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Preliminary communication

β-ELIMINATION FROM TRANSITION METAL AMIDES *

STEVEN E. DIAMOND and FRANK MARES
Allied Chemical Corporation, Chemical Research Center, Morristown, New Jersey 07960 (U.S.A.)

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Summary

Ruthenium, rhodium, and palladium phosphine complexes are found to produce metal hydrides in high yields by a β-elimination reaction from the corresponding metal amides. Evidence is presented to support the formation of an imine as the organic product. The isotope effect for the reaction is 6 ± 1 indicative of the importance of C—H bond breaking in the transition state.

The β-elimination reaction from coordinated alkyls has been of interest in organometallic chemistry for many years [1]. This reaction also provides a pathway for the decomposition of metal alkoxides to metal hydrides [2]. Several papers postulate a similar reaction for transition metal amide complexes [3], but as yet no clear evidence has been found. We would like to report the first unequivocal example of a β-elimination reaction from a transition metal amide complex.

The preparation of the amide complexes was accomplished by the addition of a stoichiometric amount of lithium amide to the metal chloride in tetrahydrofuran solution employing vacuum line techniques [4]. (The lithium amides were prepared from butyllithium and the appropriate amine.) When the reaction was initiated at dry ice/acetone temperatures visual evidence for the production of a short lived intermediate was obtained. Presumably this is the metal amide which rapidly undergoes β-elimination to produce the corresponding hydride which precipitates from the solution. This complex was isolated under inert atmosphere conditions and completely characterized.

In the case of $(Ph_3P)_3RhCl$ with added phosphine and lithium dimethylamide the known rhodium hydride [5] $(Ph_3P)_4RhH$ was isolated in approximately 75% yield. It displayed the characteristic metal—hydride absorption in the IR spectrum at 2140 cm^{-1}. Without additional phosphine present the trisphosphine com-

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* The term β-elimination in the case of alkoxides and amides refers to the β-atom from the metal (e.g. M—N—$\underline{C}$).

plex was isolated. This complex was characterized by a single crystal X-ray structure determination which will be reported in the near future. Based on these results we believe that the initial, rapid formation of the metal amide is followed by β-hydrogen elimination to generate the metal hydride (eq. 1).

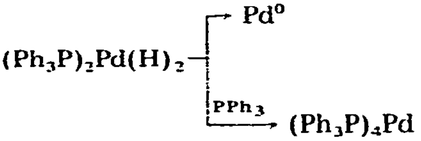
$$(Ph_3P)_3RhCl + LiN(CH_3)_2 \rightarrow [(Ph_3P)_3RhN(CH_3)_2] \rightarrow (Ph_3P)_3RhH \qquad (1)$$

In the case of $(Ph_3P)_4RuCl_2$ with two equivalents of $LiN(CH_3)_2$ the dihydride of ruthenium(II) [5] was isolated in 60% yield. As further confirmation of its identity this species was converted to the known hydride-chloride $(Ph_3P)_3Ru(H)(Cl)$ [6] by reaction with chloroform. When only one equivalent of dimethylamide is added to the tetrakisphosphine the hydride chloride is formed directly (eq. 2).

$$(Ph_3P)_4RuCl_2 + LiN(CH_3)_2 \rightarrow [(Ph_3P)_4Ru[N(CH_3)_2]Cl] \rightarrow (Ph_3P)_3Ru(H)(Cl) \qquad (2)$$

The reaction of $(Ph_3P)_2PdCl_2$ with two moles of dimethylamide produced palladium metal. This is not surprising since it is known that $(Ph_3P)_2Pd(H)_2$ is unstable [7]. However, addition of excess phosphine produced the well known complex $(Ph_3P)_4Pd$ [8] in approximately 75% yield

$$(Ph_3P)_2PdCl_2 + 2LiN(CH_3)_2 \rightarrow [(Ph_3P)_2Pd[N(CH_3)_2]_2] \rightarrow$$



$$(Ph_3P)_2Pd(H)_2 \rightarrow Pd^0 \qquad (Ph_3P)_2Pd(H)_2 \xrightarrow{PPh_3} (Ph_3P)_4Pd$$

The β-elimination reaction from dimethylamide will produce *N*-methylformylimine as the organic product. However, this species should be quite unstable under the reaction conditions making characterization difficult. In order to confirm the identity of the organic residue of this reaction lithium isopropylamide was prepared and treated with $(Ph_3P)_3RhCl$. After filtration of $(Ph_3P)_3RhH$ an excess of water was added to the solution. Gas chromatographic—mass spectral analysis confirmed the presence of acetone which would be produced by the hydrolysis of acetone imine.

$$(Ph_3P)_3RhCl + LiNHCH(CH_3)_2 \rightarrow [(Ph_3P)_3RhNHCH(CH_3)_2] \rightarrow$$

$$(Ph_3P)_3RhH + HN{=}C(CH_3)_2 \xrightarrow{H_2O} NH_3 + O{=}C(CH_3)_2$$

As a further probe into the mechanism of the β-elimination reaction lithium bis(trideuteromethyl)amide was prepared from bis(trideuteromethyl)amine $HN(CD_3)_2$. Reaction of a stoichiometric amount of this amide with $(Ph_3P)_3RhCl$ and excess phosphine resulted in the expected shift from 2140 cm^{-1} for Rh—H to 1540 cm^{-1} for Rh—D. Now $LiN(CH_3)(CD_3)$ was treated with $(Ph_3P)_3RhCl$ and excess phosphine. From the ratio of the intensities of the rhodium hydride and deuteride peaks in the IR spectra k_H/k_D was calculated to be 6 ± 1. This large deuterium isotope effect for the β-elimination reaction indicates

C—H bond breaking is the rate-determining step in the β-elimination reaction from Group VIII metal amides.

We feel that this reaction may offer a mild and convenient method for the preparation of metal hydride complexes which are otherwise accessible only by more involved syntheses. Further, we are attempting to prepare and characterize amide complexes with no β-hydrogen atoms. These results will be reported in the near future.

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