# Organometallic intermediates in dehydrobrominations catalyzed by metals and metal bromides

Angela R. Suarez, Alejandra G. Suarez, and Maria R. Mazzieri

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roundings in the monoclinic and orthorhombic crystals of ferrocene affords a simple model, based on geared rotational displacements of the molecules, to explain the phase transition at 242 K; (iii) the monoclinic → triclinic transition in ferrocene arises as a consequence of the need to preserve optimum (i.e. not repulsive) H···H intermolecular interactions at temperatures below 164 K (this is achieved by adopting, in agreement with the small barrier to internal rotation, an intermediate conformation between the eclipsed and staggered forms); (iv) this behavior is not observed in monoclinic nickelocene because the larger inter-ring separation allows easier interpenetration of the neighboring interlocked molecules than in ferrocene (similar dependence of the crystal features on the molecular size is observed on comparing the intermolecular contacts in orthorhombic ferrocene and ruthenocene); (v) the negative expansion coefficient along the *b* axis in monoclinic nickelocene can also be justified on the basis of the need to avoid repulsions between the H atoms belonging to neighboring molecules separated by a cell translation; (vi) the Cp reorientational barriers calculated by means of the atom-atom potential energy method are found in good quantitative agreement with the values of the activation energies/potential barriers obtained by spectroscopic techniques or from the anisotropic displacement parameters coming from diffraction studies.

In conclusion, the different behavior of the metallocene crystals upon cooling appears to be the result of the balance between two, not necessarily converging, factors: the striving for cohesion and the need to avoid the upsurge of "localized" repulsions. Although the metallocene molecules have nearly identical shapes (and therefore pack in nearly identical ways in their solids), there are subtle differences in size and geometry which come into play when the molecules are moved closer together as the temperature is decreased. The result is a rather dramatic change in the physical properties of these otherwise extremely similar materials.

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**Registry No.** $(C_5H_5)_2Fe$, 102-54-5; $(C_5H_5)_2Ni$, 1271-28-9; $(C_5H_5)_2Ru$, 1287-13-4; cyclopentadiene, 542-92-7.

**Supplementary Material Available:** A listing of the symmetry operations generating the ESs and of the individual contribution to ppe of each ES molecule (1 page). Ordering information is given on any current masthead page.

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# Organometallic Intermediates in Dehydrobrominations Catalyzed by Metals and Metal Bromides

Angela R. Suárez,* Alejandra G. Suárez, and María R. Mazzieri

*Departamento de Química Orgánica, Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, 5016 Córdoba, Argentina*

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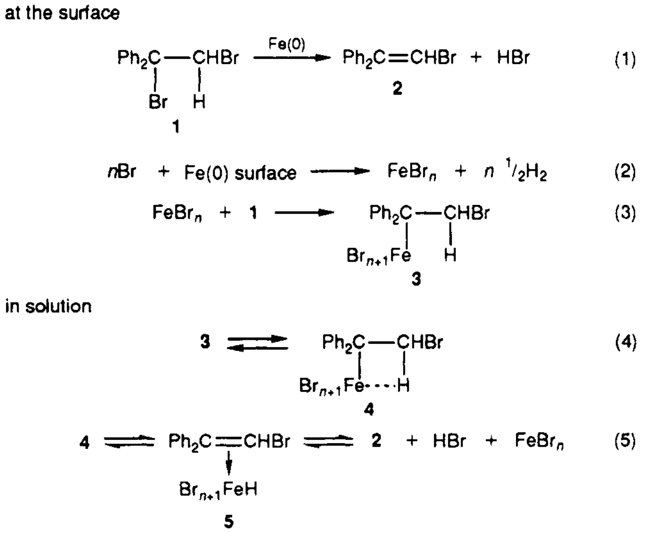
Iron, ruthenium, aluminum, and their anhydrous bromides were used as catalysts for dehydrobromination of 1,2-dibromo-1,1-diphenylethane in carbon tetrachloride solutions to give 2-bromo-1,1-diphenylethene. Organometallic species formed on the surface of the solid catalysts moved into the solution and were detected spectroscopically. The reactivity of the studied catalyst was $Al < AlBr_3 \approx Ru < RuBr_3 < FeBr_2 \approx FeBr_3 \approx Fe$.

## Introduction

Hydrogen halide abstraction from alkyl halides can be achieved under several conditions. Nevertheless, there is little work on dehydrohalogenation catalyzed by transition-metal compounds in the condensed phase, and the mechanism is still unclear. Synthetic applications of hydrogen halide elimination from alkyl halides mediated by nickel complex were reported by Smith et al.[1]

In a previous paper we reported the dehydrohalogenation of 1,2-dibromo-1,1-diphenylethane in carbon tetrachloride solutions catalyzed by powdered iron.[2] We isolated stable organoiron compounds and detected organometallic intermediates that after being formed on the metal surface moved into the solution that changed from colorless to red-brick. Steps proposed for the reaction involved the well-known oxidative addition and *β*-elimination, both very common pathways in many catalytic processes involving organometallic systems. Scheme I shows the mechanism.

### Scheme I



The participation of such organometallic intermediates was detected in several ways. Electronic absorption spectra

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[1] Henningsen, M. C.; Jeropoulos, S.; Smith, E. H. *J. Org. Chem.* **1989**, *54*, 3015.

[2] Suârez, A. R.; Mazzieri, M. R.; Suârez, A. G. *J. Am. Chem. Soc.* **1989**, *111*, 763.

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**Table I. Dehydrobromination of 1,2-Dibromo-1,1-diphenylethane Catalyzed by Metals and Metal Bromides**[a]

| catalyst | dehydrobromination, %[b] (time) 76 °C | 50 °C | 37 °C |
|---|---|---|---|
| Fe | 100 (15 min) | 100 (4 h) | 94 (8 h) |
| $FeBr_2$ | 100 (15 min) | | |
| $FeBr_3$ | 100 (15 min) | | |
| Ru | 20 (15 min) | 55 (6 h) | |
| Ru | 37 (45 min) | 86 (14 h) | 6 (14 h) |
| Ru | 100 (90 min) | 100 (16 h) | |
| $RuBr_3$ | 68 (15 min) | 86 (7 h) | 20 (14 h) |
| $RuBr_3$ | 100 (45 min) | | 27 (17 h) |
| Al | 10 (15 min) | 69 (20 h) | 20 (26 h) |
| Al | 71 (90 min) | | |
| Al | 100 (120 min) | | |
| $AlBr_3$ | 95 (90 min) | | |

[a] The informed values are the average of at least five reactions. [b] Percentage of consumed reagent.

**Table II. $^1H$ NMR Nonaromatic Proton Integration in Catalyzed Dehydrobromination Reactions**[a]

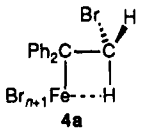
| catalyst | T, °C | % 2 | % 1 | % missing H[b] |
|---|---|---|---|---|
| Fe(0) | 76 | 65 | 33 | 2 |
| Fe(0) | 50 | 67 | 22 | 11 |
| Fe(0) | 37 | 60 | 28 | 12 |
| Fe(0) | 30 | 62 | 29 | 9 |
| $FeBr_2$ | 76 | 80 | 18 | 2 |
| $FeBr_2$ | 50 | 81 | 10 | 9 |
| $FeBr_2$ | 37 | 69 | 21 | 10 |
| $FeBr_2$ | 30 | 67 | 22 | 11 |
| $FeBr_3$ | 76 | 79 | 18 | 3 |
| $FeBr_3$ | 50 | 79 | 10 | 11 |
| $FeBr_3$ | 37 | 75 | 15 | 10 |
| $FeBr_3$ | 30 | 70 | 18 | 12 |
| Ru(0) | 76 | 57 | 40 | 3 |
| Ru(0) | 50 | 47 | 43 | 10 |
| Ru(0) | 37 | 9 | 91 | – |
| $RuBr_3$ | 76 | 55 | 43 | 2 |
| $RuBr_3$ | 50 | 45 | 44 | 11 |
| $RuBr_3$ | 37 | 24 | 67 | 9 |
| Al(0) | 76 | 58 | 39 | 3 |
| Al(0) | 50 | 18 | 72 | 10 |
| Al(0) | 37 | 20 | 70 | 10 |
| $AlBr_3$ | 76 | 87 | | 13 |

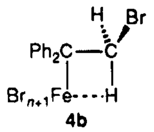
[a] The informed values are the averages of at least five reactions. [b] Lack of nonaromatic protons. Integration of aromatic protons remained unchanged during the reaction time.

**Table III. Maxima in the Visible Spectra of Reaction Mixtures**

| catalyst | wavelength (nm) band I | band II | band III |
|---|---|---|---|
| Fe(0) | 433 | 455 | 483 |
| $FeBr_2$ | 433 | 455 | 483 |
| $FeBr_3$ | 433 | 455 | 483 |
| Ru(0) | 426 | 452 | 480 |
| $RuBr_3$ | 426 | 452 | 480 |
| Al(0) | 426 | 450 | 484 |
| $AlBr_3$ | 426 | 450 | 484 |

of the reaction mixtures revealed the existence of bromine → metal electron donation.[3] Atomic absorption and mass spectrometry showed the presence of iron-containing species in the carbon tetrachloride solutions.[2] Integration of $^1H$ NMR spectra demonstrated deficiency of nonaromatic protons in mixtures of uncompleted reactions while no such deficiency was present when substrate **1** was fully transformed into product **2**. The missing protons would correspond to agostic and hydride compounds **4** and **5**. The difficulty and failure to direct detection of such proton signals at high fields may be attributable to the signal scattering arising from the coexistence of the enantiomeric forms **4a,b** and the dynamic equilibrium between the tautomeric forms **3**, **4a,b**, and **5**.[4]


**4a**


**4b**

We are at present interested in explaining the factors responsible for control of catalytic activity. From our previous report, the basic features of the mechanism proposed (Scheme I) are as follows: (i) An obvious intervention of the two different pathways for **2** formation exists, contact reaction shown in step 1 and the organometallic intermediates decomposition in step 5. (ii) Since we detected organometallic intermediates in the solution, the contact mechanism should not predominate and step 5 should take place more slowly than step 3 (Scheme I).

On the other hand, the oxidative addition of $MBr_n$ species in step 3 (Scheme I) suggests that iron bromides should carry out dehydrohalogenation with similar results, and the presence of organometallic intermediates coming from metals other than iron could be detected if they developed relatively stable agostic or hydride compounds of type **4** and **5**. All these hypotheses motivated the present study to explain the role of metals in the catalyzed dehydrobromination.

Therefore, we first performed reactions under the same conditions as those reported earlier, but using Fe(II) and Fe(III) anhydrous bromides as catalysts. Next, since it has been previously proposed that the existence of empty d orbitals is a necessary condition for the agostic structure formation,[5] we used a transition metal, Ru(0), and a non transition metal, Al(0), as catalysts. Reactions in the presence of ruthenium and aluminum tribromides were checked too.

## Results and Discussion

Results of all reactions of 1,2-dibromo-1,1-diphenylethane in the presence of metals and their bromides are listed in Table I. In Table II are typical average values of nonaromatic protons in uncompleted reactions at different temperatures, and the maxima of visible spectra are given in Table III.

Three features were observed in every case: (i) deficiency of nonaromatic protons in the $^1H$ NMR spectra of uncompleted reactions (% missing H, Table II), (ii) the presence of charge transference bands in the visible region which coincides with the lack of proton in the NMR spectra (see Table III), (iii) an initially colorless solution turning colors ranging from yellow to red-brick after heating.

Though we have not isolated metallic complexes in the present work, the above features are clear evidence that organometallic intermediates do form during the reaction. Similar intermediates have been detected by Kochi,[6] proposed by Smith,[1] and isolated by Collman[7] in elimination reactions from alkyl mono- and dibromides pro-

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[3] Hendrikson, D. N.; Kinnaird, M. G.; Suslick, K. S. *J. Am. Chem. Soc.* **1987**, *109*, 1243.

[4] Allison, J.; Ridge, D. P. *J. Am. Chem. Soc.* **1989**, *101*, 4998.

[5] (a) Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395. (b) Koga, N.; Obara, S.; Kitaura, K.; Morokuma, K. *J. Am. Chem. Soc.* **1985**, *107*, 7109.

[6] Singleton, D. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1967**, *89*, 6547.

[7] Collman, J. P.; Brauman, J. I.; Madonik, A. M. *Organometallics* **1986**, *5*, 218.

moted by Cr, Ni, and Rh complexes, respectively. Whereas these reactions yielded preferably debrominations rather than dehydrobrominations, we attribute this difference in reactivity to the different experimental conditions[8] and structure.

Results collected in Table I indicate the different reactivity of the catalysts employed. This reactivity remained unchanged despite previous activation of the metal surface with hydrogen at 400 °C, indicating that surface reaction is faster than $\beta$-elimination.

$MBr_n$ species can certainly catalyze the dehydrobromination of 1 as is demonstrated by the results shown in Table I. The ability of $MBr_2$ and $MBr_3$ to work as a catalyst of the reaction with equal ($FeBr_2$ and $FeBr_3$) or better reactivity ($RuBr_3$ and $AlBr_3$) than the corresponding metals themselves ratified the hypothesis that they would be the most effective catalyst in the present reactions.

The behavior of Ru(0) and anhydrous $RuBr_3$ was, as expected, similar to that of iron catalysts, although less reactive. At present we can only assert that the difference in reactivity between iron and ruthenium as catalysts is not originated in steps 1 or 2 but in steps 3 or 5. Further studies will be necessary to answer this difficult issue.

Experiences carried out with Al(0) and anhydrous $AlBr_3$ led to unforeseen results. Both showed catalytic activity, aluminum tribromide being more active than powdered aluminum. Noteworthy, they displayed the same behavior, including color development, as that observed with the transition-metal catalysts. These results suggested that organometallic intermediates were formed despite the absence of empty d orbital in the aluminum atoms. The Al(I) and Al(II) species originated in the oxidative sequence (step 2, Scheme I) could form carbon–aluminum $\sigma$ bonds in organometallic intermediates like 3 and 4, but trivalent aluminum atoms in $AlBr_3$ have no available valence electrons to form new bonds. So, an agostic structure similar to 4 would not be an intermediate but a transition state to a more stable hydride form such as 5. A similar four-centered transition state has been proposed by Egger[9] for the $\beta$-hydrogen elimination from $[(CH_3)_2CHCH_2]_3Al$ and by Bercaw et al.[10] in $\beta$-hydrogen elimination from permethylscandocene–alkyl complexes. An explanation of the aluminum tribromide behavior could be found if aluminum expanded its coordination sphere to include the empty d orbital as postulated previously.[11]

On performing the reactions at different temperatures, we observed an increased percentage of missing protons (see Table II). This is one of the most important results of the present work. Lower temperatures favor the accumulation of organometallic species like 4 and 5. According to our proposed mechanism, it will mean that $\beta$-elimination is slower than the oxidative addition.

In conclusion, not only Fe but also Ru and Al and even their bromides are able to catalyze dehydrobromination through an organometallic pathway. The enhanced activity of metals in their oxidized states provides support for the early mechanism proposed. Transition metals and transition-like metals can work as catalysts of HBr elimination with a marked difference in reactivity compared to a main-group metal such as Li.[12] The reactivity of the studied catalysts was $Al < AlBr_3 \approx Ru < RuBr_3 < FeBr_3 \approx FeBr_2 \approx Fe$.

## Experimental Section

$^1H$ NMR spectra were recorded in a T-60 Varian spectrometer with $SiMe_4$ as internal standard and $CCl_4$ as solvent. Electronic absorption spectra were carried out in a Shimadzu 260 spectrometer with $CCl_4$ as solvent, and atomic absorption determinations were performed on a Perkin-Elmer 372 apparatus. Particle diameters were determined with a Philips SEM microscope.

Solvents were purified by usual procedures.[13] $CCl_4$ was further dried and maintained on molecular sieves. Metal catalysts were washed with ether and vacuum-dried before use. Iron and aluminum were also treated with hydrogen at 400 °C for 5 h.

**Materials.** The catalysts employed were powdered iron (Sigma 5N) of 90–100-$\mu$m particle diameter and 2–7-$\mu$m particle diameter (Merck). Anhydrous iron(II), and iron(III), and aluminum(III) bromides and powdered Al, 5–10 $\mu$m, were supplied by Strem Chemicals Co. Powdered ruthenium of 30-$\mu$m particle diameter was purchased from Aldrich Chemical Co. and $RuBr_3$ from Johnson Mathey Inc.

**Preparation of 1.** To a $CCl_4$ solution of 1,1-diphenylethene (Aldrich) was added a $CCl_4$ solution of bromine (Merck P.A.) at −40 °C, in the dark. It was recrystallized from *n*-heptane; mp 59–59.5 °C.

**Dehydrobromination Procedure.** Reactions were carried out in air atmosphere, and the equipment was dried at 120 °C before use. A solution of 1 (1 mmol), $CCl_4$ (2 mL), and about 0.1 mmol of the catalyst was refluxed in a Pyrex tube provided with a condenser. The reaction tube was covered with aluminum foil and immersed in a bath at the reaction temperature. After the reaction finished, the mixture was filtered and evaluated by $^1H$ NMR. Solutions for UV–vis and atomic absorption spectra were prepared by dilution of an aliquot of the reaction mixture.

**Acknowledgment.** We thank the Consejo Nacional de Investigaciones Científicas y Técnicas of Argentina (CONICET) and the Consejo de Investigaciones Científicas y Tecnológicas de la Provincia de Córdoba, Argentina (CONICOR), for financial support. A.G.S. thanks CONICET for a fellowship. We also thank to Dr. J. Indovino at CIM for the SEM determinations.

**Registry No.** Fe, 7439-89-6; $FeBr_2$, 7789-46-0; $FeBr_3$, 10031-26-2; $RuBr_3$, 14014-88-1; Ru, 7440-18-8; $AlBr_3$, 7727-15-3; Al, 7429-90-5; $(Ph)_2C(Br)CH_2Br$, 40957-21-9; $(Ph)_2C{=}CH_2$, 530-48-3; $(Ph)_2C{=}CHBr$, 13249-58-6.

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[8] Collman and Kochi's experiments were carried out in homogeneous systems, at room temperature, and with a ratio of substrate to catalyst much higher than ours. When we performed reactions of 1 with the homogeneous catalyst $Fe(CO)_5$ in a ratio 1:1, the only product was 1,1-diphenylethene.

[9] Egger, K. W. *J. Am. Chem. Soc.* **1969**, *91*, 2867.

[10] Burger, B. J.; Thompson, M. E.; Cotter, W. D.; Bercaw, J. E. *J. Am. Chem. Soc.* **1990**, *112*, 1566.

[11] Köster, R.; Binger, P. *Adv. Inorg. Chem. Radiochem.* **1965**, *7*, 263.

[12] Reactions performed with Li and BuLi as catalysts gave 1,1-diphenylethene as the major product.

[13] Perrin, D. D.; Armarengo, W. L. F.; Perrin, D. R. *Purification of Laboratory Chemicals*, 2nd ed.; Pergamon Press: Oxford, 1980, pp 158, 279.