# Cationic Carbene Complexes of Nickel(II)

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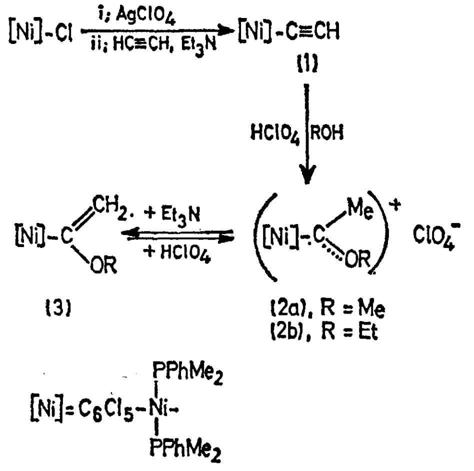
*Summary* The nickel acetylide (**1**) reacts with alcohols in the presence of perchloric acid to give stable cationic alkoxy-carbene complexes (**2**), the $^1H$ n.m.r. spectra of which show the presence of two conformational isomers; deprotonation with triethylamine occurs at the carbene methyl group.

Although the importance of nickel carbene complexes as reaction intermediates has been recognized,[1] only a few complexes have been isolated[2] and reactions of these complexes have not been reported. We have now attempted to obtain alkyl-substituted carbene complexes of nickel(II) by an analogous reaction to that used for platinum(II).[3]

Reaction of *trans*-$C_6Cl_5Ni(PPhMe_2)_2Cl$ with silver perchlorate in acetone or benzene gives a precipitate of silver chloride.[4] Addition of acetylene and triethylamine to the filtrate results in the nickel acetylide (**1**)† [ν(C–H) 3280; ν(C≡C) 1947 $cm^{-1}$ (Nujol)]. Complex (**1**) reacts with methanol in the presence of an equivalent amount of perchloric acid to give the cationic carbene complex (**2a**), 76% yield, m.p. 171—172 °C (decomp.). The $^1H$ n.m.r. spectrum of (**2a**) in nitrobenzene shows two sets of carbene methyl and methoxy proton resonances [δ(CMe) 2·21 (t, $J_{PH}$ 2·3 Hz) and 2·67 (t, $J_{PH}$ 2·3 Hz), intensity *ca.* 1:10; δ(OMe) 4·25 (t, $J_{PH}$ 1·6 Hz) and 4·89 (s), intensity *ca.* 1:10]. This result indicates the presence of two isomers for the complex in solution, and is explained by geometrical isomerism of the carbene ligand, which has the OMe group *trans* or *cis* to the CMe group,[5] probably due to considerable double bond character in the C(carbene)–O bond. The ratio of isomers varies with the solvents used. The resonances of the phosphine methyl protons of the major isomer appear



Scheme

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† The complex (**1**) thus obtained, is often contaminated with unchanged chloronickel complex; analytically pure (**1**) is prepared from *trans*-$C_6Cl_5Ni(PPhMe_2)_2OH_2{\cdot}ClO_4$, 75% yield.

as two triplets, consistent with restricted rotation about the Ni–C(carbene) bond, while those of the minor isomer are obscured by the major resonances. Deprotonation at a carbene methyl group in a transition-metal carbene complex has been reported[6] in (methylmethoxycarbene)-pentacarbonylchromium(0) using alkyl-lithium. However, deprotonation of (**2a**) occurs even with a weaker base like triethylamine to give a stable α-methoxyvinylnickel complex (**3a**), 75% yield, m.p. 118—119 °C [ν(C=C) 1578; ν(COC) 1132 cm$^{-1}$ (Nujol)]. Treatment of (**3a**) with perchloric acid results in the recovery of (**2a**) in almost quantitative yield. The $^1$H n.m.r. spectrum of (**3a**) in methylene chloride shows only one kind of methoxy group, and that the rotation about the Ni–C(vinyl) bond is free at a temperature above −40 °C. The ethoxy analogues (**2b**) and (**3b**) are also obtained, and the isomer ratio of (**2b**) in nitrobenzene is *ca.* 1:3.

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