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LETTERS

A novel hydrogen transfer hydroalumination of alkenes with triisobutylaluminum catalyzed by Pd and other late transition metal complexes

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Abstract—Hydrogen transfer hydroalumination of terminal alkenes and dienes can be achieved with 1.1 equiv. of $(i\text{-Bu})_3Al$ and catalytic amounts of $Cl_2Pd(PPh_3)_2$ and other late transition metal complexes containing Co, Rh, Ni, and Pt at ambient temperature in high yields. © 2001 Elsevier Science Ltd. All rights reserved.

Herein reported is a novel hydrogen transfer hydroalumination of alkenes with $(i\text{-Bu})_3Al$ (TIBA) and catalytic amounts of Pd and other late transition metal complexes containing Co, Rh, Ni and Pt. Although uncatalyzed hydroalumination reactions of alkenes with di- and trialkylalanes, such as $(i\text{-Bu})_2AlH$ (DIBAH) and $(i\text{-Bu})_3Al$ (TIBA), at elevated temperatures[1] as well as their Ni-catalyzed versions at room temperature[2] have long been known, their scope and limitations as well as their synthetic utility do not appear to have been explored extensively. As a consequence, relative to hydroboration[3] and hydrozirconation,[4] hydroalumination of alkenes[5] in general has been a generally sluggish reaction of limited synthetic scope. In addition to the Ni-catalyzed hydroalumination mentioned above, we developed earlier a hydrogen transfer hydroalumination of alkenes with TIBA and a catalytic amount of Cl_2ZrCp_2.[6]

Following a recent promising lead that a wide variety of Lewis acidic compounds catalyze hydrozirconation of alkenes with $i\text{-BuZrCp}_2Cl$,[7] we found that the reaction of 1-decene with 1.1 molar equiv. of TIBA in the presence of 2.5–5 mol% of the following chlorine-containing late transition metal complexes led to the formation of 1-iodododecane after treatment of the product with I_2: $Cl_2Pd(PPh_3)_2$ (90%), Li_2PdCl_4 (78–86%), K_2PtCl_4 (86%), $Cl_2Ni(PPh_3)_2$ (65%), $ClCo(PPh_3)_3$ (76%), and $ClRh(PPh_3)_3$ (79%). The cleanest results were observed with Pd and Pt catalysts. The use of $Pd(OAc)_2$ (5 mol%) in place of $Cl_2Pd(PPh_3)_2$ or Li_2PdCl_4 led to no reaction with >90% of 1-decene remaining unreacted. This may be attributable to the absence of Cl, and it is tempting to speculate that bimetallic activation[8] involving the Al–Cl–Pd bond is important. Another finding of significance is that either the use of preformed Pd(0) complexes, such as $Pd(PPh_3)_4$ (25%) in place of $Cl_2Pd(PPh_3)_2$ or Li_2PdCl_4, or strongly reducing hydride sources, such as $(i\text{-Bu})_2AlH$ (DIBAH) (25%) and $LiAlH_4$ (<5%), that can readily convert Pd(II) complexes to Pd(0) complexes in place of TIBA induced the desired hydroalumination only to a minor extent, the yield being indicated in parentheses. These results suggest *that the desired hydroalumination is catalyzed by Pd(II) but not Pd(0) complexes and that reduction of Pd(II) complexes is to be avoided. They also provide a reasonable explanation as to why TIBA rather than DIBAH serves as an effective hydride source and point to a significant advantage of hydrogen transfer hydroalumination*

Using 1.1 equiv. of TIBA and 2.5 mol% of $Cl_2Pd(PPh_3)_2$ as catalyst, the scope of the hydroalumination reaction was examined. As the results summarized in Table 1 indicate a variety of alkenes, including those that are functionally substituted, can be satisfactorily hydroaluminated. It should be mentioned, however, that retardation by strongly electron-donating functional groups in certain positions of alkenes is also noticeable. Thus, 4-bromo-1-butene, 11-iodo-1-undecene, allyl phenyl ether, allyl benzyl ether, and (3*E*)-1,3-decadiene did not provide the desired hydro-

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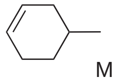
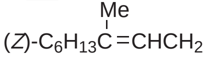
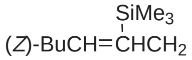
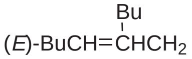
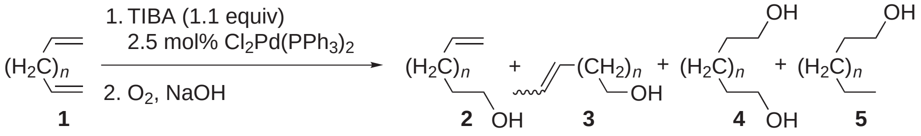
Table 1. Hydroalumination of 1-alkenes with TIBA catalyzed by $Cl_2Pd(PPh_3)_2$ [a]

R of $RCH=CH_2$	Reaction Times, h	Product yield,[b] % RCH_2CH_2I	Product yield,[b] % RCH_2CH_2OH	Unreacted alkene, %	Reduction product, %
n-C_8H_{17}	0.5	90 (85)	--	0	0
Cyclohexyl	1	--	73 (70)	0	0
Benzyl	1	--	77 (75)	0	0
$Cl(CH_2)_9$	0.5	88	--	5	0
$Br(CH_2)_9$	1	81	--	10	0
$PhS(CH_2)_3$	12	<5	--	90	--[e]
$PhS(CH_2)_3$	6[c]	--	75	0	0
	0.5	79	--	0	0
 $(Z)\text{-}C_6H_{13}\overset{Me}{C}=CHCH_2$	5	--	86 (80)	<8	--[e]
 $(Z)\text{-}BuCH=\overset{SiMe_3}{C}CHCH_2$	6	--	81 (75)	8	4
 $(E)\text{-}BuCH=\overset{Bu}{C}CHCH_2$	12	--	53	28	14
(E)-$C_6H_{13}CH=CHCH_2$	5	--	49	35	16
$Me_2C=CH(CH_2)_6$	12	--	80	0	0

[a] Unless otherwise mentioned, the reaction was carried out with 1.1 equiv of TIBA and 2.5 mol% of $Cl_2Pd(PPh_3)_2$ at 25°C in CH_2Cl_2. [b] By NMR or GLC. The numbers in parentheses are isolated yields. [c] 2.3 equiv of TIBA used. [d] An unidentified byproduct was present. Its GLC signal intensity was ca. 10% of the major product. [e] Unreacted alkene and reduction product were not distinguishable on the GLC trace.

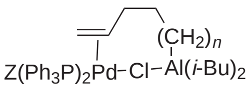
alumination products in detectable yields. α,ω-Dienes (**1**) containing two terminal vinyl groups have also been hydroaluminated. 1,5-Hexadiene undergoes a hydrometallation–cyclic carbometallation tandem process to give cyclopentylcarbinylalane which, upon oxidation with O_2, is converted to cyclopentylmethanol in 84% yield. With longer α,ω-dienes, no cyclic carbometallation has been observed. Instead, the reaction gives the expected mono- and dihydroaluminated products (**2** and **4**) as well as double bond-migrated and fully saturated monoaluminated products (**3** and **5**) formed in varying yields, as summarized in Table 2. These results shed some light on the mechanistic details of the reaction. They strongly suggest that, once hydroalumination has occurred at one end of a diene, the course of the reaction at the other double bond is significantly affected by the alkylaluminum group possibly through chelation depicted in **6** in which a Pd–Cl–Al bond is thought to be important.[8] As the dienes get longer, the chelation effect shown in **6** is expected to diminish,

Table 2. Hydroalumination of α,ω-dienes with TIBA catalyzed by $Cl_2Pd(PPh_3)_2$ [a]

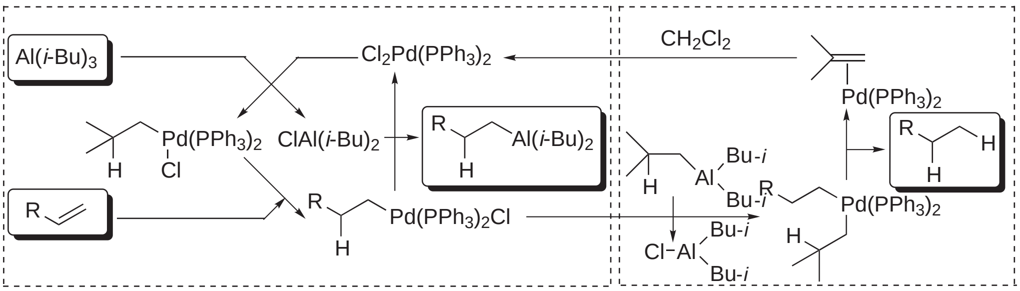


Entry	n of diene	Unreacted diene, %	Product yield, %[b] 2	3	2+3	4	5	4+5
1	3	0	32	12	44	10	22	32
2	4	0	20	23	43	14	21	35
3	5	0	12	24	36	14	25	39
4	6	0	11	24	35	16	27	43
5	10	0	0	26	26	19	54	73

[a] The reaction was carried out in CH_2Cl_2 at 25°C for 12 h. [b] By NMR and/or GLC.



6 (Z = Cl or i-Bu)



Desired non-redox catalytic cycle

Formation of alkanes by a redox process

Scheme 1.

which appears to be reflected by the decrease in the combined yield of **2** and **3** as well as the concomitant increase in the combined yield of **4** and **5**. In the reaction of 1,13-tetradecadiene, 2.26 equiv. of *i*-Bu–Al bonds are required to produce **2**–**5**, indicating that more than two *i*-Bu–Al bonds of TIBA must participate in the reaction. The overall processes may be accommodated by a combination of two catalytic cycles shown in Scheme 1. The formation of **5** is not a consequence of incomplete oxidation, since quenching the reaction mixture with D_2O after oxidation with O_2 did not incorporate D to a detectable extent. Its formation must involve cleavage of a C–Pd bond in a dialkylpalladium intermediate via dehydropalladation–reductive elimination.[9] The resulting Pd(0) complex must be reoxidized. The fact that the Pd-catalyzed hydrogen-transfer hydroalumination reported herein proceeds satisfactorily in CH_2Cl_2 but not in THF, ether, or even 1,2-dichloroethane strongly suggests that CH_2Cl_2 plays an active and significant role, such as regeneration of $Cl_2Pd(II)L_n$ from $Pd(0)L_n$. A similar oxidation of Ni(0) complexes to $Cl_2Ni(II)$ complexes by CH_2Cl_2 reported in the literature[10] provides strong support for the interpretation presented above.

Acknowledgements

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