuum Atmospheres drybox. Hydrogen reactions were performed by placing the arene complex with either toluene or benzene solvent and a magnetic stir bar in a reaction tube fitted with a Kontes Teflon stopcock. The mixture was evacuated by two freeze-evacuation-freeze cycles on a high-vacuum system. Hydrogen was then admitted to a pressure of  $\sim 1$  atm at  $-197$  °C; the stopcock was then closed. Separation and identification of volatile compounds produced in the reactions were done with a Perkin-Elmer 990 gas chromatograph. Column materials were described in the earlier articles<sup>4,5</sup> except for propane-propene (Poropack Q), for tetrahydrofuran, toluene, and methylcyclohexane and for benzene, methylcyclohexane, toluene, cyclohexane, and cyclic olefins (10 ft of OV-17, 3% on Gas Chrom Q), and for benzene and methylcyclohexane (6 ft of OV-225, 3% on Gas Chrom Z). A Finnigan 3300 GC/MS was used for definitive characterization of the chromatographically separated molecules.

**Synthesis of ( $\eta^6\text{-CH}_3\text{C}_6\text{H}_5$ )<sub>2</sub>Ti.** A metal atom (vapor) reactor<sup>14</sup> and procedures described previously<sup>15</sup> were employed to vaporize titanium (0.152 g, 3.2 mg-atom) from a tungsten boat (0.010 W) by resistive heating. The titanium vapor was codeposited at  $-196$  °C with 25 mL of purified deoxygenated toluene over a 1.5-h period. A dark red-brown matrix resulted. After completion of the reaction the matrix was warmed slightly and melted and was siphoned out at  $-50$  °C with argon pressure directly into a filtration apparatus (4–5.5  $\mu\text{m}$  fritted glass) and the deep red-purple filtrate collected in a sealable glass tube and sealed under slight vacuum with a flame. After exposure of the reactor residue to air, 0.067 g of  $\text{TiO}_2$  was recovered from the

reactor and filter. The concentration of titanium in the filtrate was about 0.11 g/25 mL of toluene, essentially all of which was in the form of bis(toluene)titanium.<sup>16</sup>

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**Registry No.** [ $\eta^3\text{-C}_3\text{H}_5\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Cl}]_2$ , 35625-66-2;  $\eta^3\text{-C}_3\text{H}_5\text{Ru}(\eta^6\text{-C}_6\text{H}_6)\text{Cl}$ , 41500-34-9;  $\text{H}_2\text{Mo}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)[\text{P}(\text{C}_6\text{H}_5)_3]_2$ , 34842-94-9;  $\text{CH}_3\text{C}_6\text{H}_5\text{TiAl}_2\text{Cl}_8$ , 56214-53-0; ( $\eta^6\text{-CH}_3\text{C}_6\text{H}_5$ )<sub>2</sub>Ti, 55527-82-7;  $\eta^3\text{-C}_3\text{H}_5\text{Ru}(\eta^6\text{-C}_6\text{H}_5\text{CH}_3)\text{Cl}$ , 69027-57-2;  $\text{Co}[(\text{C}_6\text{H}_5)_6\text{C}_2]^{2+}(\text{PF}_6^-)_2$ , 69027-58-3.

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- (7) The hydrogen reaction proceeded at 20 °C to generate a colorless solution, a metallic solid, and toluene; complete reaction was observed within 1–2 h.
- (8) A reexamination of this bis(arene)metal group confirmed earlier<sup>2</sup> observations. No hydrogenation, either stoichiometric or catalytic, was observed up to 150 °C.
- (9) The typical reaction of ( $\eta^6$ -arene)metal  $\eta^4$ -diene with hydrogen at 20 °C was a slow generation of metallic solids and free, unhydrogenated arenes.
- (10) It has been reported that  $\text{HClRu-}\eta^6\text{-C}_6\text{(CH}_3)_6[\text{P}(\text{C}_6\text{H}_5)_3]$  is a catalyst precursor for benzene hydrogenation at 50 °C and 50 atm hydrogen pressure: M. A. Bennett, T.-N. Huang, A. K. Smith, and T. W. Turney, *J. Chem. Soc., Chem. Commun.*, 582 (1978). The hexamethylbenzene ligand undergoes no hydrogenation and it is not known whether this ligand undergoes ligand exchange with benzene. Hence there are two quite different possible mechanistic scenarios. If exchange of the hexamethylbenzene ligand with benzene is not facile, then a reactive intermediate could be formed by conversion of the  $\eta^6\text{-C}_6\text{(CH}_3)_6$  ruthenium complex to a hydridoruthenium  $\eta^1$ - or  $\eta^3$ -benzyl species. If exchange is facile, then an  $\eta^6\text{-C}_6\text{H}_6\text{Ru} \rightleftharpoons \eta^4\text{-C}_6\text{H}_6\text{Ru}$  process could be operative at the reaction temperature of 50 °C.
- (11) Presence of an alane is not a sufficient condition for the hydrogenation reaction. For example, addition of trimethylaluminum to the  $(\text{CH}_3\text{-C}_6\text{H}_5)_2\text{Mo} + \text{H}_2$  reaction system in benzene or toluene did not elicit arene hydrogenation at 115 °C; there was in this instance a slow irreversible reaction of the alane and the arene complex to give a dark oil.
- (12) The structure of the (arene) $\text{TiAl}_2\text{Cl}_8$  type of complex is unknown. A probable structure is ( $\eta^6$ -arene) $\text{Ti}(\text{Cl}_2\text{AlCl}_2)_2$  with chlorine bridge bonds between aluminum and titanium, and two bridge bonds per  $\text{AlCl}_4^-$  ligand. A crystallographic investigation of the benzene complex is planned. A related complex is  $\eta^6\text{-C}_6\text{H}_6\text{UAl}_2\text{Cl}_{12}$  in which six U–Cl–Al bridge bonds are generated by uranium sharing an edge of each of the three  $\text{AlCl}_4^-$  tetrahedra (M. Cesari, U. Pedretti, A. Zazzetta, G. Lugli, and W. Marconi, *Inorg. Chim. Acta*, **5**, 439 (1971)); possibly this complex like the titanium(II) species can catalyze arene hydrogenation.
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