

Dehalogenation of Polychloroarenes with HSiEt_3 Catalyzed by an Homogeneous Rhodium–Triphenylphosphine System

Miguel A. Esteruelas,^{*,†} Juana Herrero,^{*,‡} Francisco M. López,[‡] Marta Martín,[†] and Luis A. Oro[†]

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-CSIC, 50009-Zaragoza, Spain, and Departamento de Química, Universidad de Cantabria, 39005-Santander, Spain

Received October 29, 1998

Summary: In the presence of HSiEt_3 , the rhodium system formed by addition of PPh_3 to $[\text{Rh}(\mu\text{-Cl})(\text{COE})_2]_2$ (COE = cyclooctene) simultaneously catalyzes the dehalogenation of polychloroarenes and the formation of Et_3SiCl .

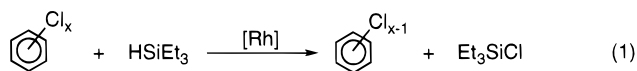
The reductive dehalogenation of aryl halides is of significant interest in connection with the neutralization of toxic polychloroarenes in the environment.¹ However, only a limited number of methods employing homogeneous transition metal catalysts have been reported.²

The catalyst formed from $\text{RhCl}_3(\text{py})_3$ and NaBH_4 in dimethylformamide has been used for the reduction of chlorobenzene to benzene with molecular hydrogen.³ Imai et al.⁴ have observed that in the presence of Pd(II) salts the C–Cl bond of chloroarenes is cleaved to give the corresponding arenes by hydrogen transfer from secondary cyclic amines. Magnesium dihydride and sodium hydride have been also used in the presence of nickel⁵ and lanthanum.⁶ Rhodium(III) biphasic and phase-transfer-catalyzed hydrogenolysis of chloroarenes under exceptionally mild conditions have been reported by Grushin and Alper,⁷ and the reduction of aryl chlorides with methanol–alkali or sodium formate in the presence of palladium complexes of 1,3-bis(diisopropylphosphino)propane has been described by Milstein and co-workers.⁸ In addition, it should be mentioned that mono- and polychloroarenes are reduced into the corresponding cycloalkanes by reaction with molecular hydrogen, in the presence of Et_3N and catalytic amounts of $[\text{Rh}(\eta^5\text{-C}_5\text{Me}_5)\text{Cl}_2]_2$.⁹

New nontoxic, economical, simple, and selective reducing systems are in constant demand. Thus, Chatgililoglu and co-workers¹⁰ have recently reported the use of an heterogeneous $\text{Et}_3\text{SiH}/\text{PdCl}_2$ system for the dehalogenation of chlorobenzene. The reaction also leads to Et_3SiCl , which is a valuable intermediate in the silicone industry and a useful reagent in organic synthesis.

In general, organosilicon halides have been prepared by group VIII metal catalyzed reactions using a variety of alkyl halides.¹¹ In particular, PdCl_2 has been employed as a catalyst for the chlorination of the silicon hydride moiety with carbon tetrachloride.¹² Kunai, Ishikawa, and co-workers have recently found that the treatment of organohydrosilanes with 2 equiv of CuCl_2 in the presence of CuI gives also organochlorosilanes in high yields.¹³

In this note we report a new rhodium homogeneous catalytic system, which simultaneously catalyzes the dechlorination of polychloroarenes and the formation of Et_3SiCl , according to eq 1.



The catalytic reactions were carried out at 78 °C, using *p*-xylene or alternatively the polychloroarene as solvent. The catalyst was generated in situ by reaction of the dimer $[\text{Rh}(\mu\text{-Cl})(\text{COE})_2]_2$ (COE = cyclooctene) with triphenylphosphine, and its homogeneity was proved by addition of mercury,¹⁴ which does not produce significant changes in the catalytic activity.

The system catalyzes the selective dechlorination of 1,2,4-trichlorobenzene to 1,2-dichlorobenzene and subsequently the dechlorination of the latter substrate to chlorobenzene and benzene. Although the formation of 1,3- and 1,4-dichlorobenzene is not observed during the dechlorination of 1,2,4-trichlorobenzene, both substrates

[†] Universidad de Zaragoza-CSIC.

[‡] Universidad de Cantabria.

(1) Entwistle, I. D.; Wood, W. W. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; Vol. 8, Chapter 4.7.

(2) (a) Grushin, V. V.; Alper, H. *Chem. Rev.* **1994**, *94*, 1047. (b) Chaloner, P. A.; Esteruelas, M. A.; Joó, F.; Oro, L. A. *Homogeneous Hydrogenation*; Kluwer Academic Publishers: Dordrecht, 1994; Chapter 4, Section 4.12.

(3) Love, C. J.; McQuillin, F. J. *J. Chem. Soc., Perkin Trans. 1* **1973**, 2509.

(4) Imai, H.; Nishiguchi, T.; Tanaka, M.; Fukuzumi, K. *J. Org. Chem.* **1977**, *42*, 2309.

(5) Carfagna, C.; Musco, A.; Pontellini, R.; Terzoni, G. *J. Mol. Catal.* **1989**, *54*, L23.

(6) Qian, Ch.; Zhu, D.; Gu, Y. *J. Mol. Catal.* **1990**, *63*, L1.

(7) Grushin, V. V.; Alper, H. *Organometallics* **1991**, *10*, 1620.

(8) Ben-David, Y.; Gozin, M.; Portnoy, M.; Milstein, D. *J. Mol. Catal.* **1992**, *73*, 173.

(9) Ferrughelli, D. T.; Horváth, I. T. *J. Chem. Soc., Chem. Commun.* **1992**, 806.

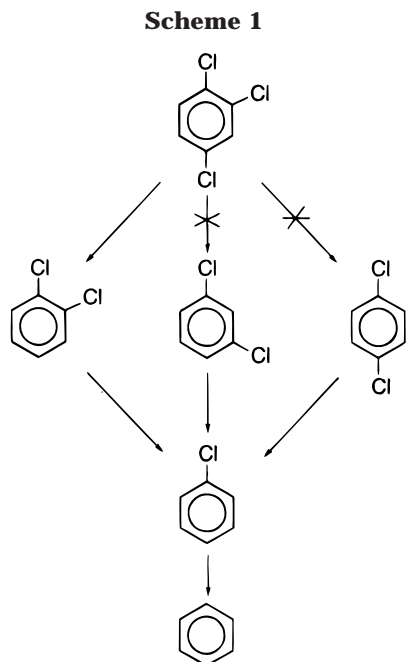
(10) Boukherroub, R.; Chatgililoglu, C.; Manuel, G. *Organometallics* **1996**, *15*, 1508.

(11) (a) Sommer, L. H.; Citron, J. D. *J. Org. Chem.* **1967**, *32*, 2470. (b) Citron, J. D.; Lyons, J. E.; Sommer, L. H. *J. Org. Chem.* **1969**, *34*, 638.

(12) (a) Seyferth, D.; Prud'homme, C. C.; Wang, W.-L. *J. Organomet. Chem.* **1984**, *277*, 203. (b) Corey, J. C.; John, C. S.; Ohmsted, M. C.; Chang, L. S. *J. Organomet. Chem.* **1986**, *304*, 93. (c) Igarashi, Y.; Kabe, Y.; Hagiwara, T.; Ando, W. *Tetrahedron* **1992**, *48*, 89.

(13) (a) Kunai, A.; Kawakami, T.; Toyoda, E.; Ishikawa, M. *Organometallics* **1992**, *11*, 2708. (b) Ishikawa, M.; Toyoda, E.; Ishii, M.; Kunai, A.; Yamamoto, Y.; Yamamoto, M. *Organometallics* **1994**, *13*, 808.

(14) Anton, D. R.; Crabtree, R. H. *Organometallics* **1983**, *2*, 855.



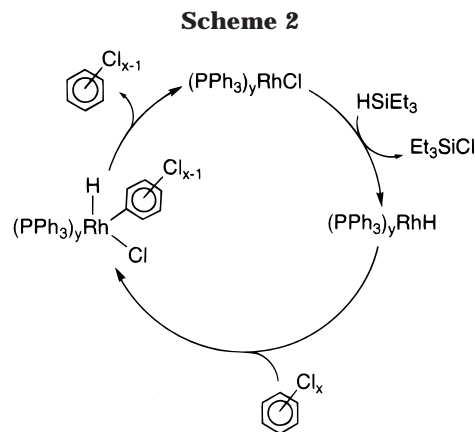
can be readily and selectively dehalogenated to chlorobenzene (Scheme 1).

The yield of the reaction of dechlorination of 1,2,4-trichlorobenzene does not depend of the solvent used, *p*-xylene or the chloroarene. However, in *p*-xylene, the dehalogenation rate is a function of the used Rh:PPh₃ molar ratio. The best results were obtained for a Rh:PPh₃ molar ratio of 1:3. For both 1:1.5 and 1:4 molar ratios, a decrease of the catalytic activity was observed (Table 1).

Complex RhCl(PPh₃)₃ is also an effective catalyst for the dehalogenation of 1,2,4-trichlorobenzene. Thus, using the polychlorobenzene as solvent, the formation of 1,2-dichlorobenzene in an amount similar to that found in the presence of [Rh(μ -Cl)(COE)₂]₂ and 6 equiv of phosphine was observed, after 65 min. This suggests that, under the catalytic conditions, the addition of triphenylphosphine to [Rh(μ -Cl)(COE)₂]₂ affords the Wilkinson's catalyst.

Equation 1 and the results shown in Table 1 can be rationalized according to the reaction sequence shown in Scheme 2. The formation of Et₃SiCl and metal-hydride compounds by reaction of chloro complexes and silanes,¹⁵ as well as the oxidative addition of aryl halides to unsaturated metallic fragments,¹⁶ is a well-known process.

The exclusive substitution of the chlorine situated in position 4 during the dehalogenation of 1,2,4-trichlo-



robenzene merits to be pointed out, because previous studies on the oxidative addition of 1,2,4-trichlorobenzene to phosphine–nickel(0) complexes show that the addition of the 4-Cl–C bond is less favored than the oxidative addition of the 2-Cl–C bond.¹⁷

In addition, it should be noted that the dechlorination of 1,2-dichlorobenzene is significantly slower and less selective than the dehalogenation of the related 1,3- and 1,4-isomers (Table 1). These observations indicate that the dechlorination of chloroarenes containing chlorines in adjacent positions is more difficult than the dehalogenation of those containing chlorines in nonadjacent positions. This difficulty could be related to the capacity for coordinating to the catalyst of the chlorine situated in the position adjacent to the activated chlorine. The coordination could occur before the Cl–C activation or/and after the cleavage of the Cl–C bond. In the first case the dihaloarene should act as a chelating *ortho*-dihalobenzene ligand,¹⁸ while in second case the dichloroarene should give rise to a σ -bonded aryl group with an *ortho*-chlorine secondary bond.¹⁹

In conclusion, we report a new and effective homogeneous catalytic system for the dehalogenation of polychloroarenes to benzene, with triethylsilane as the source of hydrogen. The reactions occur under mild conditions and without side products. Furthermore, with regard to the methods previously reported,^{3–9} the use of triethylsilane has the advantage of the formation of Et₃SiCl, which involves a significant effort economy.

Experimental Section

General Considerations. All manipulations were conducted with rigorous exclusion of air. *p*-Xylene, 1,2,4-trichlorobenzene, 1,2-dichlorobenzene, 1,3-dichlorobenzene, and chlorobenzene were dried by known procedures and distilled under argon prior to use. Triethylsilane (Fluka), *n*-octane (Merck), and 1,4-dichlorobenzene (Fluka) were used without further purification. [Rh(μ -Cl)(COE)₂]₂ was prepared by a published method.²⁰

The analysis of the products of the reactions was carried out on a Hewlett-Packard 6890 series gas chromatograph with a flame ionization detector, using a 100% cross-linked methyl

(15) See for example: (a) Chalk, A. J. *Chem. Commun.* **1969**, 1207. (b) Bennett, M. A.; Charles, R.; Fraser, P. J. *Aust. J. Chem.* **1977**, *30*, 1201. (c) Blackburn, S.; Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Chem. Res.* (5) **1980**, 170. (d) Blackburn, S. N.; Haszeldine, R. N.; Parish, R. V.; Setchfield, J. H. *J. Organomet. Chem.* **1980**, *192*, 329. (e) Fernández, M. J.; Bailey, P. M.; Bentz, P. O.; Ricci, J. J.; Koetzle, T. F.; Maitlis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 5458. (f) Campion, B. K.; Heyn, R. H.; Tilley, T. D. *J. Chem. Soc., Chem. Commun.* **1992**, 1201. (g) Aizenberg, M.; Milstein, D. *J. Chem. Soc., Chem. Commun.* **1994**, 411.

(16) See for example: (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Louie, J.; Paul, F.; Hartwig, J. F. *Organometallics* **1996**, *15*, 2794. (c) Haarman, H. F.; Ernsting, J. M.; Kranenburg, M.; Kooijman, H.; Veldman, N.; Spek, A. L.; Van Leenwen, P. W. N. M.; Vrieze, K. *Organometallics* **1997**, *16*, 887. (d) Casado, A. L.; Espinet, P. *Organometallics* **1998**, *17*, 954.

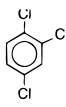













(17) Fahey, D. R. *J. Am. Chem. Soc.* **1970**, *92*, 402.

(18) Crabtree, R. H.; Faller, J. W.; Mellea, M. F.; Quirk, J. M. *Organometallics* **1982**, *1*, 1361.

(19) García, M. P.; Jimenez, M. V.; Cuesta, A.; Siurana, C.; Oro, L. A.; Lahoz, F. J.; Lopez, J. A.; Catalan, M. P.; Tripicchio, A.; Lanfranchi, M. *Organometallics* **1997**, *16*, 1026.

(20) Van der Ent, A.; Onderdelinden, A. L. *Inorg. Synth.* **1973**, *14*, 93.

Table 1. Dechlorination of Polychloroarenes with HSiEt₃ Catalyzed by [Ru(μ -Cl)(COE)₂]₂/*n*PPh₃

Polychloroarenes	Rh:PPh ₃	Solvent	arene	time (min)	yield of arene = yield of Et ₃ SiCl (%)
	1:1.5	<i>p</i> -xylene		65	11
	1:3	<i>p</i> -xylene		65	96
	1:4	<i>p</i> -xylene		65	78
	1:3	1,2,4-Cl ₂ C ₆ H ₃		65	90
	1:3	1,2-Cl ₂ C ₆ H ₄	 + 	108	61 ^a
				429	97 ^a
	1:3	1,3-Cl ₂ C ₆ H ₄		88	99
	1:3	<i>p</i> -xylene		52	92
	1:3	ClC ₆ H ₅		88	93

^a Yield of Et₃SiCl.

silicone gum column (30 m × 0.25 mm, with 0.25 μm film thickness) and *n*-octane as the internal standard. The oven conditions were 35 °C (hold 6 min) to 110 °C @ 7 °C/min (hold 4 min).

The reaction products were identified by comparison of their retention times with those observed for pure samples.

Procedure. The dehalogenation reactions were carried out at constant temperature in a two-necked flask fitted with a condenser and containing a magnetic stirring bar. The second neck was capped with a Suba seal to allow samples to be removed by syringe without opening the system. Two reaction conditions were used: (i) with *p*-xylene as solvent and (ii) with the polychloroarene as solvent.

(i) A 25.1 mg (0.035 mmol) sample of [Rh(μ -Cl)(COE)₂]₂ was dissolved in 3 mL of a *p*-xylene solution containing 0.21 mmol of triphenylphosphine, 2.4 mmol of polychloroarene, 2.4 mmol

of triethylsilane, and 150 mg of *n*-octane. The flask was then immersed in a bath at 78 °C, and the reaction solution was magnetically stirred.

(ii) A 25.1 mg (0.035 mmol) sample of [Rh(μ -Cl)(COE)₂]₂ was dissolved in 3 mL of a polychloroarene solution containing 0.21 mmol of triphenylphosphine, 2.4 mmol of triethylsilane, and 150 mg of *n*-octane. The flask was then immersed in a bath at 78 °C, and the reaction solution was magnetically stirred.

Acknowledgment. We thank the DGICYT (Projects PB94-1186 and PB95-0806, Programa de Promoción General del Conocimiento) and the Comisión Mixta Caja Cantabria, Universidad de Cantabria, for financial support.

OM9808864