Organometallics **1996,** 15, 4657−4659

^{2}H NMR Investigation of the Rhodium-Catalyzed Deuterioformylation of 1,1-Diphenylethene: Evidence for the Formation of a Tertiary Alkyl−Metal Intermediate

Raffaello Lazzaroni,[*,†] Gloria Uccello-Barretta,[†] Simone Scamuzzi,[†]
Roberta Settambolo,[‡] and Aldo Caiazzo[†]

Centro di Studio del CNR per le Macromolecole Stereordinate ed Otticamente Attive, Dipartimento di Chimica e Chimica Industriale, Università di Pisa, via Risorgimento, 35, 56126 Pisa, Italy, and Istituto di Chimica Quantistica ed Energetica Molecolare del CNR, Università di Pisa, via Risorgimento, 35, 56126 Pisa, Italy

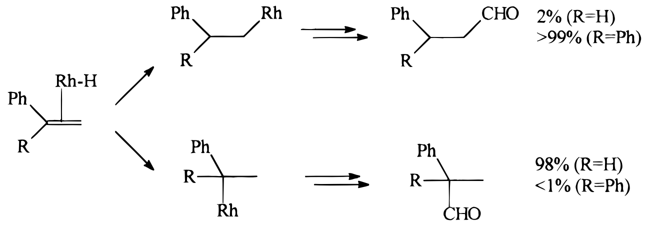
Received June 10, 1996[⊗]

Summary: Rhodium-catalyzed deuterioformylation of 1,1-diphenylethene at partial substrate conversion (15 and 34%) at 100 °C and 100 atm (CO/D_2 = 1:1) gives, in addition to the expected 3,3-diphenylpropanal-1,3-d_2, the monodeuterated olefin 1,1-diphenylethene-2-d_1 and the labeled normal aldehyde arising from this substrate. The above compounds have been detected by ^{2}H NMR analysis of the crude reaction mixtures. These findings demonstrate that a tertiary alkyl−rhodium intermediate is formed, under hydroformylation conditions, in a larger amount than the normal isomer, but it undergoes β-hydride elimination only without formation of the branched aldehyde.

Introduction

It is known that the rhodium-catalyzed hydroformylation of vinyl aromatic[1−4] and heteroaromatic[5−7] olefins is characterized by high or complete α-regioselectivity. The prevalence of the branched aldehyde is usually attributed[1,3,4] to the strongly favored formation of the branched alkyl−rhodium intermediate stabilized by a polarizable aromatic group on the carbon bonded to the metal. In this frame it is surprising that, in the case of vinylidenic olefins, such as α-methylstyrene or 1,1-diphenylethene, selective formation of the linear aldehyde has been obtained.[8,9] The branched aldehyde was formed in very low amount (<1%) in spite of the fact that one or two aromatic groups are present on the carbon linked to the metal, in the corresponding tertiary alkyl−rhodium intermediate (Scheme 1).

Scheme 1



Indeed, very few tertiary alkyl−metal compounds have been described; some of them contain a *tert*-butyl group linked to the metal;[10−12] some others are believed to be formed by isomerization of the primary alkyl−metal via reversible hydrogen 2,3-migration.[13,14]

As far as the hydroformylation of vinyl aromatic substrates is concerned, it has been shown that, at high temperature, the branched intermediate, unlike the linear one, undergoes β-hydride elimination, accounting for the α-regioselectivity decreasing with temperature. The different behavior of the two alkyl−metal intermediates has been clearly evidenced by deuterioformylation experiments at partial substrate conversion,[3,15,16] the reaction mixture being directly analyzed by ^{2}H NMR spectroscopy.[3c,17] This approach, utilized for different vinyl substrates, constitutes an excellent method to obtain direct information on both the nature and the fate of the alkyl−metal intermediates involved in the hydroformylation process.

In order to gain more insight into the “anomalous” β-regioselectivity observed for vinylidenic olefins with respect to vinyl ones of analogous structure, we carried out an investigation of the rhodium-catalyzed deuterioformylation of 1,1-diphenylethene (**1**) (Scheme 2) at partial substrate conversion, analyzing the crude reaction mixtures directly by ^{2}H NMR spectroscopy.

Results and Discussion

As substrate **1** is unreactive at room temperature, the deuterioformylation experiments were carried out in

---

[†] Dipartimento di Chimica e Chimica Industriale.

[‡] Istituto di Chimica Quantistica ed Energetica Molecolare del CNR.

[⊗] Abstract published in *Advance ACS Abstracts,* September 15, 1996.

(1) Ojima, I. *Chem. Rev.* **1988**, *88*, 1011.

(2) Tanaka, M.; Watanabe, Y.; Mitsuda, T.; Takigami, Y. *Bull. Chem. Soc. Jpn.* **1974**, *47*, 1968.

(3) (a) Lazzaroni, R.; Raffaelli, A.; Settambolo, R.; Bertozzi, S.; Vitulli, G. *J. Mol. Catal.* **1989**, *50*, 1. (b) Raffaelli, A.; Pucci, S.; Settambolo, R.; Uccello-Barretta, G.; Lazzaroni, R. *Organometallics* **1991**, *10*, 3892. (c) Uccello-Barretta, G.; Lazzaroni, R.; Settambolo, R.; Salvadori, P. *J. Organomet. Chem.* **1991**, *417*, 111.

(4) Van Rooy, A.; Orij, E. N.; Kamer, P. C. J.; Van Leeuwen, P. W. N. M. *Organometallics* **1995**, *14*, 34.

(5) Lapidus, A. L.; Rodin, A. P.; Pruidze, I. G.; Ugrak, B. I. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1990**, *7*, 1661; *Chem. Abstr.* **1990**, *113*, 171816. (b) Kalck, P.; Serein-Spiran, F. *New J. Chem.* **1989**, *13*, 515.

(6) Browning, A. F.; Bacon, A. D.; White, C. *J. Mol. Catal.* **1993**, *83*, L11.

(7) (a) Settambolo, R.; Pucci, S.; Bertozzi, S.; Lazzaroni, R. *J. Organomet. Chem.* **1995**, *489*, C50. (b) Settambolo, R.; Caiazzo, A.; Lazzaroni, R. *J. Organomet. Chem.* **1996**, *506*, 337.

(8) Matsui,Y.; Orchin, M. *J. Organomet. Chem.* **1983**, *246*, 57.

(9) (a) Botteghi, C.; Paganelli, S.; Bigini, L.; Marchetti, M. *J. Mol. Catal.* **1994**, 93, 279. (b) Botteghi, C.; Cazzolato, L.; Marchetti, M.; Paganelli, S. *J. Org. Chem.* **1995**, *60*, 6612.

(10) Tamaki, A.; Magennis, S. A.; Kochi, J. K. *J. Am. Chem. Soc.* **1974**, *96*, 6140.

(11) Reger, D. L.; Garza, D. G.; Baxter, J. C. *Organometallics* **1990**, *9*, 873.

(12) Reger, D. L.; Garza, D. G.; Libioda, L. *Organometallics* **1992**, *11*, 4285.

(13) Reger, D. L.; Culbertson, E. C. *Inorg. Chem.* **1977**, *16*, 3104.

(14) Bennett, M. A.; Crisp, G. T. *Organometallics* **1986**, *5*, 1792.

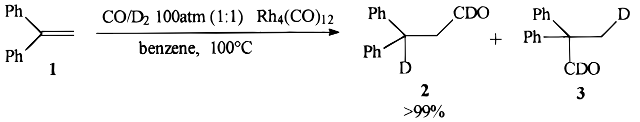
(15) (a) Lazzaroni, R.; Uccello-Barretta, G.; Benetti, M. *Organometallics* **1989**, *8*, 2323. (b) Casey, C. P.; Petrovich, L. M. *J. Am. Chem. Soc.* **1995**, *117*, 6007.

(16) Consiglio, G. *Organometallics* **1988**, *7*, 778.

(17) Lazzaroni, R.; Settambolo, R.; Uccello-Barretta, G. *Organometallics* **1995**, *14*, 4644.

S0276-7333(96)00462-1 CCC: $12.00

Scheme 2



benzene at 100 °C, constant total gas pressure of 100 atm (CO/D_2 = 1/1) and employing $Rh_4(CO)_{12}$ as the catalyst precursor. The substrate conversion and the composition of the reaction mixtures were evaluated by GC analysis, using benzophenone as internal standard. At the two selected conversion degrees (15 and 34%), both the regioselectivity and chemoselectivity were high, the former being greater than 99% in favor of the linear aldehyde, the latter ranging from 98 to 95% at 15 and 34% conversion, respectively. (The signals, of low intensity, present at 1.21 and 3.68 ppm in the ^2H NMR spectrum of the crude product of the reaction at 34% conversion have been assigned to 1,2-dideuterio-1,1-diphenylethane.) The determination of HD and/or H_2 species in the residual reaction gases was carried out by MS analysis, following the same procedure as for the deuterioformylation of styrene.[3]

As reported by many authors for the hydroformylation, the deuterioformylation of **1** in the presence of $Rh_4(CO)_{12}$ gives the linear aldehyde as exclusive reaction product. In fact, in the ^2H NMR spectra relative to the deuterioformylation experiments at 15% conversion (Figure 1), two signals at 9.07 and 4.08 ppm are present due to the deuterium atom of the aldehyde group and to the deuterium on the carbon in α-position to the phenyl groups, respectively.

Surprisingly, a resonance of high intensity is present at 5.16 ppm which can be assigned to a deuterium atom bonded to the terminal carbon atom of 1,1-diphenylethene (**1**-*2*-d_1).

As reported in Scheme 3, the branched alkyl–rhodium intermediate, **t**, gives, via β-hydride elimination, the complex π_2 in which the deuterated olefin **1**-*2*-d_1 undergoes fast exchange with the unlabeled one, **1** (the prevalent species at low conversion). As in the residual reaction gases HD is already present at low conversion, it must be concluded that the reaction of rhodium hydride with D_2 to give rhodium deuteride and HD is a fast process with respect to the aldehyde formation.

As a consequence, the tertiary alkyl–rhodium intermediate, **t**, originates the monodeuterated olefin **1**-*2*-d_1 and HD and regenerates the π_1 complex. On the basis of the relative intensities of the deuterium signals of the **1**-*2*-d_1 olefin and aldehydic species, we can also establish that at low conversion (~15%) ~2 mol of olefin is formed for each mole of aldehyde. On this basis, we can assume that the branched intermediate is formed in a larger amount with respect to the expected linear isomer, **p**, but the formation of the acyl–rhodium intermediate from the tertiary alkyl to give the corresponding branched aldehyde is probably sterically hindered. The ^2H NMR spectra of the deuterioformylation run at 34% conversion shows, in addition to the signals already present at low conversion, a new signal at 2.38 ppm assigned to a deuterium atom bonded to the carbon atom in α-position to the carbonyl group. This aldehydic species arises from the deuterioformylation of the monodeuterated olefin **1**-*2*-d_1 whose amount in solution increases with the conversion. This signal, although of very low intensity, is already present in the ^2H NMR spectrum of the deuterioformylation run at 15% conversion.

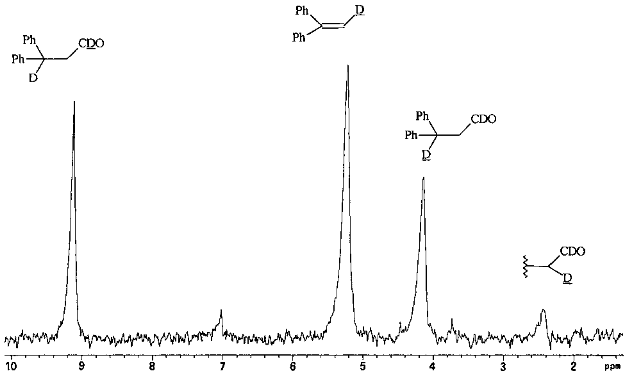


Figure 1. 2H NMR spectrum (46 MHz, 25 °C, C_6D_6 as external standard) of the crude reaction mixture in benzene, obtained by deuterioformylation of 1,1-diphenylethene (**1**) at 100 °C and 15% substrate conversion.

The above findings clearly confirm the efficacy and also simplicity of our approach for the understanding of the mechanistic aspects of the hydroformylation. In fact, it must be stressed that the classical approach based on the sole analysis of regioisomeric ratios would have led to the erroneous conclusion that no tertiary metal–alkyl intermediate was formed in the hydroformylation of 1,1-diphenylethene, as no branched aldehyde is obtained.

It is of interest to compare these results with those previously reported for the deuterioformylation of styrene under the same experimental conditions (100 °C, $Rh_4(CO)_{12}$). For this last substrate, the formation of the primary alkyl is not reversible as it is completely transformed into the linear aldehyde. On the contrary, the secondary rhodium–alkyl intermediate partially undergoes β-hydride elimination and partially generates the branched aldehyde. In the case of **1**, the formation of the tertiary alkyl is reversible and gives β-hydride elimination only.

In conclusion, the ^2H NMR analysis of crude hydroformylation products coming from vinyl or vinylidenic aromatic substrates is a direct and simple way to detect the different behavior of a primary, secondary, or tertiary metal–alkyl intermediate related to the β-hydride elimination under typical rhodium-catalyzed hydroformylation conditions.

Experimental Section

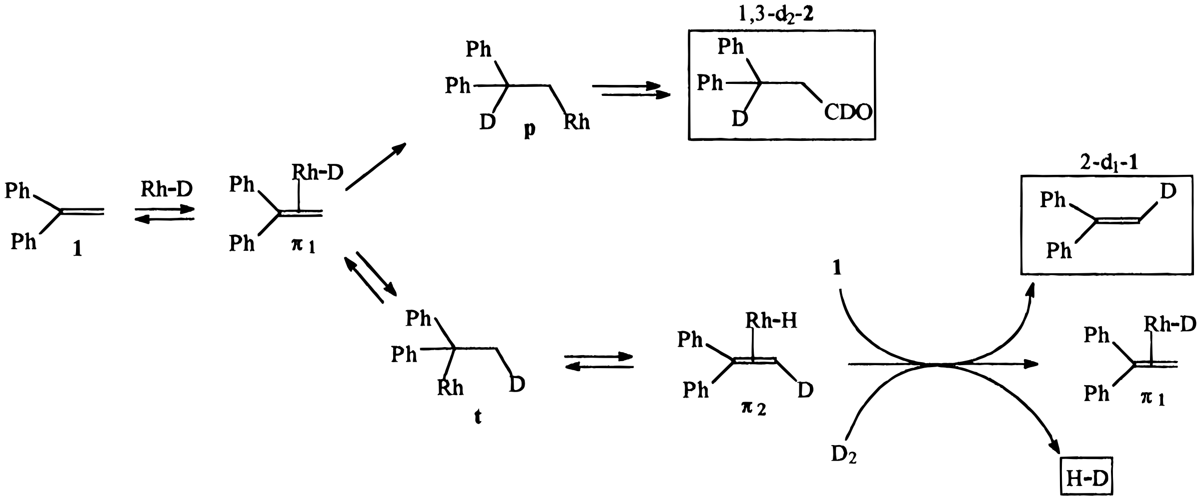
Benzene was dried over molecular sieves and distilled under nitrogen. The starting 1,1-diphenylethene was commercially available. $Rh_4(CO)_{12}$ was prepared as reported in the literature.[18] GC analyses of the reaction mixtures were performed on a Perkin-Elmer 8500 chromatograph equipped with a 12 m × 0.22 mm BP1 capillary column, using helium as carrier gas. ^2H NMR spectra of the crude products in benzene were carried out on a Varian VXR 300 spectrometer operating at 46 MHz for ^2H. Chemical shifts were referred to C_6D_6 as external standard.

Hydroformylation or Deuterioformylation of 1,1-Diphenylethene: General Procedure. A solution of 1,1-diphenylethene (500 mg, 2.78 mmol) and $Rh_4(CO)_{12}$ (20 mg, 0.027 mmol) in benzene (5 mL) was introduced by suction into

---

[18] McCleverty, J.; Wilkinson, G. *Inorg. Synth.* **1966**, *8*, 211.

Scheme 3



an evacuated 25 mL stainless steel autoclave. Carbon monoxide was introduced, the autoclave was then rocked and heated to 100 °C, and hydrogen or deuterium was rapidly introduced up to 100 atm total pressure. When the gas absorption reached the value corresponding to the fixed conversion,[19] the reaction mixture was siphoned out. The degree of conversion was measured by GLC, using benzophenone as internal standard.

Acknowledgment. This work was partially supported by the Ministero dell'Università e della Ricerca Scientifica e Tecnologica (60 and 40% funds).

OM960462E

---

[19] Substrate conversion of 15 and 34% were reached after 3 and 10 h, respectively.