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Reversibility of Metal–Alkyl Intermediate Formation in the Rhodium-Catalyzed Deuterioformylation of 1-Hexene

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Rhodium-catalyzed deuterioformylation of 1-hexene, at partial substrate conversion, has been investigated at different temperatures and pressures, and the incorporation of deuterium in the residual substrate has been detected by MS and ^{2}H NMR analyses. At room temperature, 1-hexene does not isomerize to internal olefins nor is deuterium present in the residual 1-hexene. At high temperature, 1-hexene incorporates deuterium mainly at carbon atom C_2 and isomerization to 2-hexene, nondeuterated or deuterated at carbon atom C_1, occurs. These findings indicate that the formation of alkylrhodium intermediates is not reversible at room temperature. At high temperature a β-hydride elimination process occurs to an extent which is greater for the branched than for the linear alkyl accounting for the influence of the reaction parameters on the regio- and chemoselectivity of the reaction.

Introduction

Metal hydride addition to the olefinic double bond to give the isomeric metal–alkyl intermediates as well as their rearrangement into the olefin and metal hydride are well-known processes in organometallic chemistry.[1-4] They are also regarded as important steps in many homogeneously catalyzed organic reactions, namely, isomerization, hydrogenation, and hydroformylation of unsaturated substrates.[5-11] For example, in the rhodium- and cobalt-catalyzed hydroformylation of 1-alkenes, the reversibility of formation of the metal–alkyl intermediate accounts for the isomerization of the substrate as well as for the intermolecular and intramolecular protium–deuterium exchange observed in the hydroformylation of labeled alkenes and in the deuterioformylation of unlabeled ones.[12-15]

A recent investigation of the rhodium-catalyzed styrene deuterioformylation showed that a β-hydride elimination process, which occurs selectively for the branched alkylrhodium intermediate, strongly affects the regioselectivity of the reaction.[16,17] By contrast, no systematic studies have been reported on the factors affecting the rearrangement of the metal–alkyl intermediate in the hydroformylation of alkyl olefins.

In order to gain a deeper insight into this aspect of the reaction, which could be of relevance for the regioselectivity of 1-alkene hydroformylation, the deuterioformylation of 1-hexene at various temperatures and gas pressures has been investigated. All the experiments were performed at partial substrate conversion, and the unconverted substrate was carefully analyzed for the presence of isomerized olefins and for incorporation of deuterium in both the terminal and internal olefin. Deuterium content was determined by GC–MS techniques; deuterium distribution was obtained by ^{2}H NMR spectroscopy.

Results

Deuterioformylation of 1-hexene was carried out in benzene at 20, 80, and 100 °C, under 80 or 140 atm of CO and D_2 (1:1) at constant pressure (±2 atm). All experiments were stopped at partial 1-hexene conversion after approximately the same drop of gas pressure corresponding to a 35–40% substrate conversion to aldehydes. Polymeric compounds and hydrogenation products of olefins or aldehydes were not observed. Composition of reaction mixtures was determined by GC analysis. Conversion of 1-hexene to 2-hexenes and aldehydes was evaluated by GC analysis using benzene, the reaction solvent, as internal standard.

The results, reported in Table I, show the following features: 1-hexene conversion to aldehydes is very similar in all the experiments (35–40%), while the isomerization of 1-hexene to (*E*)- and (*Z*)-2-hexene increases with increasing temperature and decreasing gas pressure. Thus the chemoselectivity to aldehydes is practically complete at 20 °C, but it strongly decreases at 100 °C and 80 atm, the isomerization (52%) predominating over the aldehyde formation (48%) under these experimental conditions. The regioselectivity of reaction, i.e. the isomeric ratio (N/B) between *n*-heptanal (N) and 2-methylhexanal (B), is low at room temperature (56/44) but increases noticeably at higher temperature (74/26 at 100 °C and 140 atm).

No effect of gas pressure on the regioselectivity was observed at 20 °C, and its influence was also very low at higher temperatures (76/24 at 100 °C and 80 atm).

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Table I. Chemo- and Regioselectivity in the Rhodium-Catalyzed Deuterioformylation of 1-Hexene, after Partial Conversion,[a] as a Function of Temperature and Gas Pressure[b]

			composition of reaction products,[c] mol %						
			olefins			aldehydes			
T, °C	P_{CO}, atm	P_{H_2}, atm	E_1	(*E*)-E_2	(*Z*)-E_2	N	B	$(N + B)/E_2$[d]	N/B[e]
20	70	70	63	...	...	21	16	100/...	56/44
20	40	40	64	...	...	20	15	100/..	56/44
80	70	70	59	4.5	1.5	23	12	85/15	66/34
100	70	70	46	11	3	30	10	74/26	74/26
100	40	40	23	30	10	28	9	48/52	76/24

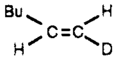
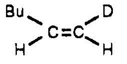
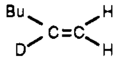
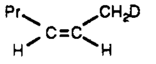
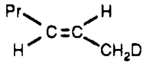
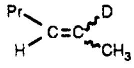
[a] The amount of 1-hexene (E_1) converted to aldehydes (N + B) was similar for all runs (about 35–40%). [b] Reaction conditions: 2.0 g of 1-hexene, 10.0 g of benzene, 0.5 mg of $Rh_4(CO)_{12}$. In the runs at 20 °C the amount of $Rh_4(CO)_{12}$ was 5 mg. [c] E_1 = 1-hexene; E_2 = 2-hexene; N = *n*-heptanal; B = 2-methylhexanal; accuracy ±1%. [d] Chemoselectivity. [e] Regioselectivity.

Table II. Deuterium Content via MS Analyses of 1-Hexene and 2-Hexene Recovered from the Rhodium-Catalyzed Deuterioformylation of 1-Hexene, after Partial Conversion[a]

			isotopic species distribution[b]											
			1-hexene				(*Z*)-2-hexene				(*E*)-2-hexene			
T, °C	P_{CO}, atm	P_{H_2}, atm	d_0	d_1	d_2	NDM[c]	d_0	d_1	d_2	NDM[c]	d_0	d_1	d_2	NDM[c]
20	70	70	100	...	...	...	...	...	...	...	...	...	...	...
20	70	70	100	...	...	...	...	...	...	...	...	...	...	...
80	70	70	97	3	...	0.03	27	73	...	0.73	27	73	...	0.73
100	70	70	89	11	...	0.11	49	48	3	0.54	50	47	3	0.53
100	40	40	78	21	1	0.24	65	32	3	0.38	64	33	3	0.39

[a] Composition of reaction products is reported in Table I. [b] d_0, d_1, and d_2 are respectively nondeuterated and mono- and dideuterated species; estimated accuracy ±1%. [c] Average number of deuteriums per molecule.

Table III. ^2H NMR Chemical Shifts (δ, ppm)[a] (46 MHz, CCl_4, 25 °C) of Monodeuterated Substrates[b] Originating from the Rhodium-Catalyzed Deuterioformylation of 1-Hexene

	 (*E*)-E_1-*1*-d_1	 (*Z*)-E_1-*1*-d_1	 E_1-*2*-d_1	 (*Z*)-E_2-*1*-d_1	 (*E*)-E_2-*1*-d_1	 (*E*,*Z*)-E_2-2-d_1
δ	4.84	4.90	5.69	1.93	1.98	5.27

[a] Referred to $CDCl_3$ as external standard. [b] E_1 = 1-hexene; E_2 = 2-hexene; d_1 = monodeuterated substrate.

Table IV. Deuterium Distribution, from ^2H NMR Analysis, in the 1-Hexene and (*E*)- and (*Z*)-2-Hexene Recovered from the Rhodium-Catalyzed Deuterioformylation of 1-Hexene, after Partial Conversion[a]

			deuterium content[b] at vinyl and allyl carbon atoms of							
			1-hexene				2-hexene			
			$R - C_3 - C_2 = C_1$				$R - C_3 = C_2 - C_1$			
T, °C	P_{CO}, atm	P_{H_2}, atm	C_3	C_2	C_1	NDM[c]	C_3	C_2	C_1	NDM[c]
20	70	70	...	...	...	...	...	...	...	...
20	40	40	...	...	...	...	...	...	...	...
80	70	70	...	0.02	0.01	0.03	...	...	0.73	0.73
100	70	70	...	0.08	0.03	0.11	...	0.06	0.47	0.53
100	40	40	0.01	0.18	0.05	0.24	...	0.11	0.26	0.37

[a] Composition of reaction products is reported in Table I. [b] No deuterium is present on the carbon atom of the alkyl group R (R = *n*-propyl); estimated accuracy ±3%. [c] Average number of deuterium atoms per molecule determined from MS analyses (see Table II).

3-Hexene and 2-ethylpentanal were not found among the products, so long as 1-hexene was present in the reaction mixture.

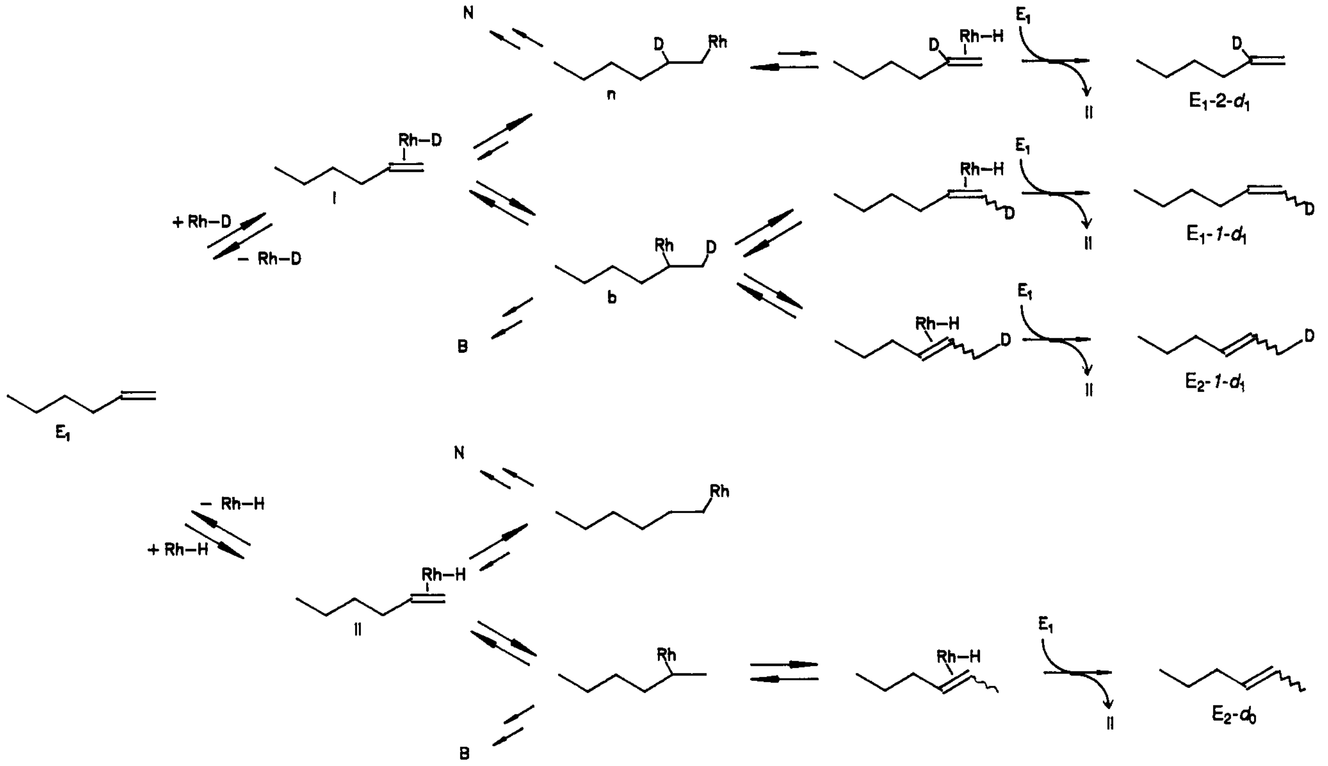
Deuterium Content and Distribution of Unconverted Hexenes. Chemically pure samples of unconverted 1-hexene and samples enriched in 2-hexene were obtained by a careful fractional distillation of the reaction mixture at atmospheric pressure through a spinning band column.

MS Analyses. The deuterium content of deuterated species in the residual olefins was determined by GC–MS analyses of both the crude reaction products and enriched samples. When the reaction was carried out at 20 °C, 2-hexene is not formed and no detectable amount of deuterated 1-hexene was observed (Table II). At higher temperatures, monodeuterio-1-hexene was formed, but less than 1% of dideuterated species was present in the unconverted substrate. The average number of deuterium atoms per molecule (NDM), in the case of 1-hexene, increased on increasing the temperature and decreasing the gas pressure.

Mono-, di-, and nondeuterated species were found for 2-hexene when the reaction was carried out at higher temperature; in contrast to what was observed for 1-hexene, the NDM decreased with increasing temperature and decreasing pressure. The amount of dideuterated species was low (<3%). The monodeuterated species predominated at 80 °C and 140 atm, whereas the nondeuterated product predominated at 100 °C and 80 atm. The distribution of deuterated species was the same for the (*E*)- and (*Z*)-2-hexene (Table II).

NMR Analysis. Deuterium distribution in 1-hexene and 2-hexene recovered from deuterioformylation experiments at high temperature was very easily determined by ^2H NMR analysis of pure or enriched samples of the olefins. The high sensitivity of ^2H NMR enabled the labeled species to be easily detected even if present in a very low

Scheme I



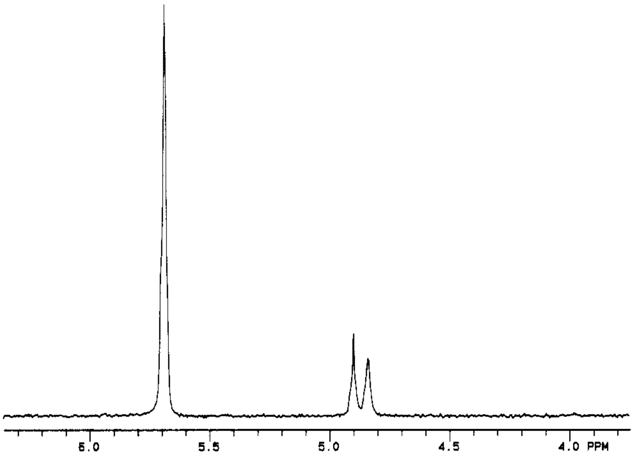


Figure 1. ^2H NMR spectrum (CCl_4, 46 MHz, 25 °C) of a pure sample of 1-hexene, recovered from the deuterioformylation experiment at 100 °C and 140 atm.

amount. ^2H NMR parameters of the deuterated olefins are reported in Table III. The absolute amount of deuterium in each position was evaluated by combining ^2H NMR data, which give the corresponding relative amount, with MS data giving the total amount of deuterium incorporated (NDM); the results are summarized in Table IV.

In Figure 1 the ^2H NMR spectrum of a pure sample of 1-hexene, recovered from the deuterioformylation experiment at 100 °C and 140 atm, is reported. Three resonances at 4.84, 4.90, and 5.69 ppm are present; according to MS data (Table II) they are due to three monodeuterated species where the deuterium is incorporated in the vinyl moiety. The signal at 5.69 ppm is due to the monodeuterated compound having the deuterium in position 2 (E_1-*2*-d_1), while the absorptions at 4.84 and 4.90 ppm are respectively due to the two geometrical isomers of monodeuterio-1-hexene ((*E*)-E_1-*1*-d_1 and (*Z*)-E_1-*1*-d_1) having the deuterium on the terminal carbon atom (Table III).

As shown in Figure 1 and reported in Table IV, in the case of 1-hexene the deuterium is incorporated almost exclusively in the vinyl moiety, no significant amount (<1%) of deuterium being present on the saturated carbon atoms. Furthermore, the amount of deuterium on position 2 is higher than on the terminal carbon atom; thus, 1-hexene-*2*-d_1 predominates over 1-hexene-*1*-d_1.

The ^2H NMR spectrum of a mixture of 1-hexene and 2-hexene, enriched in the latter, recovered from the experiments at 100 °C and 140 atm, shows in addition to the signals of monodeuterated 1-hexenes, two resonances partially superimposed at 1.93 and 1.98 ppm (Figure 2), which are respectively attributed to *Z* and *E* isomers of monodeuterated 2-hexenes (Table III). The signal of low intensity at 5.27 ppm is due to small amounts of mono- and dideuterated 2-hexenes containing a deuterium atom on the olefinic carbon in position 2 (Table IV). Therefore, in the case of 2-hexene, most of the deuterium is incorporated on the terminal carbon atom. Only at 100 °C and 80 atm is a significant amount of deuterium detectable on the carbon atom in position 2.

The formation of all monodeuterated hexenes as well as of nondeuterated (*E*)- and (*Z*)-2-hexenes can be rationalized on the basis of the reaction sequence depicted in Scheme I. The π-complex I, formed by coordination of 1-hexene to a rhodium deuteride species, gives rise to the isomeric alkylrhodium complexes. At high temperatures this step is reversible for both isomers, which yields, via a β-hydride elimination process, the π-complexes between deuterated olefins and rhodium hydride. Exchange of labeled olefins with unlabeled 1-hexene (E_1) gives the nondeuterated π-complex II and the free deuterated olefins E_1-*2*-d_1 (from the linear alkyl), (*E*)- and (*Z*)-E_1-*1*-d_1 and (*E*)- and (*Z*)-E_2-*1*-d_1 (from the branched one).

An analogous sequence from complex II accounts for the formation of unlabeled (*E*)- and (*Z*)-2-hexene (Scheme I), while complex III, originating from monodeuterated 1-hexene-*2*-d_1 and a rhodium hydride or deuteride (Scheme

Scheme II

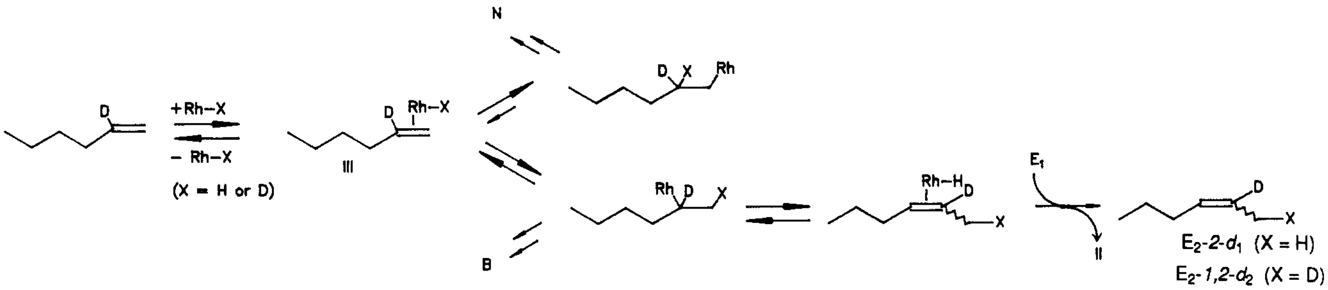


Table V. Distribution of Reaction Products[a] Arising from the Linear (n) and Branched (b) Alkylrhodium Intermediates

		products, mol %									n		b	
T, °C	P_{tot}, atm	N	B	E_1-*2*-d_1	E_1-*1*-d_1	E_2-*1*-d_1	E_2-d_0	E_2-*2*-d_1	E_2-*1,2*-d_2	E_1-d_0	N	E_n[b]	B	E_b[b]
20	140	21	16	...	...	...	...	...	...	63	56	...	44	...
80	140	20	15	1.2	0.6	4.4	1.6	...	...	57.2	53	4	27	16
100	140	30	10	3.7	1.4	6.2	6.6	0.8	0.4	40.9	50	8	17	25
100	80	28	9	4.1	1.1	10.5	25	3.5	1	17.8	32	10	10	48

[a] N = *n*-heptanal; B = 2-methylhexanal; E_1 = 1-hexene; E_2 = 2-hexene; d_0, d_1, and d_2 are respectively nondeuterated and mono- and dideuterated species. [b] E_n = E_1-*2*-d_1 + E_2-*2*-d_1 + E_2-*1,2*-d_2; E_b = E_1-*1*-d_1 + E_2-*1*-d_1 + E_2-d_0 + E_2-*2*-d_1 + E_2-*1,2*-d_2.

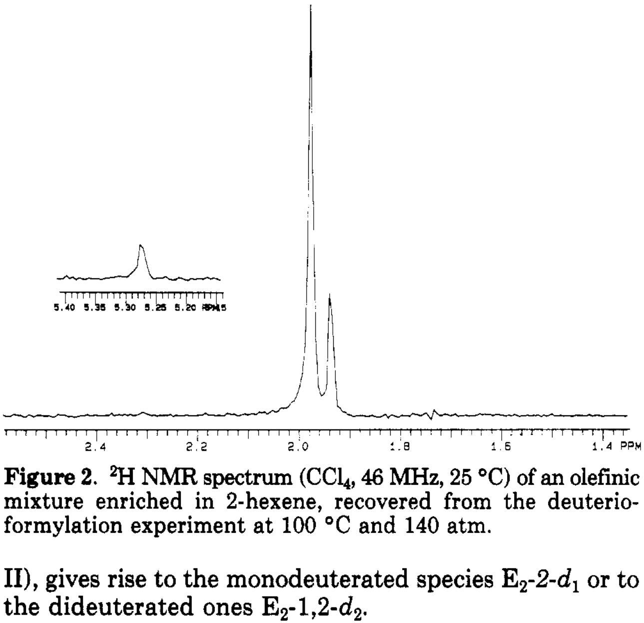


Figure 2. ^{2}H NMR spectrum (CCl$_4$, 46 MHz, 25 °C) of an olefinic mixture enriched in 2-hexene, recovered from the deuterioformylation experiment at 100 °C and 140 atm.

II), gives rise to the monodeuterated species E_2-*2*-d_1 or to the dideuterated ones E_2-1,2-d_2.

It should be noted that the predominance of nondeuterated 2-hexene over deuterated 2-hexene observed at 100 °C (Table II) indicates that the concentration of nondeuterated complex II is higher than that of I or III under these experimental conditions.

Discussion

The results of this investigation clearly show that the rearrangement of the isomeric metal–alkyl intermediates under hydroformylation conditions strongly depends on the reaction parameters as well as on the structure of the alkyl group bonded to the metal.

At low temperature no 2-hexene is found in the unconverted substrate and no deuterium is present in the residual 1-hexene. Hence the olefin addition to the metal hydride is not reversible in these conditions.

At higher temperatures (*E*)- and (*Z*)-2-hexenes, as well as monodeuterated 1-hexenes, are formed as a consequence of the metal–alkyl intermediate rearrangement (Scheme I).

The data obtained from GC, MS, and ^{2}H NMR analyses discussed above (see Tables I–IV) allow evaluation of the relative amounts of products (aldehydes[18] or hexenes) arising from the linear or the branched alkylrhodium intermediate (Table V).

At low temperature the metal alkyls are completely transformed into aldehydes (N and B), while at higher temperature they are partially converted into aldehydes and partially dissociate into rhodium hydride and olefins. It is noteworthy that the amount of rearrangement products is higher for the branched than for the linear metal alkyl.[19] In the case of the linear alkyl, the aldehyde formation predominates over rearrangement in all experiments. In contrast, for the branched alkyl rearrangement predominates over aldehyde formation in the experiments carried out at 100 °C.

As far as the regioselectivity of 1-hexene hydroformylation is concerned,[8,9,12,13,20] the above findings lead to some important conclusions. (i) At room temperature the regioselectivity of formation of isomeric aldehydes reflects the regioselectivity of formation of the metal–alkyl intermediate. The low value of regioselectivity observed under these conditions (isomeric ratio 56/44) suggests that the rate of formation of the isomeric alkylrhodium compounds is little affected by their primary or secondary structure. (ii) The different behavior of branched and linear metal alkyls toward the β-hydride elimination accounts for the increase of regioselectivity observed at high temperature. The linear alkyl is mainly converted to linear aldehyde, while the branched one partially converts into branched aldehyde and partially regenerates a π metal complex, from which both the linear and branched alkyl can again originate.

Comparison of the above results with those previously reported for the rhodium-catalyzed deuterioformylation of styrene[16,17] allows us to point out the following. (i) At low temperature the metal–alkyl formation is irreversible for styrene as well as for 1-hexene. (ii) At high temperature alkyl formation is reversible for the branched and linear

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[18] The distribution of deuterated species in the isomeric aldehydes and their characterization by MS and ^{1}H NMR analyses will be reported in details in a forthcoming paper.

[19] It is to point out that the amounts of hexenes arising from the linear alkyl do not include the 1-hexene arising from rearrangement of the nondeuterated linear alkyl. Both E_n and E_b values do not include monodeuterated 1-hexene converted into aldehydes.

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alkyl in the case of 1-hexene, but only for the branched one in the case of styrene.

These findings satisfactory explain the influence of reaction temperature on the regioselectivity. For both substrates an increase in temperature produces an increasing linear isomer, the effect being stronger in the case of styrene.[16,17]

Isomerization of metal–alkyl intermediates has been often invoked in rhodium- and cobalt-catalyzed hydroformylation of alkenes[10,14,20-23] in order to explain the influence of reaction parameters on the product distribution. However, experimental evidence for differing behavior of isomeric metal alkyls toward β-hydride elimination, during the hydroformylation of 1-alkenes is reported here for the first time.

Experimental Section

Benzene was dried over molecular sieves and distilled under nitrogen. $Rh_4(CO)_{12}$ was prepared as reported in the literature.[24] GC analysis of the deuterioformylation mixtures were performed on a Dani 6800 chromatograph equipped with 2 m × 0.4 cm columns of 10% SE30 on 60/80 mesh Chromosorb WAW DCMS or 5% UCON LB 550X on 60/80 Chromosorb WAW DCMS and a flame-ionization detector; nitrogen was used as carrier gas. The analysis of the olefinic products was also carried out by using a 8500 Perkin-Elmer gas chromatograph equipped with a 12 m × 0.22 mm BP1 capillary column, using helium as carrier gas.

Mass spectra were measured with a VG 70/70E spectrometer at 70 eV: the accelerating voltage was 6 kV, and the emission current was 100 μA. GC–MS analyses of olefinic mixtures were performed by use of the same spectrometer coupled with a DANI 3800 gas chromatograph equipped with a silica capillary column SE30 (50 m × 0.53 mm).

^2H NMR spectra were recorded in CCl_4 solutions on a Varian VXR 300 spectrometer, operating at 46 MHz for ^2H. $CDCl_3$ was used as external standard.

Deuterioformylation of 1-Hexene: General Procedure. Deuterioformylation of 1-hexene, at partial substrate conversion, was performed following a general procedure previously described for other substrates.[16] In a 50-mL evacuated stainless-steel autoclave, a solution of $Rh_4(CO)_{12}$ (0.5 mg, 6.7×10^{-4} mmol) and 1-hexene (2.0 g, 23.8 mmol) in benzene (10.0 g) was introduced by suction. Carbon monoxide was introduced to the desired pressure: the autoclave was then rocked and heated to the reaction temperature, and deuterium was rapidly introduced to the desired total pressure. When the reaction started, the drop in pressure was restored by injection of a carbon monoxide–deuterium mixture (1:1) from a high-pressure container. Progress in the reaction was followed by the pressure drop in the high-pressure gas reservoir. When the gas absorption reached the value corresponding to the desired conversion to aldehydes, the autoclave was rapidly cooled, the reaction mixture was siphoned out, and GC was used to determine the isomeric composition. The degree of 1-hexene conversion was measured by GC, using benzene as an internal standard.

Unreacted substrate and benzene were separated from aldehydic products by fractional distillation at atmospheric pressure.

Chemically pure samples of unconverted 1-hexene and samples enriched in 2-hexene were obtained by careful fractional distillation of the reaction mixture at atmospheric pressure through a spinning band column.

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A Heteroatom-Stabilized Neutral Imine Organoactinide Complex: X-ray Structure of Dichlorobis(pentamethylcyclopentadienyl)uranium(IV) Phosphine Imine

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$Cp^*{}_2UCl_2(HNPPh_3)$ is formed from the reaction between $Cp^*{}_2UCl_2$ and 1 equiv of $HNPPh_3$ in toluene. The complex is of the "Cp_2MX_2Y type" and has been characterized by the usual spectroscopic and chemical methods and by single-crystal X-ray diffraction. $Cp^*{}_2UCl_2(HNPPh_3)$ crystallizes in the triclinic space group $P\bar{1}$ with a = 11.387 (4) Å, b = 17.048 (6) Å, c = 10.116 (2) Å, α = 102.15 (3)°, β = 110.28 (3)°, γ = 77.59 (3)°, Z = 2, R = 0.0554, and R_G = 0.0615. The U–N bond distance of 2.43 (1) Å is short for the separation of U(IV) and a neutral nitrogen donor ligand. The position of H(1), located by using low-angle X-ray data, indicates an agostic interaction with the uranium and hydrogen bonding with one of the chlorines. Consistent with this model, the N–H stretch occurs at a low frequency.

We are interested in nitrogen donors that may be good coligands in organometallic complexes of electron-poor, high-valent actinides.[1,2] In this context, we have been drawn to phosphine imines, $[R_3PNH]$, which are isoelectronic with $[R_3PCH]^-$, a ligand we have studied a great deal.[3,4] There is very little known about the coordination chemistry of phosphine imines, $RNPR'_3$. In addition to a copper(II) chloride complex of *N*-phenyltriphenylphosphine imine[5] and a copper(I) chloride complex of

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