Reductive Elimination of Hydrogen Chloride from Chloro Hydrido Transition Metal Complexes: An Efficient and Simple Method for Generation of Electron-Rich, Coordinatively Unsaturated, Reactive Intermediates

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Oxidative addition (OA; eq 1) and the reverse process, reductive elimination (RE; eq 2), are important transformations in chemistry and are key processes in the catalysis with transition metals.[1-3] It is not surprising, therefore, that numerous profound studies have been undertaken in order to understand the detailed mechanisms of both processes.

$$[L_nM] + XY \rightleftarrows [L_{n-m}M(X)Y] + mL \qquad (1)$$

$$[L_nM(X)Y] \rightleftarrows [L_nM] + XY \qquad (2)$$

L = neutral ligand, e.g., tertiary phosphine

X, Y =
H, alkyl, aryl, CN, I, Br, Cl, in various combinations

The number of publications on oxidative addition reactions substantially exceeds that on reductive elimination. This situation finds a clear reflection in modern books on organometallic chemistry[1-3] where the chapters concerning OA are at least two to three times larger by volume than those on RE reactions. Evidently, OA processes are generally easier to study. By starting with relatively stable compounds such as Vaska's complex, [(Ph₃P)₂Ir(CO)Cl], Wilkinson's catalyst, [(Ph₃P)₃RhCl], or zero-valent phosphine complexes of Pt and Pd, one obtains Ir(III), Rh(III), Pt(II), and Pd(II) species, respectively, which are usually more stable than the original complexes and can be fully characterized. On the contrary, reductive elimination from a transition metal center leads to electron-enriched, coordinatively unsaturated complexes of metals in low oxidation states. An exceedingly high reactivity of such complexes toward even relatively inert molecules makes the RE reactions difficult to study and, at the same time, very attractive to chemists. Due to their high reactivity, the [LₙM] species (eq 2) can be successfully used in organometallic

and inorganic synthesis, catalysis, and activation of inert bonds, including aromatic and aliphatic C-H bonds.[4]

How could the equilibrium (eq 2) be controlled? In a number of cases, RE occurs spontaneously at ambient or even lower temperatures, especially when X = H and Y = alkyl or aryl. Most σ-alkyl (aryl) transition metal hydrides are too unstable to be convenient to work with. A skillful synthetic design along with expensive, sophisticated ligands is required to create a σ-organometallic hydride which is stable at room temperature, but smoothly eliminates the hydrocarbon upon slight heating.[5] Although the transition metal polyhydrides (X = Y = H) are quite promising, it is now clear that either UV irradiation or stoichiometric amounts of a dihydrogen trap are necessary to effectively shift equilibrium 2 to the right. In addition, the H₂-acceptors known (e.g., *tert*-butylethylene[4a,d,6] and the uranium hydrogen sponge[7]) are expensive.

Chloro hydrido transition metal complexes (X = Cl, Y = H) seem to be a special case. More than 100 chloro hydrido complexes are known, especially for catalytically important late transition metals. Many of these compounds are very easy to prepare and handle; usually they are not only thermally stable but also relatively insensitive to air and moisture. What seems to be significant in this case is the possibility of shifting equilibrium 2 to the right by adding to the system inexpensive inorganic or organic bases which can trap the hydrogen chloride. Reductive elimination of HCl from chloro hydrido transition metal complexes has never been reviewed. The goal of this Account is to show the potential of this reaction in synthesis and

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(1) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley and Sons: New York, 1988.
(2) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Application of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987.
(3) Yamamoto, A. *Organotransition Metal Chemistry. Fundamental Concepts and Applications*; John Wiley and Sons: New York, 1986.
(4) For reviews, see: (a) Crabtree, R. H. *Chem. Rev.* 1985, 85, 245. (b) Halpern, J. *Inorg. Chim. Acta* 1985, 100, 41. (c) Deem, M. L. *Coord. Chem. Rev.* 1986, 74, 101. (d) Ephritikhine, M. *New J. Chem.* 1986, 10, 9. (e) Jones, W. D.; Feher, F. J. *Acc. Chem. Res.* 1989, 22, 91. (f) Ryabov, A. D. *Chem. Rev.* 1990, 90, 403.
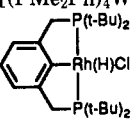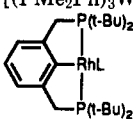(5) Hackett, M.; Ibers, J. A.; Jernakoff, P.; Whitesides, G. M. *J. Am. Chem. Soc.* 1986, 108, 8094. Hackett, M.; Ibers, J. A.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 1436. Hackett, M.; Whitesides, G. M. *J. Am. Chem. Soc.* 1988, 110, 1449.
(6) Crabtree, R. H.; Mihelcic, J. M.; Quirk, J. M. *J. Am. Chem. Soc.* 1979, 101, 7738.
(7) Mimoun, H.; Brazi, E.; Cameron, C. J.; Benazzi, E.; Meuner, P. *New J. Chem.* 1989, 13, 713.

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Table I. Reductive Elimination of HCl from Chloro Hydrido Transition Metal Complexes under Homogeneous Conditions

entry	chloro hydrido complex	base	added ligand	product	ref
1	$[(Ph_3P)_2Pt(H)Cl]$	KOH/EtOH	PPh_3	$[(Ph_3P)_3Pt]$	14
2		NH_3 or N_2H_4	CO	$[Pt_3(CO)_3(Ph_3P)_4]$	15
3		DBU	Ph_2C_2	$[(Ph_3P)_2Pt(Ph_2C_2)]$	16
4	$[L_2Ir(CO)(H)X_2]$ (L = PMe_3, PEt_3, PMe_2Ph, $AsMe_2Ph$; X = Cl, Br, I)	KOH/MeOH or Et_3N	none	$[L_2Ir(CO)X]$	17
5	$[(Ph_3P)_2Ir(CSe)(H)Cl_2]$	Et_3N	none	$[(Ph_3P)_2Ir(CSe)Cl]$	18
6	$[(Ph_3P)_2Ir(CO)(H)_2Cl]$	KOH/EtOH	PPh_3	$[(Ph_3P)_3Ir(CO)(H)]$	19
7	$[(Ph_3P)_3Ru(CO)(H)Cl]$	1. $AgClO_4$ 2. NaOH/EtOH	CNR	$[(Ph_3P)_3Ru(CO)(CNR)]$	20
8			$CNR + O_2$	$[(Ph_3P)_2Ru(O_2)(CO)(CNR)]$	20
9			$CO + PPh_3$	$[(Ph_3P)_3Ru(CO)_2]$	21
10		DBU	CO	$[(Ph_3P)_2Ru(CO)_3]$	16
11	$[(Ph_3P)_3Os(CO)(H)Cl]$	1. $AgClO_4$ 2. NaOH/EtOH	$CO + PPh_3$	$[(Ph_3P)_3Os(CO)_2]$	21
12		DBU	CO	$[(Ph_3P)_2Os(CO)_3]$	16
13	$[(PMe_2Ph)_4W(H)_2Cl_2]$	Et_3N	L (CO, RNC, C_2H_4)	$[(PMe_2Ph)_3W(L)_3]$	22
14		$NaN(SiMe_3)_2$	L(CO, C_2H_4)		23

catalysis. Some mechanistic aspects of the process will also be discussed.

Reductive Elimination of HCl under Homogeneous Conditions.

In the late 1950s and early 1960s the addition of dry HCl to $[L_2Pt(H)Cl]$ (L = Et_3P) in ether (eq 3) was reported.[8] The adduct, presumably an octahedral Pt(IV) complex, $[L_2Pt(H)_2Cl_2]$, is stable under hydrogen chloride; however, it easily loses one molecule of HCl if heated or treated with water, to give the original Pt(II) monohydride. Similar transformations were observed later for a number of other square-planar phosphine complexes of Pt(II).[9,10]

$$[L_2Pt^{II}(H)Cl] + HCl \underset{\text{heat or } H_2O}{\overset{HCl,\ Et_2O}{\rightleftharpoons}} [L_2Pt^{IV}(H)_2Cl_2] \quad (3)$$
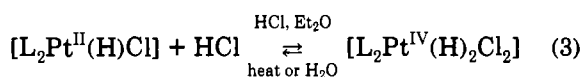
A few years later Ugo, Cariati, and LaMonica claimed the preparation of bis(triphenylphosphine)platinum by a number of reactions including RE of HX from the corresponding complexes (eq 4).[11] The formation of $[(Ph_3P)_2Pt]$ was confirmed by some ligand addition reactions, although no yields were reported.[12] However, later it was concluded that "subsequent attempts to prepare $[Pt(Ph_3P)_2]$ in *monomeric form* under conditions where it is sufficiently stable for direct detection and characterization, either in solution or as a solid, appear to have been unsuccessful".[13]

As seen, these first examples (eqs 3 and 4) were quite far from certainty with respect to the characterization of the complexes. However, the significant feature was

$$[L_2Pt(H)X] + B: \underset{-HX}{\rightarrow} \text{"[}L_2Pt]\text{"} \quad (4)$$

X = Cl, B: = n-BuLi, N_2H_4; X = CN, B: = KOH

in demonstrating clearly the *principal possibility* of reductively eliminating HCl from chloro hydrido transition metal compounds in the presence of a base. Since the early 1960s a number of reactions have been published where reductive elimination of HCl from different transition metal complexes was successfully applied to inorganic and organometallic synthesis (Table I). The reactions shown in Table I were conducted mostly as one-step processes; however, in a few cases (entries 7–9, 11) a stepwise technique was employed. Some of the transformations are of significant synthetic value. Dehydrochlorination of {2,6-bis[(di-*tert*-butylphosphino)methyl]phenyl}chloro-hydridorhodium (entry 14) gives rise to an extremely reactive 14-electron species which is able to activate aliphatic and aromatic C–H bonds.[23] Unfortunately, the majority of papers cited in Table I were published as brief communications, providing the reader with no experimental detail.

Some chloro transition metal complexes react smoothly with H_2 in the presence of base to give the corresponding products in high yields (e.g., eqs 5 and 6).[24,25] Both reactions are of high importance as the resulting complexes are excellent catalysts for the hydrogenation

(8) Chatt, J.; Duncanson, L. A.; Shaw, B. L. *Chem. Ind. (London)* 1958, 859. Chatt, J.; Shaw, B. L. *J. Chem. Soc.* 1962, 5075.
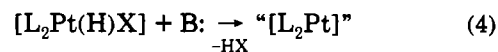
(9) Anderson, D. W. W.; Ebsworth, E. A. V.; Rankin, D. W. H. *J. Chem. Soc., Dalton Trans.* 1973, 854.

(10) Ramprasad, D.; Yue, H. J.; Marsella, J. A. *Inorg. Chem.* 1988, 27, 3151.

(11) Ugo, R.; Cariati, F.; LaMonica, G. *J. Chem. Soc., Chem. Commun.* 1966, 868. Keubler, M.; Ugo, R.; Cenini, S.; Conti, F. *J. Chem. Soc., Dalton Trans.* 1975, 1081.

(12) Ugo, R.; LaMonica, G.; Cariati, F.; Cenini, S.; Conti, F. *Inorg. Chim. Acta* 1970, 4, 390.

(13) (a) Sen, A.; Halpern, J. *Inorg. Chem.* 1980, 19, 1073. (b) Abis, L.; Sen, A.; Halpern, J. *J. Am. Chem. Soc.* 1978, 100, 2915.

(14) Cariati, F.; Ugo, R.; Bonati, F. *Inorg. Chem.* 1966, 5, 1128.

(15) Booth, G.; Chatt, J. *J. Chem. Soc. A* 1969, 2131.

(16) Grundy, K. R. *Inorg. Chim. Acta* 1981, 53, L225.

(17) Deeming, A. J.; Shaw, B. L. *J. Chem. Soc. A* 1968, 1887.

(18) Roper, W. R.; Town, K. G. *J. Organomet. Chem.* 1983, 252, C97.

(19) Harrod, J. F.; Gilson, D. F. R.; Charles, R. *Can. J. Chem.* 1969, 47, 1431.

(20) Christian, D. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* 1971, 1271.

(21) Cavit, B. E.; Grundy, K. R.; Roper, W. R. *J. Chem. Soc., Chem. Commun.* 1972, 60.
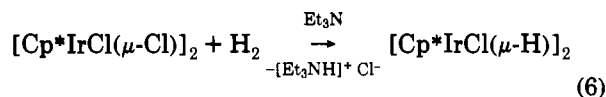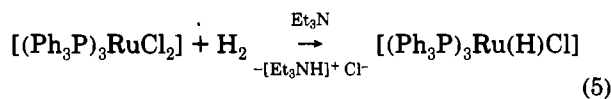
(22) Dadkhah, H.; Kashef, N.; Richards, R. L.; Hughes, D. L.; Pombeiro, A. J. L. *J. Organomet. Chem.* 1983, 255, C1.

(23) Nemeh, S.; Jensen, C.; Binamira-Soriaga, E.; Kaska, W. C. *Organometallics* 1983, 2, 1442.

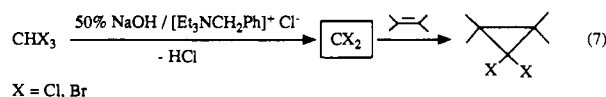(24) Hallman, P. S.; McGarvey, B. R.; Wilkinson, G. *J. Chem. Soc. A* 1968, 3143.

(25) Gill, D. S.; Maitlis, P. M. *J. Organomet. Chem.* 1975, 87, 359.

of olefins. Transformations 5 and 6 likely proceed via coordination of H_2 with the transition metal centers, followed by elimination of HCl from the η^2-H_2 complexes formed (see below).

$$[(Ph_3P)_3RuCl_2] + H_2 \xrightarrow[-[Et_3NH]^+ Cl^-]{Et_3N} [(Ph_3P)_3Ru(H)Cl] \tag{5}$$

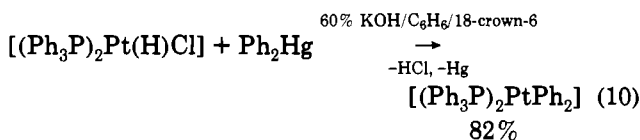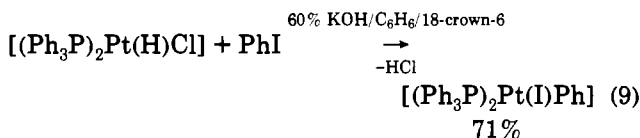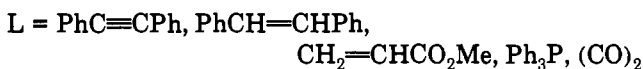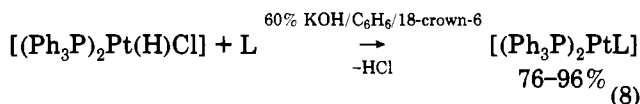$$[Cp^*IrCl(\mu\text{-}Cl)]_2 + H_2 \xrightarrow[-[Et_3NH]^+ Cl^-]{Et_3N} [Cp^*IrCl(\mu\text{-}H)]_2 \tag{6}$$

Reductive Elimination of HCl under Biphasic or Phase Transfer Catalysis (PTC) Conditions

Coordinatively unsaturated complexes of transition metals in low oxidation states, $[L_nM]$ (eq 2), are regarded[26] as $\sigma^0\pi^2$ carbene analogues. The most efficient and simple method to generate dihalocarbenes from the corresponding haloforms is known to be the phase transfer catalyzed reaction discovered by Makosza and Wawryzniewicz (eq 7).[27] The resemblance between eqs 2 and 7 pushed us to apply PTC conditions to eliminate HCl from chloro transition metal hydrides.

$$CHX_3 \xrightarrow[-HCl]{50\% \text{ NaOH} / [Et_3NCH_2Ph]^+ Cl^-} \boxed{CX_2} \longrightarrow \searrow = \diagdown \quad \diagup\!\!\diagdown_{X \quad X} \tag{7}$$

X = Cl, Br

Readily available, air- and moisture-stable in both the solid state and solution, the platinum(II) complex, $[(Ph_3P)_2Pt(H)Cl]$, smoothly undergoes reductive elimination of HCl under PTC conditions.[28,29] Both Pt(0) and Pt(II) complexes were obtained in high yields when the reaction was conducted in the presence of appropriate ligands and substrates (eqs 8–10).

$$[(Ph_3P)_2Pt(H)Cl] + L \xrightarrow[-HCl]{60\% \text{ KOH}/C_6H_6/18\text{-crown-6}} [(Ph_3P)_2PtL] \atop 76\text{-}96\% \tag{8}$$

L = $PhC\equiv CPh$, $PhCH\!=\!CHPh$,

$CH_2\!=\!CHCO_2Me$, Ph_3P, $(CO)_2$

$$[(Ph_3P)_2Pt(H)Cl] + PhI \xrightarrow[-HCl]{60\% \text{ KOH}/C_6H_6/18\text{-crown-6}}$$

$$[(Ph_3P)_2Pt(I)Ph] \tag{9}$$
$$71\%$$

$$[(Ph_3P)_2Pt(H)Cl] + Ph_2Hg \xrightarrow[-HCl, -Hg]{60\% \text{ KOH}/C_6H_6/18\text{-crown-6}}$$

$$[(Ph_3P)_2PtPh_2] \tag{10}$$
$$82\%$$

Iridium,[30,31] rhodium,[31] and ruthenium[31,32] polyhydrides can be prepared in quantitative yields from their

chloro hydrido precursors and H_2 under PTC conditions (eqs 11–13).

$$[L_2Ir(H)Cl_2] + 3H_2 \xrightarrow[-2HCl]{50\% \text{ NaOH}/C_6H_6/[Et_3NCH_2Ph]^+ Cl^-} [L_2IrH_5] \tag{11}$$

L = $i\text{-}Pr_3P$, Cy_3P

$$[L_2Rh(H)Cl_2] + H_2 \xrightarrow[-HCl]{50\% \text{ NaOH}/C_6H_6/[Et_3NCH_2Ph]^+ Cl^-}$$

$$[L_2Rh(H)_2Cl] \tag{12}$$

L = $i\text{-}Pr_3P$, Cy_3P

$$[L_2L'Ru(H)Cl] + 2H_2 \xrightarrow[-HCl]{PTC} [L_2L'Ru(H_2)(H)_2] \tag{13}$$

L = L' = Ph_3P; L = $i\text{-}Pr_3P$, L' = CO

PTC = 50% NaOH/benzene/$[Et_3NCH_2Ph]^+$ Cl⁻,

or KOH/toluene (dichloromethane)/18-crown-6

The synthetic methods (eqs 8–13) possess a number of advantages over previously known procedures. Since the reactions are straightforward and clean, leading to no byproducts, the resulting complexes are very easy to isolate in pure form. The PTC method seems to be the best for preparing such compounds as $[(Ph_3P)_2Pt(CO)_2]$, $[(Ph_3P)_2Pt(CH_2\!=\!CHCO_2Me)]$, and $[(Ph_3P)_2Pt(Ph)_2]$. It is noteworthy that the well-known complex $[L_3Pt]$ (L = PPh_3), which is widely used in organometallic synthesis, was obtained for the first time in pure form without contamination by $[L_4Pt]$.[29] When the $[L_3Pt]$ was synthesized by the common literature method, the room temperature ^{31}P NMR showed only a very broad, unresolved signal due to the ligand exchange between residual $[L_4Pt]$ and the tricoordinated complex, $[L_3Pt]$.[13a] In contrast, sharp lines were observed at 25 °C in both the ^{31}P and ^{195}Pt NMR spectra of $[L_3Pt]$ when synthesized from chloroplatinum hydride under PTC conditions.[29] With respect to the synthesis of the polyhydrides, it is obvious that to work with alkali and reagent-grade benzene is more convenient than handling complex hydrides ($LiAlH_4$, $NaBH_4$) in oxygen-free, dry ether or THF, which are commonly used for this purpose.

Another phase transfer catalyzed reaction (eq 14) is quite remarkable as it represents the first example of RE of HCl from a binuclear transition metal hydride.[33] The process can be formally regarded as the loss of two HCl molecules from the dihydride, followed by OA of the triphenylphosphine C–H and C–P bonds to the iridium centers. It was established that the *o*-phenylene ligand originates from triphenylphosphine, not the solvent (benzene). The structure of the resulting complex with three bridging ligands was determined by a single-crystal X-ray diffraction study.[33]

(26) Varshavsky, Yu. S. *Metalloorg. Khim.* **1988**, *1*, 249; *Organomet. Chem. USSR* **1988**, *1*, 135 (English translation).
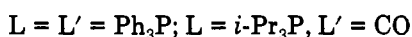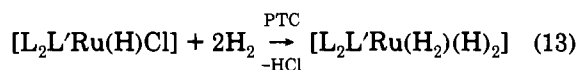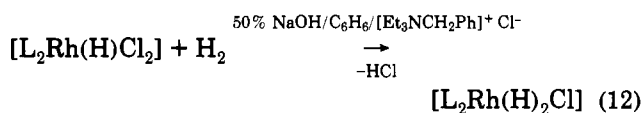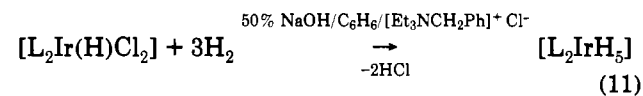
(27) Makosza, M.; Wawryzniewicz, W. *Tetrahedron Lett.* **1969**, 4659.

(28) Grushin, V. V.; Akhrem, I. S.; Volpin, M. E. *Metalloorg. Khim.* **1988**, *1*, 474; *Organomet. Chem. USSR* **1988**, *1*, 260 (English translation).

(29) Grushin, V. V.; Akhrem, I. S.; Vol'pin, M. E. *J. Organomet. Chem.* **1989**, *371*, 403.

(30) Grushin, V. V.; Bakhmutov, V. I.; Akhrem, I. S.; Volpin, M. E. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1988**, 494; *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1988**, *37*, 415 (English translation).

(31) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *J. Organomet. Chem.* **1990**, *382*, 185.

(32) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *Inorg. Chem.* **1992**, *31*, 1.

(33) Grushin, V. V.; Vymenits, A. B.; Yanovsky, A. I.; Struchkov, Yu. T.; Vol'pin, M. E. *Organometallics* **1991**, *10*, 48.
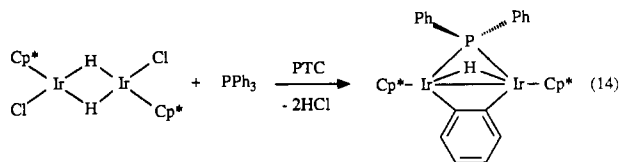
$$Cp^* = \eta^5\text{-}C_5Me_5; \quad PTC = 60\% \ KOH/C_6H_6/[Et_3NCH_2Ph]^+ \ Cl^-$$

The PTC process (eq 14) competes successfully with the known[25] homogeneous reaction between the original dihydride and PPh_3 which leads to the mononuclear complex, $[Cp^*Ir(H)(PPh_3)Cl]$ (ca. 30% yield). Interestingly, the latter does not undergo reductive elimination of HCl under PTC conditions. When the PTC reaction of the dimer, $[Cp^*{}_2Ir_2Cl_2(\mu\text{-}H)_2]$, was carried out in the absence of PPh_3, a complicated mixture of hydridoiridium species was obtained. The experiment conducted with benzene-d_6 as the organic phase revealed that these iridium hydrides were formed via the solvent (benzene) C–H or C–D bond cleavage.[33]

Reductive Elimination of HCl from Transition Metal Complexes in Homogeneous Catalysis

Reductive elimination of hydrogen chloride from various complexes of platinum metals is of high relevance to homogeneous catalysis. For instance, in a number of cases a base is necessary for in situ generation of catalytically active hydrido complexes from the reaction between their non-hydrido precursors and H_2 (e.g., eqs 5 and 6). Markó and co-workers[34] widely investigated catalytic aspects of the base-promoted hydrogenation of olefins and ketones catalyzed by phosphine rhodium complexes. The well-known beneficial effect of water on the rate of hydrogenation of diverse substrates was for the first time accounted for by Joó.[35] It was proposed that the extraction of HCl·base (e.g., $[Et_3NH]^+$ Cl^-, which arises from reductive elimination of HCl from the rhodium complex) into the aqueous phase shifts the equilibrium in favor of the catalytically active species.[35] Slow equilibrium (eq 15) was observed in toluene solutions of the rhodium monohydrides, $[L_2Rh(H)Cl_2]$ (L = $i\text{-}Pr_3P$, Cy_3P), under H_2.[36] These readily available, air-stable monohydrido complexes of rhodium are catalytically inactive for the hydrogenation of the C=C bond. The corresponding dihydrides, however, are isostructural and isoelectronic with the species which are believed to be responsible for the olefin reduction with Wilkinson's catalyst. Equilibrium 15 can be shifted to the right not only by strong bases (e.g., alkali under PTC conditions,[31] see above) but also by an excess of a readily absorbing HCl aqueous phase.

$$[L_2Rh(H)Cl_2] + H_2 \rightleftharpoons [L_2Rh(H)_2Cl] + HCl \quad (15)$$

L = $i\text{-}Pr_3P$, Cy_3P

Since, in this case, elimination of HCl does not require a strong base, the system (eq 15) can be successfully

(34) Nagy-Magos, Z.; Vastag, S.; Heil, B.; Markó, L. *Transition Met. Chem.* **1978**, *3*, 123. Heil, B.; Törös, S.; Bakos, J.; Markó, L. *J. Organomet. Chem.* **1979**, *175*, 229. Törös, S.; Kollár, L.; Heil, B.; Markó, L. *J. Organomet. Chem.* **1983**, *253*, 375; *255*, 377.
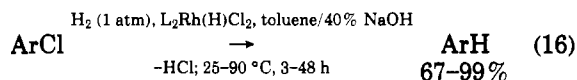(35) Joó, F.; Trócsányi, E. *J. Organomet. Chem.* **1982**, *231*, 63.
(36) Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *175*, 19.

applied to the hydrogenation of α,β-unsaturated aldehydes and ketones at 25 °C and 1 atm of H_2.[37] The efficient catalytic reaction (1–5% of $[(Cy_3P)_2Rh(H)Cl]$) in benzene(m-xylene)–water biphasic systems is highly selective, leading to reduction of only C=C bonds in unsaturated carbonyl compounds. Unlike Wilkinson's catalyst, the hydridorhodium complexes of bulky triisopropylphosphine and tricyclohexylphosphine do not decarbonylate aldehydes at room temperature. Thus, possessing a number of important advantages, this biphasic hydrogenation can be considered as one of the best catalytic methods for the reduction of α,β-unsaturated aldehydes.

There is another type of catalytic reaction where alternating formation of a chloro hydrido transition metal species and subsequent reductive elimination of HCl from the complex occur continuously. For example, such a reaction sequence was proposed for secondary steps in the Heck arylation of olefins with haloarenes catalyzed by Pd complexes.[2] Recently, the first processes were purposely developed which are based on formation of chloro hydrido transition metal complexes and their decomposition via loss of HCl, as *key catalytic steps*.

Complexes $[L_2Rh(H)Cl_2]$ and $[L_2Ru(CO)(H)Cl]$ (L = $i\text{-}Pr_3P$, Cy_3P) in the presence of alkali efficiently catalyze the H/D exchange between benzene or toluene and D_2.[38] It seemed logical to apply these systems to hydrogenolysis of the carbon–chlorine bond in chloroarenes. Indeed, the chlorohydridorhodium complexes of triisopropylphosphine or tricyclohexylphosphine (usually 1–5 mol%) were found to effectively catalyze the reduction of chloroarenes to arenes[39] (eq 16). The catalytic biphasic reaction occurs under exceedingly mild conditions, affording the desired products in almost quantitative yields. The catalytic system is tolerant of many functional groups. It works well with heterocyclic compounds and even carboxylic acids which exist as the corresponding anions under the reaction conditions. The process is biphasic in nature; however, in a few cases the addition of benzyltriethylammonium chloride to the biphasic systems improved yields slightly. The hydrogenolysis selectivity is very high, with no biaryl formation or aromatic ring hydrogenation observed in any of these transformations.[39]

$$\text{ArCl} \xrightarrow[\substack{-HCl;\ 25-90\ °C,\ 3-48\ h}]{H_2\ (1\ atm),\ L_2Rh(H)Cl_2,\ toluene/40\%\ NaOH} \text{ArH} \quad (16)$$
$$67-99\%$$

ArCl = chlorobenzene, 1-chloronaphthalene, 3- and 4-chlorotoluenes, 4-chloroaniline, 4-chloroanisole, 4-chloro-1-(trifluoromethyl)benzene, 4-chlorobenzophenone, p-chlorobenzoic acid, p-chlorophenylacetic acid, carprofen, 5-chlorobenzodioxole, 5-chloro-1-ethyl-2-methylimidazole, tetrachloro-m-xylene

Reaction 16 represents the first example of an efficient catalytic hydrogenolysis of the carbon–chlorine bond in chloroarenes. Dechlorination of chloroaromatics could be effectively used in organic synthesis. For instance (Scheme I), o-methylbenzophenone cannot be

(37) Grushin, V. V.; Alper, H. *Organometallics* **1991**, *10*, 831.
(38) Grushin, V. V.; Vymenits, A. B.; Vol'pin, M. E. *Metalloorg. Khim.* **1990**, *3*, 702.
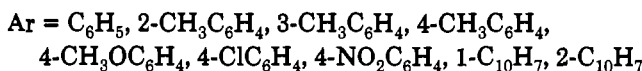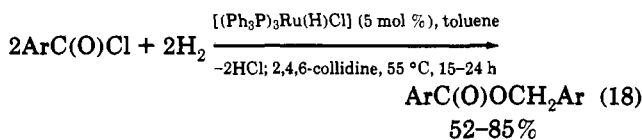(39) Grushin, V. V.; Alper, H. *Organometallics* **1991**, *10*, 1620.

Scheme I
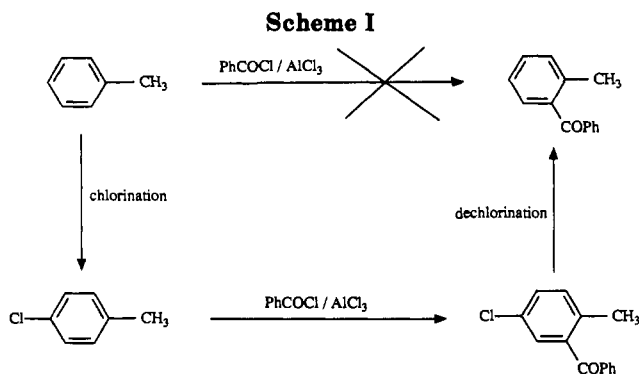
prepared by direct Friedel–Crafts benzoylation of toluene because the electrophile will attack the para position of the ring. By introducing chlorine to the para position of the toluene molecule (which is easy to do), one protects this site against electrophilic attack. Benzoylation of the prepared *p*-chlorotoluene followed by removal of the chlorine atom affords the desired compound. Therefore, chlorine could be used as a protecting group, offering chemists a unique opportunity to alter the orientation rules of aromatic electrophilic substitution.

It seemed worth applying the catalytic system [$L_2Rh(H)Cl_2$] + H_2 + alkali to the reduction of acid chlorides to aldehydes. Clearly, for this purpose it was necessary to replace the aqueous alkali for another base which is substantially less reactive toward carboxylic acid chlorides. When triethylamine was used as the base in the Rh-catalyzed reaction between 2-naphthoyl chloride and H_2, 2-naphthaldehyde was obtained in 61% isolated yield[40] (eq 17).
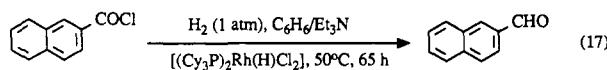
Reaction 17 represents the first example of homogeneously catalyzed Rosenmund-type reduction. Since yields of other aldehydes were too low (0–30%), the search was made for a more efficient catalyst for the reduction of acid chlorides. Eventually, it was found that the well-known chloro hydrido complex of ruthenium, [($Ph_3P)_3Ru(H)Cl$], is able to simultaneously catalyze the Rosenmund and the Tishchenko reactions.[40] This process (eq 18) is formally best characterized as the reduction of acid chlorides to aldehydes followed by the disproportionation of the aldehyde formed to the corresponding ester. A number of aroyl chlorides containing electron-withdrawing and electron-donating substituents were successfully converted into esters in the presence of the ruthenium catalyst (5 mol %) and 2,4,6-collidine as base.

$$2ArC(O)Cl + 2H_2 \xrightarrow[\text{-2HCl; 2,4,6-collidine, 55 °C, 15-24 h}]{[(Ph_3P)_3Ru(H)Cl]\ (5\ \text{mol}\ \%),\ \text{toluene}}$$

$$ArC(O)OCH_2Ar \quad (18)$$
$$52-85\%$$

Ar = C_6H_5, 2-$CH_3C_6H_4$, 3-$CH_3C_6H_4$, 4-$CH_3C_6H_4$,
4-$CH_3OC_6H_4$, 4-ClC_6H_4, 4-$NO_2C_6H_4$, 1-$C_{10}H_7$, 2-$C_{10}H_7$

(40) Grushin, V. V.; Alper, H. *J. Org. Chem.* **1991**, *56*, 5159.

The catalytic transformation (eq 18) is the first example of a one-pot Rosenmund-type reduction and Tishchenko dimerization reaction. The reaction sequence affords valuable esters directly from acid chlorides and H_2.

## Mechanistic Considerations and Studies

Before analyzing the pathways of reductive elimination of HCl from the transition metal complexes, let us consider, briefly, possible mechanisms for the reverse process (eq 1), which has been studied in more detail.

Synchronous oxidative addition (eq 19) can take place when some platinum(II) compounds[8-10] or Vaska's complex[41] is treated with dry HCl in a low-polarity medium or without any solvent.[42] This concerted process is believed to be similar to the oxidative addition of other bonds (e.g., H–H, C–halogen, C–H) to transition metal centers.[1-3]

$$[L_nM] + HCl \rightarrow \text{``}[L_nM(HCl)]\text{''} \rightarrow [L_nM(H)(Cl)] \quad (19)$$

No transition metal complexes with molecular HCl as a ligand have been described so far. However, existence of stable transition metal complexes with molecular hydrogen[43] and organic halides[44] suggests that some molecular HCl complexes might be sufficiently stable for isolation and characterization. Several examples of intramolecular E–H–Cl (E = N, S, O) hydrogen bonding in complexes of Ir, Ru, and Pd have been reported.[45,46] Some are capable of losing HCl in the presence of base and, therefore, can be regarded as HCl complexes stabilized by the intramolecular hydrogen bond.[46a]

Electrophilic oxidative addition of HCl (eq 20) to electron rich transition metal complexes in low oxidation states is probably the most common mechanism. The reactions of Pt(0) phosphine complexes with acids are among the most extensively studied and understood examples.[47] Metal centers of some relatively stable complexes are quite basic; e.g., solutions of [($Et_3P)_3Pt$] in aqueous THF were estimated to have pH of ca. 14.[48]

$$[L_nM] \xrightarrow{H^+} [L_nMH]^+ \xrightarrow{Cl^-} [L_nM(H)(Cl)] \quad (20)$$
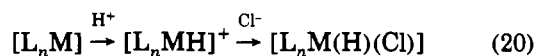
When *hydrido* complexes are subject to protonation,

(41) Vaska, L. *J. Am. Chem. Soc.* **1966**, *88*, 5325.

(42) Pearson, R. G.; Kresge, C. T. *Inorg. Chem.* **1981**, *20*, 1878 and references cited therein.

(43) For reviews, see: Kubas, G. T. *Acc. Chem. Res.* **1988**, *21*, 120. Crabtree, R. H.; Hamilton, D. G. *Adv. Organomet. Chem.* **1988**, *28*, 299. Henderson, R. A. *Transition Metal Chem.* **1988**, *13*, 474. Ginzburg, A. G.; Bagatur'yants, A. A. *Metalloorg. Khim.* **1989**, *2*, 243. Crabtree, R. H. *Acc. Chem. Res.* **1990**, *23*, 95. Jessop, P. G.; Morris, R. H. *Coord. Chem. Rev.* **1992**, *121*, 155.

(44) For a review, see: Kulawiec, R. J.; Crabtree, R. H. *Coord. Chem. Rev.* **1990**, *99*, 89.

(45) (a) Fryzuk, M. D.; MacNeil, P.; Rettig, S. J. *J. Am. Chem. Soc.* **1987**, *109*, 2803. (b) Fryzuk, M. D.; Montgomery, C. D.; Rettig, S. J. *Organometallics* **1991**, *10*, 467.

(46) (a) Sellmann, D.; Barth, I.; Moll, M. *Inorg. Chem.* **1990**, *29*, 176. (b) Kiers, N. H.; Feringa, B. L.; Kooijman, H.; Spek, A. L.; Van Leeuwen, P. W. N. M. *J. Chem. Soc., Chem. Commun.* **1992**, 1169.

(47) Roundhill, D. M. *Adv. Chem. Ser.* **1978**, *167*, 160. Thomas, K.; Dumler, J. T.; Renoe, B. W.; Nyman, C. J.; Roundhill, D. M. *Inorg. Chem.* **1972**, *11*, 1795.

(48) Yoshida, T.; Matsuda, T.; Okano, T.; Kitani, T.; Otsuka, S. *J. Am. Chem. Soc.* **1979**, *101*, 2027.

the metal atom and/or hydrido ligands can be attacked by the proton.[49]
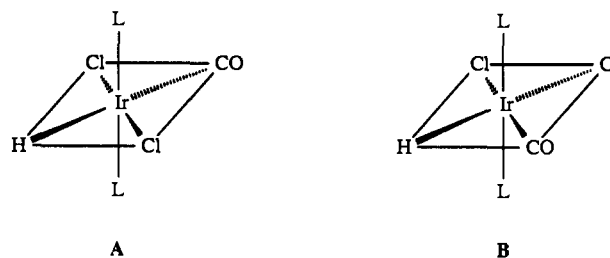
Nucleophilic addition of HCl (eq 21) is rare, however reliably established by Louw's[50] and Crabtree's[51] groups. It is interesting that not only cationic but also some neutral complexes exhibit substantial Lewis acidity at the metal centers. Pearson and Kresge[42] have proved by equilibrium and kinetic studies that the addition of HCl to Vaska-type complexes in methanol proceeds via such a path.

$$[L_nM] \xrightarrow{Cl^-} [L_nMCl]^- \xrightarrow{H^+} [L_nM(H)(Cl)] \qquad (21)$$
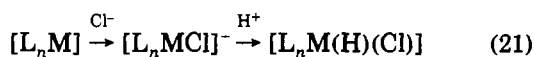
Neutral chloro hydrido transition metal complexes exhibit neither well-pronounced acidity[52] nor obvious "hydridic" properties.[53] Mechanistic aspects of reductive elimination of HCl from the transition metal complexes are more complicated than those of the reverse process. In a number of cases the HCl elimination reactions require not just base but also an added ligand. The latter is likely to be responsible not only for simply trapping the coordinately unsaturated species but also for facilitating the process of reductive elimination. Possessing lone electron pair(s), the base and the ligand may penetrate the inner coordination sphere of chloro hydrido complexes and cause substantial rearrangements before the loss of HCl occurs.

Besides photochemically induced elimination of HCl from [(Ph₃P)₂Ir(CO)(H)Cl₂],[54] only a few reactions are known which proceed in the absence of base. James[55] mentioned spontaneous conversion of the octahedral complex A (L = Cy₃P) to its isomer B, accompanied by a modest loss of HCl; the reaction conditions were not reported. We found that complex A (L = *i*-Pr₃P) slowly loses HCl in the solid state under CO or argon (months at room temperature and atmospheric pressure in the dark). In benzene, A readily isomerizes to B in the presence of air; however, neither elimination of HCl nor isomerization was observed under inert (Ar) atmosphere, even in the presence of aqueous HCl or concentrated alkali containing the phase-transfer catalyst [Et₃NCH₂Ph]⁺ Cl⁻.[56] Complexes B are more stable toward loss of HCl in the solid state than those of type A.

The reactivity pattern reverses itself when one considers the base-promoted elimination of HCl from hydrides A and B in solution. Deeming and Shaw[17] clearly demonstrated that it is adduct B, not A, which smoothly undergoes elimination of HCl in the presence of triethylamine or sodium methoxide. The elimination reactions were found to be first-order in both complex and Et₃N, with rate constants in the order Cl > Br >

(49) Oglieve, K. E.; Henderson, R. A. *J. Chem. Soc., Chem. Commun.* 1992, 441.

(50) Ashworth, T. V.; Singleton, J. E.; de Waal, D. J. A.; Louw, W. J.; Singleton, E.; van der Stok, E. *J. Chem. Soc., Dalton Trans.* 1978, 340.

(51) Crabtree, R. H.; Quirk, J. M.; Fillebeen-Khan, T.; Morris, G. E. *J. Organomet. Chem.* 1979, 181, 203.

(52) Kristjánsdóttir, S. S.; Norton, J. R. Acidity of Hydrido Transition Metal Complexes in Solution. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991; p 309.

(53) Labinger, J. A. Nucleophilic Reactivity of Transition Metal Hydrides. In *Transition Metal Hydrides*; Dedieu, A., Ed.; VCH: New York, 1991; p 361.

(54) Geoffroy, G. L.; Hammond, G. S.; Gray, H. B. *J. Am. Chem. Soc.* 1975, 97, 3933.

(55) James, B. R.; Preece, M.; Robinson, S. D. *Inorg. Chim. Acta* 1979, 34, L219.

(56) Grushin, V. V. Unpublished observations, 1988–1989.

A   B

I for the ligand trans to the hydrogen. These observations are highly consistent with the conclusion made by Pearson and Kresge[42] of a *nucleophilic* mechanism for the ionic addition of HCl to Vaska-type complexes, [L₂Ir(CO)Cl]. The addition starts with the coordination of the Cl⁻ to iridium, followed by protonation. Such ionic reactions lead to adducts B which can be deprotonated to give [L₂Ir(CO)Cl₂]⁻. Subsequent decomposition of the latter leads to the corresponding Ir(I) square-planar complex along with Cl⁻. Thus, reductive elimination of HCl from adducts B is mechanistically similar to the generation of dichlorocarbene from chloroform in the presence of base.[57] Adducts A do not lose HCl via such a pathway. It is conceivable that the slow loss of HCl from the solid complexes A (L = *i*-Pr₃P, Cy₃P) is due to a non-ionic, concerted elimination.

Although very weak C–H acids with pK_a ≤ 38 can undergo an H/D exchange with NaOD/D₂O in the presence of [Bu₄N]⁺ HSO₄⁻,[58] most neutral transition metal "classical" hydrides are not sufficiently acidic[52,59,60] to undergo deprotonation even under such PTC conditions. Indeed, the chlorohydridoplatinum complex [(Ph₃P)₂Pt(H)Cl] does not exchange its "hydrido" hydrogen for deuterium when treated in benzene with 40% NaOD/D₂O in the presence of 18-crown-6.[29] Notwithstanding, the complex readily loses HCl in the presence of some ligands under PTC conditions. The reaction path (eq 22) is likely to be the reverse of that shown in eq 20. Owing to the strong trans influence of the hydrido ligand, the chloro ligand easily leaves the inner coordination sphere of the complex. Subsequent deprotonation of the resulting cationic platinum hydrides under PTC conditions affords the corresponding complexes of Pt(0) in high yield.[29]

$$[L_2Pt(H)Cl] + L' \rightleftharpoons [L_2Pt(L')H]^+ Cl^- \xrightarrow[-HCl]{OH^-} [L_2PtL'] \qquad (22)$$
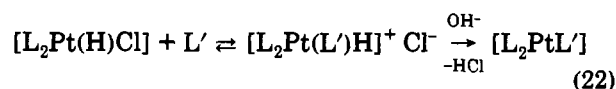
L = Ph₃P; L' = Ph₃P, CO, alkenes, alkynes, etc.

When [L₂Pt(H)Cl] is treated with alkali under PTC conditions in the absence of added ligands, replacement of the chloro ligand by the hydroxide anion probably occurs,[61] followed by reductive elimination of water.[29] This path can compete to some extent with that described in eq 22, when the reaction is conducted in the presence of added ligands.

In contrast to the 16-electron square-planar chloroplatinum hydride, octahedral 18-electron complexes are

(57) Dehmlow, E. V.; Dehmlow, S. S. *Phase Transfer Catalysis*; Verlag Chemie: Weinheim, 1983.

(58) Feldman, D.; Rabinovitz, M. *J. Org. Chem.* 1988, 53, 3779.

(59) Pearson, R. G. *Chem. Rev.* 1985, 85, 41.

(60) Crabtree, R. H. In *Comprehensive Coordination Chemistry*; Wilkinson, G., Ed.; Pergamon Press: Oxford, 1987; Vol. 2, p 689.

(61) Chaudret, B. N.; Cole-Hamilton, D. J.; Nohr, R. S.; Wilkinson, G. *J. Chem. Soc., Dalton Trans.* 1977, 1546.

not prone to bimolecular substitution of the chloro ligand. Roper and co-workers[20,21] used $AgClO_4$ for removal of the Cl⁻ from $[(Ph_3P)_3M(CO)(H)Cl]$ (M = Ru, Os; see Table I). The following step (treatment with RO⁻) was shown to involve alkoxide anion coordination to the metal rather than simple deprotonation. Reductive elimination of the alcohol resulted in the desired zerovalent complexes of Ru and Os.

The so-called "nonclassical" hydrides (molecular dihydrogen complexes) are substantially more acidic (kinetic acidity) than most of the "classical" hydrido complexes of transition metals.[43,62] An η^2-H_2 ligand can be efficiently deprotonated not only in the case of cationic complexes but also in the case of neutral complexes. For instance, the nonclassical ruthenium hydride $[(Ph_3P)_3RuH_4]$ is reversibly deprotonated by RO⁻ (R = cyclohexyl) in THF.[63] The crucial role of the sufficiently acidic molecular dihydrogen complexes in elimination of HCl when some transition metal chlorides react with H_2 (e.g., eqs 5 and 6) has been clearly demonstrated by Morris and co-workers.[64] Dihydride complexes $[L_2MH_2]$ [L = bis(tertiary phosphine), M = Fe, Ru, Os] were obtained in 45-80% yield from the corresponding dichlorides and H_2 in the presence of 2 equiv of base (EtONa or t-BuONa).[64] Both η^2-H_2 complexes $[L_2M(X)(H_2)]^+$, where X = Cl and H, were spectrally (NMR) shown to be intermediates in the process, the complex with X = Cl having been proposed to be as acidic as HCl.

The synthesis of $[(i\text{-}Pr_3P)_2Ir(H)_5]$ from $[(i\text{-}Pr_3P)_2Ir(H)Cl_2]$[30,31] (eq 11) is remarkable since not only the starting monohydride and the final pentahydride[65] but also the reaction intermediates have been structurally characterized by either X-ray or neutron diffraction. Treatment of monohydride 1 with H_2 in benzene or toluene (20 °C, 1 atm) leads to fast, reversible formation of the octahedral, nonclassical trihydride 2 with the H_2 ligand trans to the hydrido ligand (Scheme II).[66] In the presence of water, a competition between H_2 and H_2O for occupying the vacant coordination site at the iridium atom was observed.[67] Both 2 and the aqua complex 3 are too unstable for isolation; however, they have been reliably characterized in solution (^1H, ^2H, ^{31}P NMR).[66,67] A prolonged exposure of 1 to H_2 in dry benzene results in almost quantitative formation of another nonclassical hydride, 4, i.e., the cis isomer of 2. In contrast with 2, the cis complex 4 is stable and can be easily isolated in analytically pure form.[66] Before the neutron diffraction study of 4 was carried out by Koetzle, Klooster, and McMullan,[68] the complex was

Scheme II *
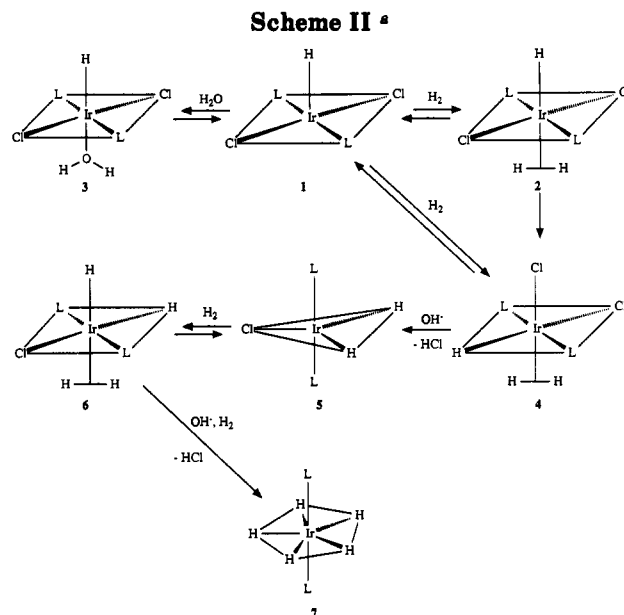
a L = *i*-Pr₃P.

erroneously characterized as a classical trihydride[69] and a molecular HCl complex.[66,70] When treated with KOH, the nonclassical hydride 4 undergoes deprotonation of the η^2-H_2 ligand followed by elimination of Cl⁻, to give the classical dihydride 5.[66,71] Reversible addition of an H_2 molecule to 5 results in formation of the nonclassical tetrahydride 6, which was characterized by NMR (high-resolution spectra and T_1 measurements)[66,72] and single-crystal X-ray diffraction.[72] Similarly to 4, 6 loses HCl and adds a molecule of H_2 in the presence of alkali, to give the pentahydride 7.[31,73] It is quite possible that not only 4 but also 2 loses HCl to give 5 in the course of the PTC synthesis of 7 from 1.[30,31] All the transformations shown in Scheme II are exceedingly smooth, proceeding without formation of byproducts. This is why the yield of 7 (eq 11) is quantitative.

Unlike the iridium complex 1, a similar five-coordinated ruthenium monohydride, $[L_2Ru(CO)(H)Cl]$ (L = t-Bu₂MeP), readily reacts with alkali.[74] The resulting hydroxo hydride, $[L_2Ru(CO)(H)(OH)]$, eliminates H_2O straightforwardly upon treatment with H_2 to give the tetrahydride, $[L_2Ru(CO)(H_2)(H)_2]$, in quantitative yield.[75] Thus, in such cases (eq 13)[32] initial replacement of the chloro ligand by the OH⁻ takes place, followed by formation of $[L_2Ru(CO)(H_2)(H)(OH)]$ and intramolecular deprotonation of its η^2-H_2 ligand by the OH ligand. Subsequent elimination of water from the aqua complex and addition of dihydrogen leads to the tetrahydride.

It was assumed[36] that reactions of chlorohydrido-rhodium complexes which are isostructural and isoelec-

(62) Morris, R. H. *Inorg. Chem.* **1992**, *31*, 1471 and references cited therein.

(63) Linn, D. E.; Halpern, J. *J. Am. Chem. Soc.* **1987**, *109*, 2969.

(64) Cappellani, E. P.; Maltby, P. A.; Morris, R. H.; Schweitzer, C. T.; Steele, M. R. *Inorg. Chem.* **1989**, *28*, 4437. Similar results were later reported by Rigo's group: Mezzetti, A.; Del Zotto, A.; Rigo, P.; Farnetti, E. *J. Chem. Soc., Dalton Trans.* **1991**, 1525.

(65) Garlaschelli, L.; Khan, S. I.; Bau, R.; Longoni, G.; Koetzle, T. F. *J. Am. Chem. Soc.* **1985**, *107*, 7212.

(66) Gusev, D. G.; Bakhmutov, V. I.; Grushin, V. V.; Vol'pin, M. E. *Inorg. Chim. Acta* **1990**, *177*, 115.

(67) Bakhmutov, V. I.; Gusev, D. G.; Vymenits, A. B.; Grushin, V. V.; Vol'pin, M. E. *Metalloorg. Khim.* **1991**, *4*, 164; *Organomet. Chem. USSR* **1991**, *4*, 88 (English translation).

(68) Albinati, A.; Bakhmutov, V. I.; Caulton, K. G.; Clot, E.; Eckert, J.; Eisenstein, O.; Grushin, V. V.; Gusev, D. G.; Hauger, B. E.; Klooster, W.; Koetzle, T. F.; Loughlin, T. J. O.; McMullan, R. K.; Pelissier, M.; Ricci, J. S.; Sigalas, M. P.; Vymenits, A. B. To be submitted.

(69) Bergamini, P.; Sostero, S.; Traverso, O.; Mura, P.; Segre, A. *J. Chem. Soc., Dalton Trans.* **1989**, 2367.

(70) Gusev, D. G.; Vymenits, A. B.; Bakhmutov, V. I. *J. Chem. Soc. Mendeleev Commun.* **1991**, 24.

(71) Complex 5 was previously prepared and characterized by Werner et al. See: Werner, H.; Wolf, J.; Höhn, A. *J. Organomet. Chem.* **1985**, *287*, 395.

(72) Mediati, M.; Tachibana, G. N.; Jensen, C. M. *Inorg. Chem.* **1992**, *31*, 1827.

(73) Esteruelas, M. A.; Herrero, J.; López, A. M.; Oro, L. A.; Schulz, M.; Werner, H. *Inorg. Chem.* **1992**, *31*, 4013.

(74) Poulton, J. T.; Folting, K.; Streib, W. E.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3190.

(75) Caulton, K. G.; Poulton, J. T. Private communication, Aug 1992.

tronic with 1 (eqs 12 and 15) proceed via similar (η^2-H$_2$)Rh intermediates. However, the latter is too labile for isolation and characterization in solution. Molecular dihydrogen complexes of ruthenium are likely to mediate the sequential Rosenmund–Tishchenko reaction catalyzed by [(Ph$_3$P)$_3$Ru(H)Cl].[40]

The mechanism of PTC for reductive elimination of HCl from transition metal centers is not very clear, although in a number of cases it was demonstrated that phase-transfer catalysts do accelerate such reactions.[29–33,38] Generally, PTC is known to greatly facilitate many inorganic and organometallic reactions, i.e., deprotonation, ligand exchange, cleavage of bridging bonds, etc.[76] Here we would like to consider briefly one more mechanistic aspect of this problem. The transfer of OH$^-$ from an aqueous phase to an organic phase of low polarity is still questionable.[58,76] At the same time, other "softer" anions, including Cl$^-$, can be successfully transferred by crown ethers or quaternary ammonium cations to such solvents as benzene, chloroform, and methylene chloride. It is known[57,76] that anions are transferred to the organic media in their *hydrated* form. These molecules of water could therefore be responsible for formation of some aqua complexes of transition metals and for deprotonation of acidic, nonclassical hydrides which, as we have seen, can be intermediates of reductive elimination in a number of cases.

Conclusions

The present Account is the first attempt to review synthetic, catalytic, and mechanistic aspects of the reductive elimination of HCl from chloro hydrido

(76) Goldberg, Yu. *Phase Transfer Catalysis: Selected Problems and Applications*; Gordon and Breach Science Publishers: Singapore, 1992.

transition metal complexes. Although these reactions do not always lead to coordinatively unsaturated species as initially expected, they can be successfully applied to stoichiometric and catalytic inorganic, organometallic, and organic reactions. Therefore, transition metal complexes carrying both chloro and hydrido ligands deserve to be considered as valuable *synthons* of highly reactive, electron rich species. Nowadays application of PTC and biphasic systems to reductive elimination of HCl from transition metal hydrides seems most promising due to the simplicity and high efficiency of this modern technique. Mechanistic analysis shows the crucial role of vacant coordination sites and/or η^2-coordinated H$_2$ ligands in elimination of HCl from the transition metal centers, accounting for the low reactivity of coordinately saturated, 18-electron complexes, such as [Cp*Ir(PR$_3$)(H)Cl], under PTC conditions. Nonetheless, such complexes might appear reactive in the presence of other HCl-binding agents, among which wet silver oxide deserves serious consideration. The potential of chloro transition metal hydrides in chemistry has not been fully realized yet, opening a wide area for useful, challenging, enjoyable research.