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On the Mechanism of the Reduction of Primary Halides with Grignard Reagents in the Presence of (dppf)PdCl$_2$ or (dppf)Pd(0)[†]

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Reaction of primary alkyl halides with Grignard reagents in the presence (dppf)PdCl$_2$ or (dppf)Pd(0) leads to reduction of the halide. The mechanism of the reduction is dependent on the solvent and the Grignard reagent. In tetrahydrofuran, reduction is independent of palladium. The alkyl halide is largely reduced by β-hydride transfer from the Grignard reagent. Competing with hydride transfer is a halogen–metal exchange reaction, which converts the alkyl halide into the corresponding Grignard reagent. Protonation of reaction mixture then gives the observed products. Grignard reagents that do not possess β-hydrogens undergo the halogen–metal exchange exclusively, but still lead to reduction of the alkyl halide. At subambient temperatures and in diethyl ether, reduction of primary alkyl halides with Grignard reagents in the absence of palladium catalysts is very slow. That reduction which does occur is almost exclusively the product of β-hydride transfer. The addition of (dppf)PdCl$_2$ markedly accelerates the rate of reduction of alkyl halides in diethyl ether. The catalytic effect is proposed to occur through a catalytic cycle involving oxidative addition of the alkyl halide, hydride-transfer, and reductive-elimination steps. The order of the first two steps remains unclear.

Carbon–carbon bond-forming reactions remain the most useful synthetic methods available to the organic chemist. Palladium and nickel catalysts have become increasingly popular for mediating the coupling reactions of organic halides or pseudohalides that contain sp or sp^2 carbons at or immediately adjacent to the electrophilic center.[1] Presumably, this allows the catalyst to undergo a precomplexation with a π-system prior to oxidative addition. There have been few reports on the use of Group 10 metal complexes to catalyze the cross-coupling reactions of unactivated sp^3 electrophiles. This can be attributed to the lack of reactivity of the catalysts and to the expectation of the formation of side products. Pearson has shown that low-valent palladium species react with methyl iodide or methyl tosylate at relatively slow rates,[2] indicating that oxidative addition of unactivated electrophiles may be a difficult process. Should oxidative addition occur, the newly formed alkyl metal species can then undergo a β-hydride elimination reaction in competition with desired reaction processes. It has been commonly assumed that β-hydride elimination is a very rapid process, and therefore coupling cannot compete with olefin formation.[1]

For the development of a general reaction utilizing unactivated sp^3 electrophiles, one must employ a catalyst that possesses sufficient nucleophilicity to allow oxidative addition with the electrophile and electronic or steric constraints that minimize β-hydride elimination from either the electrophile or the nucleophile. A major advance occurred with the finding that β-hydride elimination from the nucleophilic partner in a cross-coupling reaction can be largely suppressed on use of substoichiometric amounts of dichloro[1,1′-bis(diphenylphosphino)ferrocene]palladium(II) ((dppf)PdCl$_2$) as the catalyst.[3] Widdowson later reported that prereduction of (dppf)PdCl$_2$ to the (dppf)-Pd(0) analogue using 2 equiv of DIBAL afforded a catalyst capable of mediating the coupling of primary halides with Grignard reagents.[4]

While developing a program directed toward the development of Group 10 metal catalysts for the formation of carbon–carbon bonds using unactivated primary neopentyl electrophiles, we discovered that either (dppf)PdCl$_2$ or (dppf)Pd(0) will effectively catalyze the Grignard-mediated reduction of both primary neopentyl iodides and n-alkyl iodides in diethyl ether.[5,6] Because the palladium-catalyzed reduction appeared to circumvent the problems of slow oxidative addition and rapid β-hydride elimination, we felt that an understanding of the mechanism of reduction might facilitate the development of conditions that optimize cross-coupling.

Table I. Reaction of 1-Iododecane with (3-Phenyl-1-propyl)magnesium Bromide[a]

entry	temp (°C)	solvent	catalyst	yield (%)	product ratio R-H:R(-H):R-R′
1	67	THF	none	96	92:8:0
2	67	THF	(dppf)Pd(0)	100	100:0:0
3	67	THF	(dppf)PdCl$_2$	100	86:14:0
4	25	THF	none	100	88:11:1
5	25	THF	(dppf)Pd(0)	100	84:16:0
6	25	THF	(dppf)PdCl$_2$	100	88:11:1
7	25	Et$_2$O	none	10[b]	99:1:0
8	25	Et$_2$O	(dppf)Pd(0)	83[b]	85:15:0
9	25	Et$_2$O	(dppf)PdCl$_2$	66[b]	96:4:0

[a] Reaction of 1-iododecane (1.0 mmol) and bibenzyl (GC standard) with 3 equiv of Ph(CH$_2$)$_3$MgBr and 2 mol % of catalyst (if added) in solvent indicated (10 mL) for 24 h. Reaction was begun at −78 °C and warmed to the temperature indicated. Yields and ratios were determined by gas chromatography using internal standards. R = CH$_3$(CH$_2$)$_9$, R′ = Ph(CH$_2$)$_3$. [b] Reaction was run for 91 h.

Results

Initial investigations of the reduction of 1-iododecane (1) indicated that there was little difference between use of (dppf)PdCl$_2$ and (dppf)Pd(0) (Table I).[5] In our hands,

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[†] This work is dedicated to the memory of John Kenneth Stille who was tragically lost in an airplane crash on July 19, 1989. John was a scientist, scholar, teacher, mentor, and friend. He will be missed.

(1) (a) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA; 1987. (b) Colquhoun, H. M.; Holton, J.; Thompson, D. J.; Twigg, M. V. *New Pathways for Organic Synthesis. Practical Applications of Transition Metals*; Plenum Press: New York; 1984. (c) Heck, R. F. *Palladium Reagents in Organic Synthesis*; Academic Press: New York; 1985.

(2) Pearson, R. G.; Figdore, P. E. *J. Am. Chem. Soc.* **1980**, *102*, 1541–1547.

(3) Hayashi, T.; Konishi, M.; Korobi, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158–163.

(4) Castle, P. L.; Widdowson, D. A. *Tetrahedron Lett.* **1986**, *27*, 6013–6016.

(5) Yuan, K.; Scott, W. J. *Tetrahedron Lett.* **1989**, *30*, 4779–4782.

(6) Professor Widdowson has also encountered difficulties with the (dppf)Pd(0)-catalyzed coupling reaction.[7] Recent results from his laboratories indicate that the reaction produces alkane/alkene mixtures in agreement with our findings.

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Table II. Effect of Varying Reaction Conditions on the Reduction of 1-Iododecane with (3-Phenyl-1-propyl)magnesium Bromide in THF[a]

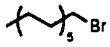
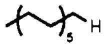
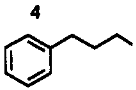
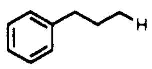
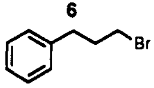
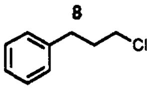
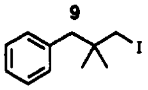
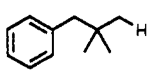
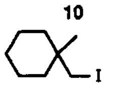
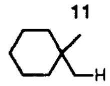
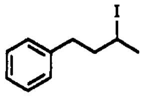
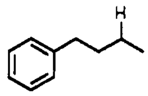
entry	catalyst	amount (mol %)	temp (°C)	yield (%)	product ratio R–H:R(–H):R–R′
1	(dppf)Pd(0)	4.9	0	100	91:9:0
2	(dppf)Pd(0)	5.2	25	100	84:16:0
3	(dppf)Pd(0)	4.6	67	100	100:0:0
4	none		0	30	60:2:14
5	(dppf)Pd(0)	0.6	0	44	100:0:0
6	(dppf)Pd(0)	16.4	0	100	93:7:0
7	(dppf)Pd(0)	34.7	0	100	100:0:0
8	(dppf)Pd(0)	52.4	0	100	100:0:0

[a] Reaction of 1-iododecane (1.0 mmol) and bibenzyl (GC standard) with 3 equiv of $Ph(CH_2)_3MgBr$ and catalyst (if added) in THF (10 mL) for 24 h. Reaction was begun at −78 °C and warmed to the temperature indicated. Yields and ratios were determined by gas chromatography using internal standards. $R = CH_3(CH_2)_9$, $R' = Ph(CH_2)_3$.

neither $(dppf)PdCl_2$ nor (dppf)Pd(0) were found to catalyze the cross-coupling of alkyl halides with Grignard reagents. The choice of solvent appears to be central to the course of the reaction. In tetrahydrofuran (THF) at room temperature and above, reaction of halide **1** with an excess of (3-phenyl-1-propyl)magnesium bromide (**2**) affords high yields of decane, whether in the presence or absence of added palladium. In contrast, in diethyl ether reaction of halide **1** with Grignard **2** in the absence of a catalyst returned starting material in 90% yield (Table I). Similarly, in THF at 0 °C in the absence of catalyst, starting material was returned in 70% yield (Table II, entry 4).

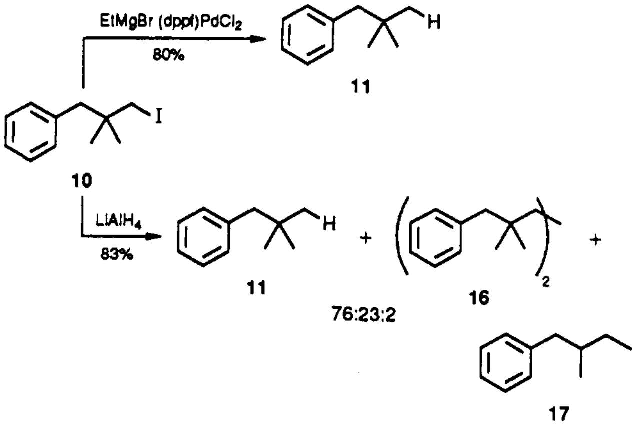
Attempts were made to vary reaction conditions in order to increase yields of cross-coupled products. In THF, variation of the reaction temperature above room temperature had little effect on the product ratio (Table II, entries 1–3). As the concentration of catalyst is increased at 0 °C, conversion to products increases (Table II, entries 1, 4–8). Only in the absence of catalyst at 0 °C was cross-coupling observed, albeit at low levels. Addition of catalytic or stoichiometric amounts of a Lewis acid to facilitate coupling met with little success. Though Fe(III)[8] and Zn(II)[9] salts are known to cause or participate in the catalysis of coupling reactions, neither $Fe(acac)_2$, $ZnCl_2$, $ZnBr_2$, nor ZnI_2 in the presence of (dppf)Pd(0) acted to couple iodide **1** with **2**. Use of either catalytic or stoichiometric amounts of CuI led to a 2:1 ratio of coupled to reduced products.[10,11]

Table III. $(dppf)PdCl_2$-Catalyzed Reduction of Alkyl Halides Using Ethylmagnesium Bromide in THF at 67 °C[a]

entry	alkyl halide	product	yield (%)[b]
1	 **4**	 **5**	76
2	 **6**	 **7**	76 (100)
3	 **8**		91 (100)
4	 **9**		76 (100)
5	 **10**	 **11**	80 (100)
6	 **12**	 **13**	57 (90)
7	 **14**	 **15**	– (50)[c]

[a] Reaction of alkyl halide (1.0 mmol) with 5 equiv of ethylmagnesium bromide and 2 mol % of catalyst in THF (10 mL) for 24 h. Reaction was begun at −78 °C and warmed to 67 °C. [b] Numbers in parentheses indicate yields for separate experiments determined by gas chromatography using bibenzyl as internal standard. [c] Butylbenzene was contaminated with approximately 50% of a mixture of 4-phenyl-1-butene and (*E*)- and (*Z*)-1-phenyl-2-butene.

As shown in Table III, the reduction process is a general one. Reactions were run with 2 mol % of $(dppf)PdCl_2$ and excess ethylmagnesium bromide (**20**) to optimize isolation of the reduction products. This procedure avoided complications resulting from quenched Grignard reagents and byproducts related to the use of DIBAL. Primary chlorides, bromides, and iodides are all reduced, as are sterically hindered primary halides (entries 4 and 5). Secondary halides undergo elimination processes in competition with reduction (entry 6). Reduction of 3-iodo-1-phenyl-2,2-dimethylpropane (**10**) using this procedure afforded no products of rearrangement. the analogous reduction using lithium aluminum hydride led to a 3:1 mixture of reduced product **11** and the corresponding dimer, **16**, along with a small amount of the rearranged, reduced compound **17**.



The product distribution varies considerably depending on the Grignard reagent employed (Table IV). *n*-Alkyl Grignard reagents, such as **2**, lead to reduction of 1-iododecane. With methylmagnesium chloride (**18**), products of elimination predominate. Phenylmagnesium bromide (**19**) afforded decane in 56% yield, along with 1-decene and the coupling product, 1-phenyldecane. Neopentyl iodide (**10**) afforded lower conversions for all three Grignard reagents (Table IV, entries 7–9). Notably, for both hin-

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(7) Widdowson, D. A. Private communication.

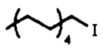
(8) For examples of Fe(III)-catalyzed coupling processes, see: Neumann, S. M.; Kochi, J. K. *J. Org. Chem.* **1975**, *40*, 599–606. Smith, R. S.; Kochi, J. K. *J. Org. Chem.* **1976**, *41*, 502–509.

(9) For reviews of the use of zinc nucleophiles in Group 10 metal-catalyzed coupling reactions, see: Negishi, E.-i. *Acc. Chem. Res.* **1982**, *15*, 340–348. Negishi, E.-i.; Takahashi, T.; King, A. O. *Org. Synth.* **1987**, *66*, 67–74, and references therein.

(10) For a review on substitution reactions using organocopper reagents, see: Posner, G. H. *Org. React.* (*N.Y.*) **1975**, *22*, 253–400.

(11) The palladium catalyst actually appears to hinder the Cu(I)-catalyzed Gilman-coupling reaction of 1-iododecane with methylmagnesium chloride. As expected, reaction of **1** with MeMgCl in the presence of catalytic CuI and in the absence of palladium catalysts afforded quantitative yields of undecane.

Table IV. Effect of Varying Grignard Reagent on the (dppf)Pd(0)-Catalyzed Reduction[a]

entry	alkyl halide RX	Grignard reagent	solvent	yield (%)	ratio R–H:R(–H):R–R′
1	 1	$Ph(CH_2)_3MgBr$	THF	63	100:0:0
2		PhMgBr	THF	100	57:19:24
3		MeMgCl	THF	100	21:77:2
4[b]		MeMgCl	THF	16	4:7:5
5[c]		MeMgCl	THF	41	3:3:35
6[d]		MeMgCl	THF	100	61:4:35
7		$Ph(CH_2)_3MgBr$	Et_2O	12	100:0:0
8		PhMgBr	Et_2O	100	20:65:15
9		MeMgCl	Et_2O	100	55:18:27
10	10	$Ph(CH_2)_3MgBr$	THF	19	100:0:0
11		PhMgBr	THF	79	89:0:11
12[e]		MeMgCl	THF	85	100:0:0

[a] Reaction of the alkyl halide (1.0 mmol) and bibenzyl (GC standard) with 1.2–2.0 equiv of Grignard reagent and 2–5 mol % of (dppf)Pd(0) in THF (10 mL) for 24 h. Reaction was begun at −78 °C and warmed to 0 °C. Yields and ratios were determined by gas chromatography using internal standards. [b] Reaction was warmed to 0 °C and run in the absence of catalyst. [c] Reaction was warmed to 25 °C and run in the absence of catalyst. [d] Reaction was warmed to 67 °C and run in the absence of catalyst. [e] Reaction was run for 74 h.

Table V. Deuterium Incorporation Studies of the Reduction of 3-Iodo-1-phenylpropane in the Absence of Palladium Catalysts[a]

entry	Grignard reagent	solvent	reactn quench	product ratio R–H:R–R′	deuterium incorpn in R–H (%)
1	EtMgBr	d_8-THF	H_2O	83:14	2
2	EtMgBr	THF	D_2O	100:0	32
3	EtMgBr	d_8-THF	D_2O	84:14	31
4	d_5-EtMgBr	THF	H_2O	100:0	2
5	d_5-EtMgBr	THF	D_2O	100:0	31
6	EtMgBr	THF	D_2O	92:8	0[b]
7	EtMgBr	THF	D_2O	96:4	18[c]
8	EtMgBr	THF	D_2O	98:2	36[d]
9	EtMgBr	THF	D_2O	98:2	45[e]

[a] Reaction of 3-iodo-1-phenylpropane (1.0 mmol) and bibenzyl (GC standard) with ethylmagnesium bromide (3.0 mmol) and 2 mol % of catalyst in THF (10 mL) for 24 h. Reaction was begun at −78 °C and warmed to 25 °C. Yields and ratios were determined by gas chromatography using internal standards. All reactions proceeded to afford the product mixture in 100% yield except entry 7, which returned 5% starting alkyl halide in addition to the product mixture. R = $Ph(CH_2)_3$, R′ = CH_3CH_2. [b] 1.0 mmol of ethylmagnesium bromide was used. [c] 2.0 mmol of ethylmagnesium bromide was used. [d] 5.0 mmol of ethylmagnesium bromide was used. [e] 10.0 mmol of ethylmagnesium bromide was used.

Table VI. Deuterium Incorporation Studies of the Reduction of 3-Iodo-1-phenylpropane with Ethylmagnesium Bromide in Diethyl Ether Followed by D_2O Quench[a]

entry	reactn temp (°C)	catalyst	yield (%)	ratio R–H:R–R′	deuterium incorpn in R–H
1	0	none	24	17:83	
2	25	none	36	74:26	89
3	33	none	64	89:11	89
4	0	$(dppf)PdCl_2$	92	95:5	75
5	25	$(dppf)PdCl_2$	95	94:6	54
6	33	$(dppf)PdCl_2$	95	93:7	67

[a] Reaction of 3-iodo-1-phenylpropane (1.0 mmol) and bibenzyl (GC standard) with 3 equiv of ethylmagnesium bromide and 2 mol % of catalyst (if added) in diethyl ether (10 mL) for 24 h. Reaction was begun at −78 °C and warmed to the temperature indicated. Yields and ratios were determined by gas chromatography using internal standards. Starting alkyl halide accounted for the remainder of the observed material in the product mixture. R = $Ph(CH_2)_3$, R′ = CH_3CH_2.

dered and unhindered primary halides, coupling proved to be a minor pathway with all Grignard reagents studied.

Mechanistic Studies on Reduction in Tetrahydrofuran. Labeling studies were conducted to determine the mode of hydrogen transfer for the reduction of 3-iodo-1-phenylpropane (**6**) with 3 equiv of ethylmagnesium bromide (**20**) in the absence of palladium catalysts (Table V). Little or no deuterium was incorporated into the isolated phenylpropane when the reaction was run in d^8-THF. Use of d^5-EtMgBr as the Grignard reagent also had little effect on the level of deuterium incorporated into the reduced product. Quenching of the reaction with a D^+ source caused incorporation of deuterium in 30% of the phenylpropane isolated (entry 2). Reaction of iodide **6** with EtMgBr in d^8-THF followed by quenching with D_2O (entry 3) afforded phenylpropane with deuterium levels similar to those observed from the EtMgBr/THF/D_2O example (entry 2). These results suggest that although H^+ is an important source of the hydrogen transferred during the reduction, it is not the major source. As the amount of ethylmagnesium bromide initially added to the reaction mixture is increased, the amount deuterium incorporated into the product on quenching the reaction mixture with D_2O also increases (entries 2, 6–9), indicating the existance of multiple competing mechanisms of reduction.

Reduction of alkyl halides with other Grignard reagents is also consistent with the concept of multile competing mechanisms. Reduction of 3-iodo-1-phenylpropane in THF using methylmagnesium chloride, which is incapable of β-hydride delivery, led to the formation of 1-decene and decane (Table IV, entries 4–6). When the reaction was run at 0 °C, 1-decene/decane were formed in a 1.75:1 ratio. At 67 °C, decane becomes the major product of the reaction with only trace amounts of 1-decene observed. Reaction of 1-iodododecane with 3 equiv of PhMgBr in THF in the presence of 5 mol % of (dppf)Pd(0) gave a 1:3 mixture of 1-decene and decane after 24 h, along with a 24% yield of 1-phenyldecane (Table IV, entry 2). This was the first case in which moderate levels of cross-coupling were observed. It is noteworthy that the 1-decene/decane ratio is the inverse of that obtained with MeMgBr.

Mechanistic Studies on Reduction in Diethyl Ether. In Et_2O, the reduction of alkyl halides is facilitated by palladium catalysts (Table I, entries 4–6). In the absence of catalyst, the yield of reduced product in Et_2O is temperature dependent (Table VI, entries 1–3). Incorporation of deuterium in the propylbenzene on quenching the reaction mixture with D_2O is very high, indicating that the hydrogen source for the small amount of reduction that does occur in the absence of a palladium catalyst is largely H^+. Addition of 2 mol % $(dppf)PdCl_2$ increases the yield of propylbenzene at all temperatures studied (Table VI, entries 4–6). The palladium-catalyzed reduction causes levels of deuterium incorporation on quenching with D_2O to decrease.

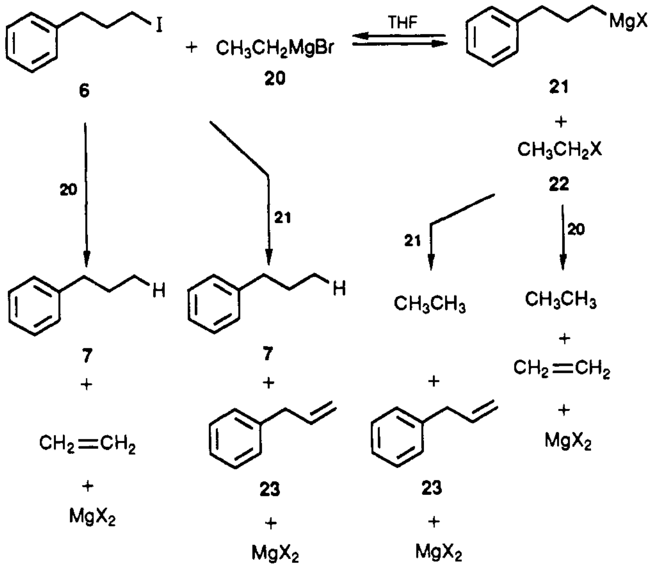
Discussion

The reduction of primary alkyl halides with Grignard reagents in THF at room temperature and above need not be a palladium-catalyzed process. The hydrogen required for the reduction could be transferred to the electrophile in the form of a hydrogen atom, a hydride, or a proton. Grignard reagents are well known to be single electron donors.[12] Electron transfer to the alkyl halide, followed by carbon–halogen bond dissociation would generate an alkyl radical. Abstraction of a hydrogen atom from the solvent would then lead to the reduced product. Seyferth proposed a radical pathway for the reduction of *gem*-dibromocyclopropanes with methylmagnesium bromide.[13] Ashby has shown that the reduction of 1-iodo-2,2-dimethylhexene with metal hydrides takes place by a single-electron-transfer pathway.[14] Similarly, Ashby proposed that the reduction of dimesityl ketone with Grignard reagents involves a solvent cage radical pair mechanism,[15] essentially a single-electron-transfer version of Whitmore's polar six-centered transition-state mechanism.[16,17] On the basis of low levels of incorporation of deuterium when the reduction was run in d^8-THF (entry 1), the mechanism of hydrogen transfer does not appear to involve abstraction of a hydrogen atom from the solvent.

Halogen–metal exchange would reduce the alkyl iodide to the corresponding Grignard reagent. Quenching of this material with a proton source would then afford the alkane. Halogen–metal exchange with Grignard reagents in diethyl ether is well precedented for alkyl halides containing strong electron-withdrawing groups.[18] Zakharkin and co-workers showed that in THF, dimethoxyethane or diglyme an equilibrium based on halogen–metal exchange is rapidly established.[19] Exchange was proposed to proceed through a mechanism similar to that of alkyllithium-based exchange.[20-22] Formation of Grignard reagents followed by aqueous quench has long been a useful method for the reduction of alkyl halides.[23] Quenching of the reaction mixture formed on treatment of 3-iodo-1-phenylpropane with 3 equiv of EtMgBr with D_2O afforded approximately 30% incorporation of deuterium in the isolated propylbenzene. Thus, while important, halogen–metal exchange does not account for the majority of the hydrogen transferred during reduction.

Alkyl halides have long been known to be susceptible to hydride-based reduction.[24,25] Johnson found that hydride transfer with lithium aluminum hydride was sluggish in diethyl ether but fast in THF.[25b] Organometallic reagents, such as butyllithium[26] and lithium diisopropylamide,[27] have been shown to act as reducing reagents through delivery of a β-hydride. Whitmore first proposed that Grignard reagents containing β-protons reduce ketones in the "abnormal" Grignard reaction[16] via a six-centered transition state.[17] Thus, the Grignard reagent might be acting as a hydride-transfer agent.

Scheme I. Proposed Mechanism for the Reduction of 3-Iodo-1-phenylpropane with Ethylmagnesium Bromide in THF



The results of the deuterium incorporation studies are best explained by postulating two competing mechanisms for the reduction of the alkyl halide. We propose that hydride transfer and transmetalation are both on-going processes as shown in Scheme I. On treatment with an excess of EtMgBr (**20**), iodide **6** undergoes rapid halogen–metal exchange,[19] generating Grignard reagent **21** and ethyl halide **22**. The reverse reaction must also occur, thus affording an equilibrium mixture of halides and Grignard reagents. Reduction of halide **6** with ethylmagnesium bromide (**20**) affords propylbenzene and ethylene. Ethyl halide must also be reduced by the Grignard reagents to afford ethane and olefinic products. Due to lessened steric constraints, the latter reduction should be more rapid. Because an excess of the Grignard reagent was employed, the reduction of halides **6** and **22** can continue until all of the electrophile is consumed. The mixture of Grignard reagents remaining after the hydride-transfer phase of the reaction is then quenched with a proton source to afford ethane and propylbenzene. The D_2O quench of the reaction mixture must then indicate the amount of **21** remaining after consumption of the iodides (approximately 30% in this case). Use of 3–5 equiv of ethylmagnesium bromide insures that the concentration of Grignard **20** is greater than the concentration of Grignard **21**. Thus, even if one assumes similar hydride-transfer rates, Grignard **21**, derived from the electrophile, should not compete effectively as a reductant.

If Grignard **21** does act as the hydride-transfer agent, an equivalent of allylbenzene must also produced. Small amounts of allylbenzene have been observed in some reaction mixtures (5–15%, Table II). The concept of equilibrating Grignard reagents is supported by the finding that on treatment of 3-iodo-2,2-dimethyl-1-phenylpropane (**10**) with (3-phenylpropyl)magnesium bromide, followed

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[13] Seyferth, D.; Prokai, B. *J. Org. Chem.* **1966**, *31*, 1702–1704.

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[21] For an excellent review on the mechanism of lithium–halogen exchange, see: Bailey, W. F.; Patricia, J. J. *J. Organomet. Chem.* **1988**, *351*, 1–46.

[22] No attempt has been made to distinguish between polar, concerted, and single-electron mechanisms of metal–halogen exchange.

[23] Noller, C. R. *Organic Synthesis*; Wiley: New York, 1943; Collect. Vol. 2, pp 478–480.

[24] No attempt has been made to distinguish between a polar hydride-transfer mechanism and hydride transfer via a solvent-cage single-electron-transfer mechanism.

[25] For examples, see: (a) $LiAlH_4$. Krishnamurthy, S. *J. Org. Chem.* **1980**, *45*, 2550–2551; and references therein. (b) $LiAlH_4$/LiH. Johnson, J. E.; Blizzard, R. H.; Carhart, H. W. *J. Am. Chem. Soc.* **1948**, *70*, 3664–3665. (c) $NaBH_4$. Bell, H. M.; Vanderslice, C. W.; Spehar, A. *J. Org. Chem.* **1969**, *34*, 3923–3926.

[26] Eastham, J. F.; Gibson, G. W. *J. Org. Chem.* **1963**, *28*, 280.

[27] (a) Benkeser, R. A.; DeBoer, C. E. *J. Org. Chem.* **1956**, *21*, 281–284. (b) Wittig, G.; Schmidt, H.-J.; Renner, H. *Chem. Ber.* **1962**, *95*, 2377–2383. (c) Kowalski, C.; Creary, X.; Rollin, A. J.; Burke, M. J. *J. Org. Chem.* **1978**, *43*, 2601–2608.

by a protic quench prior to consumption of all of the halide, afforded 3-iodo-1-phenylpropane (**6**) along with starting iodide **10**.

Key to this mechanistic proposal are the concepts of equilibrating Grignard reagents **20** and **21** and competing reduction mechanisms. On use of d^5-EtMgBr, two effects are expected. First, the equilibrium constant for the halogen–metal exchange processes should shift somewhat to increased concentrations of Grignard **21** and perdeuterioethyl halide (d^5-**22**) to reflect the destabilization of the Grignard reagent in the perdeuterio case. Second, consideration of kinetic isotope effects for transfer of D^- suggests that reduction of **6** and perdeuterio-**22** with d^5-EtMgBr should be slowed considerably.[28] The result is that virtually none of the hydrogen transferred to the alkyl halide is delivered by d^5-EtMgBr (Table V, entries 4 and 5).

A number of experiments have been run to test the proposal of competitive reduction mechanisms. As the number of equivalents of EtMgBr is increased to 10.0, unreacted Grignard reagent increases and deuterium incorporation the propylbenzene increases to 45% (Table V, entries, 2, 6–9). If hydride transfer were the only operative mechanism of reduction and deuterium incorporation on quenching reaction mixtures with D_2O was the result of a side reaction, one would predict that increasing the initial concentration of EtMgBr would either maintain or lower the amount of deuterium incorporation. In contrast, based on the proposed halogen–Grignard reagent exchange/β-hydride-transfer mechanism, one would predict that as the starting ratio of EtMgBr to 3-iodo-1-phenylpropane is increased, the equilibrium should favor formation of ethyl halide. Accordingly, hydride-transfer-based reduction of ethyl halide with ethylmagnesium halide should increase and halide **6** should be increasingly converted into (3-phenyl-1-propyl)magnesium halide. Thus, on quenching with D_2O, increased initial Grignard reagent leads to increased deuterium incorporation in the reduced product.

The halogen-Grignard reagent exchange/β-hydride-transfer mechanism allows one to predict that Grignard reagents which do not possess β-hydrogens should undergo halogen–metal exchange and that the newly formed alkyl Grignard reagent should be the only species capable of hydride donation. Thus, alkene formation should become more pronounced. Reaction of 1-iodododecane with 3 equiv of MeMgCl in THF at 0 °C produced 1-decene and decane in a 1.75:1 ratio (Table IV, entry 4). The ratio observed is the result of the reduction of methyl halide with decylmagnesium halide to form 1-decene in competition with the reduction of 1-iodododecane to form decene and decane. At room temperature the 1-decene/decane ratio becomes 1:1 and at 67 °C the ratio shifts to 1:16.5 (Table IV, entry 6). The relationship of the 1-decene/decane ratio on temperature indicates that the methyl halide being formed is volatilized, shifting the equilibrium toward formation of decylmagnesium halide. A water quench then gives the reduced product. Trapping of the off-gases of a 67 °C reaction afforded a THF solution of CH_3I (^{1}H NMR δ 2.23) and CH_3Cl (^{1}H NMR δ 3.23, ^{13}C NMR δ 22.4) in approximately a 6:1 ratio.

Reaction of 1-iodododecane with 3 equiv of PhMgBr in THF in the presence of 5 mol % of (dppf)Pd(0) gave a 3:1 mixture of decane and 1-decene after 24 h, along with 24% of 1-phenyldecane (Table IV, entry 2). This was the first case in which moderate levels of cross-coupling were observed. It is noteworthy that the 1-decene/decane ratio is the inverse of that obtained with MeMgBr. After equilibration, the only halide amenable to reduction is 1-iodododecane and the only hydride source is decylmagnesium halide. The reduction should lead to a 1:1 mixture of products. However, the reduction appears to be slow and remaining Grignard reagent is quenched to afford decane.

In THF at 0 °C and in Et_2O, the reduction of alkyl halides is facilitated by palladium catalysts. In the absence of catalyst, the yield of reduced product is temperature dependent. In Et_2O, high deuterium incorporation on quenching the reaction mixture with D_2O indicates that the reduction occurred mainly through a halogen–metal exchange/protonation mechanism. Addition of (dppf)-$PdCl_2$ increases the yield of propylbenzene at all temperatures studied (Table VI, entries 4–6). The palladium-catalyzed reduction causes levels of deuterium incorporation on quenching with D_2O to decrease somewhat. This suggests that the catalyst is aiding halogen–metal exchange, ultimately leading to moderate levels of deuterium incorporation. Transition-metal-catalyzed halogen–metal exchange has been described by Noller, although the solvents employed in those studies were not disclosed.[30] Should the palladium-catalyzed halogen–metal exchange afford a major pathway toward reduction, the D_2O quench of the reaction would necessarily have increased or maintained the high levels of deuterium incorporation observed in the absence of catalysts. The drop in deuterium incorporation can only be explained in terms of a second competing mechanism.

Homogeneous palladium catalysts are well known to catalyze hydride-transfer reactions, principally from hydroaromatics, trialkylsilanes, trialkylstannanes, and formic acid derivatives.[31] Palladium-catalyzed reduction of allylic electrophiles and aryl halides with sodium borohydride,[32] sodium cyanoborohydride,[33] or lithium triethylborohydride[34] proceeds in good to excellent yields. We propose that (dppf)$PdCl_2$ catalyzes the reduction in Et_2O following a catalytic cycle common to many cross-coupling reactions (Scheme II).[1] Thus, (dppf)$PdCl_2$ is reduced in situ to (dppf)Pd(0) complex **24**[1,3] which oxidatively adds the electrophile. Hydride transfer from the Grignard reagent to the resulting Pd(II) complex generates an olefin, magnesium halide, and an organopalladium(II) hydride (**26**). Reductive elimination affords the alkane with concomitant regeneration of (dppf)Pd(0) catalyst **24**.

The order of the oxidative-addition and hydride-transfer steps is not yet clear. Preliminary oxidative addition followed by reaction with a nucleophile, as illustrated in Scheme II, is well precedented for palladium-catalyzed cross-coupling reactions, especially in the presence of moderate to weak nucleophiles.[1] However, oxidative addition of an unactivated electrophile should be very slow, as indicated by the lack of a palladium-catalyzed reaction in THF. Preliminary hydride transfer to afford a palladate

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[28] San Fillipo reported a kinetic isotope effect of 3.3 to 3.7 for the thermal β-hydride elimination of octyllithium at 120 to 150 °C to generate octene and lithium hydride.[29] This process is believed to involve a four-centered transition state. Assuming that transition state of hydride transfer from the Grignard reagent to the alkyl halide is more symmetrical and more nearly linear, one would expect the isotope effect to increase.

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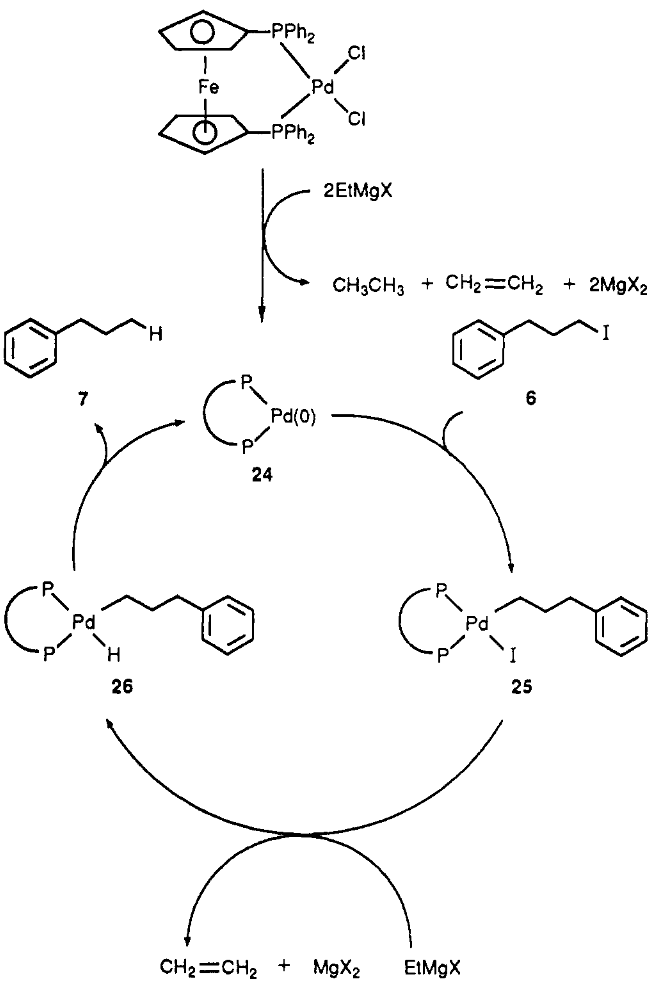
Scheme II. Proposed Mechanism for the Reduction of 3-Iodo-1-phenylpropane with Ethylmagnesium Halide in Diethyl Ether



complex would be expected to enhance the nucleophilicity of the metal, facilitating oxidative addition.

Conclusions

In our hands Grignard reagents act to reduce alkyl electrophiles in the presence of either (dppf)PdCl$_2$ or (dppf)Pd(0). In THF at room temperature or above, the course of the reaction is not affected by the absence of palladium. In this case, reduction occurs through halogen–metal exchange to form a mixture of Grignard reagents followed by β-hydride transfer to the resulting mixture of alkyl halides. After consumption of the alkyl halides, any remaining Grignard reagents are quenched with an aqueous workup.

In THF at low temperatures and in Et$_2$O at all temperatures studied, palladium catalyzes the reduction of alkyl halides. The catalyzed reduction may also involve two competing pathways. Palladium may act to accelerate halogen–metal exchange. The catalyst also increases the rate of β-hydride delivery from the Grignard reagent. We propose that the latter reaction involves oxidative addition of the electrophile, β-hydride transfer from the Grignard reagent to form an intermediate organopalladium hydride complex, and reductive elimination of the alkane to regenerate the catalyst.

Experimental Section

^{1}H NMR spectra were obtained on a JEOL FX-90Q or a Bruker WM-360 spectrometer in CDCl$_3$ with tetramethylsilane as internal standard. ^{13}C NMR spectra were recorded on a JEOL FX-90Q or a Bruker WM-360 spectrometer with CDCl$_3$ as solvent and internal standard. Infrared spectra were taken on a Beckman Acculab 1 spectrometer. Capillary gas chromatographic analyses were run on a Hewlett Packard 5890A gas chromatograph equipped with 0.53 mm × 5 m methyl silicone column and a flame ionization detector. GC-mass spectra (GC-MS) were obtained on a Hewlett-Packard 5985B or a VG TRIO 1 instrument at an ionization potential of 70 eV. Thin-layer chromatography was performed on EM silica gel 60F-254 plates. Column chromatographic purification of reaction mixtures were performed with Woelm 230–400-mesh silica gel. Spinning band distillations were conducted with an ACE/Bowdoin microscale spinning band column (10 cm).

Methylmagnesium chloride was purchased from the Aldrich Chemical Co. Other Grignard reagents were prepared by the reaction of magnesium turnings with the alkyl halide in THF or diethyl ether. After consumption of the halide, the resulting ethereal solution was usually tranferred via cannula through a type C sintered glass frit into a dry storage bottle. All Grignard reagents were titrated prior to use by employing a modification of the procedure of Watson and Eastham.[35] Tetrahydrofuran (THF) was doubly distilled from potassium. Diethyl ether was distilled from LiAlH$_4$. (dppf)PdCl$_2$ was prepared as described in the literature.[3] Ethyl bromide, phenyl bromide, 3-iodo-1-phenylpropane, 3-bromo-1-phenylpropane, 3-chloro-1-phenylpropane, 1-iodododecane, and 1-bromododecane were purchased from the Aldrich Chemical Co. 3-Iodo-2,2-dimethyl-1-phenylpropane,[36] 1-(iodomethyl)-1-methylcyclohexane, and 3-iodo-1-phenylbutane[37] were prepared by using a modification of a literature procedure.[38] Alkyl halides were passed through a short column of neutral alumina prior to use. ^5d-Ethyl bromide (99% D) was purchased from MSD Isotopes and used as received. Decane, undecane, dodecane, 1-decene, butylbenzene, propylbenzene, allylbenzene, and 1,1-dimethylcyclohexane were purchased from the Aldrich Chemical Co. and used as GC and spectral standards without further purification. All reactions were conducted under a positive argon pressure.

General Procedure for the Reduction of Organohalide Compounds (Tables I, II, and IV–VI). A mixture of a GC standard (usually 0.130 g of dibenzyl, 0.700 mmol) and (dppf)PdCl$_2$ (if catalyst was employed, 0.0366 g, 0.050 mmol, 5 mol %) was placed under Ar using 2 cycles of an evacuate/quench protocol, and the reaction vessel was cooled to −78 °C. To this mixture was added solvent (10 mL), followed by DIBAL (if catalyst was pre-reduced, 0.150 mL, 1.5 M in toluene, 0.225 mmol). The resulting solution was stirred at −78 °C under argon while the alkyl iodide (1.0 mmol) and then the Grignard reagent (1.5–2.5 mmol, 1–2 mL) were rapidly added by syringe. The cooling bath temperature was then allowed to raise to the desired temperature over 2 h. After reaching this temperature, 0.5-mL samples were periodically acquired from the reaction solution by syringe. These were treated with a 1% HCl solution and extracted with hexanes, and the organic phase was analyzed by using GC.

General Procedure for Reduction of Alkyl Halides with Ethylmagnesium Bromide (Table III, Entry 1). To (dppf)PdCl$_2$ (0.015 g, 0.021 mmol, 2.2 mol %) that had been placed under an argon atmosphere using 2 cycles of an evacuate/quench protocol and cooled to −78 °C was added THF (8 mL), followed by the 1-iodododecane (0.24 g, 0.95 mmol), ethylmagnesium bromide (1.4 mL, 2.5 M in THF, 3.5 mmol), and finally additional THF (2 mL). This mixture was slowly raised to room temperature over 4–6 h, followed by heating in a 75 °C oil bath for 8–12 h. The resulting black slurry was cooled to room temperature and diluted with pentane (15 mL). Unreacted Grignard reagent was quenched by the dropwise addition of water and the reaction mixture was washed with water (20 mL). The aqueous layer was back-extracted with pentane (15 mL), and the combined organic layers were washed sequentially with water (3–6 × 20 mL) and a saturated

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sodium chloride solution (2 × 20 mL). The organic layer was dried over anhydrous $MgSO_4$, filtered through a small pad of silica gel, and concentrated by removal of the solvent through a 100-cm Vigreux column. Remaining solvent was removed by placing the oil under reduced pressure for short periods of time. Purification by bulb-to-bulb distillation gave dodecane (0.12 g, 76% yield) as a clear colorless oil.

The purity of compounds 5, 7, 11, and 13 was ≥95% as determined by GC and by ^{13}C and ^{1}H NMR determinations. GC retention times and all spectra were identical with those of commercial standards.

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Registry No. **1**, 2050-77-3; **4**, 143-15-7; **6**, 4119-41-9; **8**, 637-59-2; **9**, 104-52-9; **10**, 40548-64-9; **12**, 129848-86-8; **14**, 59456-20-1; **20**, 925-90-6; **21**, 1462-75-5; PhMgBr, 100-58-3; MeMgCl, 676-58-4; (dppf)Pd(0), 127140-10-7; $(dppf)PdCl_2$, 72287-26-4.

Supplementary Material Available: Spectral characteristics of compounds **5**, **7**, **10**, **12**, **13**, and **14**, the GC/MS data arising from the mixture obtained on reduction of 3-iodo-1-phenylbutane, more detailed experimental information for the reduction of iodides **12** and **14**, and ^{1}H and ^{3}C NMR spectra of **11**, **12**, and **14** (10 pages). Ordering information is given on any current masthead page.

New Desulfurizations by Nickel-Containing Complex Reducing Agents

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Desulfurizations of saturated aliphatic or aromatic sulfoxides or sulfones are efficiently performed with nickel complex reducing agents (NiCRA's). The complete desulfurization of dithioketals can be effected in high yields with these reagents, while their half-desulfurization is efficiently achieved with 2,2′-bipyridine-modified nickel complex reducing agents (NiCRA-bpy). The desulfurization of vinyl thioethers, sulfoxides, and sulfones have been shown to be chemoselective, leaving the C–C double bond intact. The desulfurization of (*E*)-$PhSO_2(CH_3)C{=}CHPh$ to *cis*-$CH_3CH{=}CHPh$ with NiCRA in the presence of quinoline is 95% enantioselective.

Introduction

Desulfurization of organic compounds is important in the production of nonpolluting fuels and is also a cornerstone of organic synthesis using sulfur chemistry.[1] Among numerous desulfurizing reagents, heterogeneous nickel reagents occupy an important position. A number of Raney nickels[2,3] and in situ generated nickel boride[4] have been the most widely used nickel reagents. Drawbacks of Raney nickels include their tedious preparation, hazards in handling, difficulty in determining the weight of Ni, and the large Ni/S ratio necessary.[3] Nickel boride is more convenient but less reactive. Both reagents suffer from a lack of chemoselectivity.[4b,c] Literature data[1,2b,3a,5,6] indicates that the desulfurizing properties of nickel reagents are mainly due to hydrogen adsorbed on the surface of the finely divided reagents and to single-electron-transfer (SET) ability. The easily prepared nonpyrophoric nickel-containing complex reducing agents (NiCRA's and NiCRAL's)[7a] appeared interesting as new candidates for desulfurizing reagents, since they are strong "hydrogen transmitters"[8] and effect SET reactions.[9] These prop-

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0022-3263/90/1955-6194$02.50/0