

## TRANSITION METAL ALKYL AND HYDRIDES

### XI\*. EVIDENCE FOR THE EXISTENCE OF HYDRIDO CARBENE NICKEL COMPLEXES

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#### SUMMARY

In the reaction of ethereal methylmagnesium iodide with anhydrous nickel chloride, ethylene is apparently formed through an intermediate hydrido carbene complex.

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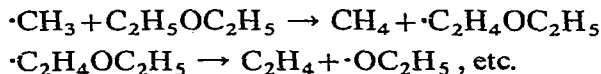
#### RESULTS

As a continuation of our studies on the alkyl-olefin exchange reaction of various Grignard reagents with olefinic hydrocarbons in the presence of anhydrous nickel chloride<sup>1-3</sup>, we have now examined systems containing ethereal CH<sub>3</sub>MgI. In the gas phase above a reaction mixture consisting of CH<sub>3</sub>MgI, NiCl<sub>2</sub> and olefins, some ethylene and ethane could always be detected in addition to the chief component, methane. The reaction of CH<sub>3</sub>MgI with NiCl<sub>2</sub> in absence of olefin leads to the same result, but ethylene and ethane are not formed when phenyl- or benzylmagnesium halides are used instead of CH<sub>3</sub>MgI (Table 1).

#### DISCUSSION

The formation of methane and ethane can plausibly be explained by the decomposition of methylmetal species (see eqns. (1) and (3)).

The formation of ethylene has been explained by Abraham and Hogarth<sup>4</sup> by assuming the decomposition of the radical formed from the solvent, diethyl ether:



However, the fact that PhMgBr and PhCH<sub>2</sub>MgCl give no gaseous product shows that ethylene does not originate from the solvent.

Another possible source of ethylene in systems containing methylmetal derivatives may be transition metal hydrido carbene complexes formed in the reaction

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\* For Part X see Ref. 3.



reflux condenser, under nitrogen in the presence of anhydrous nickel chloride. Gas samples were taken with a syringe through a silicone rubber membrane from the gas phase above the reaction mixture before and after the addition of  $\text{NiCl}_2$  to the Grignard reagent. The samples were analyzed by GLC on a 1 m activated  $\text{Al}_2\text{O}_3$  column at  $20^\circ$ . Absolute quantities of the gases evolved were not determined; Table 1 shows the hydrocarbon content of the gas phase in the reaction flask.

#### ACKNOWLEDGEMENT

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