

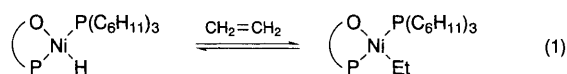
The Reaction of [Ni(acac)₂] with Triethoxysilane in the Presence of PPh₃: a New Method for Synthesis of [Ni(acac)Et(PPh₃)]

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The reaction of [Ni(acac)₂] with triethoxysilane in the presence of PPh₃ is examined under oxygen-free conditions, permitting isolation of [Ni(acac)Et(PPh₃)] **1** formed by elimination of one acac ligand (as protonated and hydrosilylated product) from the nickel complex with its simultaneous silylation which is followed by C–O bond cleavage in triethoxysilyl ligand *via* a mechanism involving transfer of an ethyl group to Ni with elimination of pentaethoxyhydrodisiloxane in the excess of triethoxysilane.

Bidentate nickel complexes of the general formula [Ni(chelate)R(PPh₃)₂] are well-known efficient catalysts for homogeneous oligomerization and polymerization of α -olefins,^{1,2} *e.g.* conversion of ethene to α -olefins (C₆–C₂₀) during the SHOP process. The involved mechanism is mostly discussed in terms of formation of a hydride intermediate.^{3,4} Keim and coworkers⁴ described the isolation and *in situ* NMR measurements of such model intermediates, for which in the presence of ethene the equilibrium given by eqn. (1) was observed.



The first synthesis of [Ni(acac)Et(PPh₃)] was by Yamamoto⁵ and Nesmeyanov⁶ and their coworkers from [Ni(acac)₂] and Al(OEt)Et₂ at –30 °C (–35 °C) in 30–40% yield (40 h in toluene or ether solution) and it was characterized spectroscopically by Cotton⁷ and Yamamoto.⁸ In nonpolar solvents, atypical singlet signals for the ethyl protons in the ¹H and ¹³C NMR spectra were observed and commented upon.^{5,7,8}

It is known that the reaction of [Ni(acac)₂] with triethoxysilane under a variety of conditions leads mainly to either metallic nickel deposition or isolation of the unreacted complex.⁹ One paper¹⁰ reported the reaction of [Ni(acac)₂] with a hydrosilane, Cl₃SiH, and H₂ evolution and, surprisingly, formation of a grey solid characterized as Ni[OC(Me)C(SiCl₃)C(Me)=O]₂. However, elemental analysis and spectroscopic data are far from those expected for such a formulation.

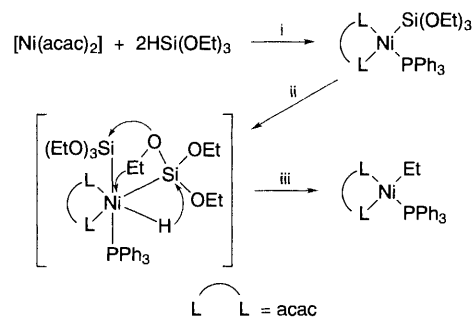
In view of the lack of literature data and on the basis of the results of catalytic examinations of the system [Ni(acac)₂]–HSi(OEt)₃–vinylsilane,¹¹ it seems that the only way to retard Ni^{II} reduction to Ni black in the presence of hydrosilane is stabilization of the system by introduction of tertiary phosphine and in this paper we present the results obtained with the [Ni(acac)₂]–HSi(OEt)₃–PPh₃ system. The reaction was studied at room temperature in benzene. Triethoxysilane was added under argon under Schlenk-line conditions to a benzene solution of [Ni(acac)₂] containing a small excess of triphenylphosphine (1 or 2 mol equiv.) After several seconds, the yellowish-green solution turned intensely blood-red. With a stoichiometric Ni:HSi(OEt)₃ ratio the same effect was seen after a longer period (hours). No traces of reduction to metallic Ni were observed. GC–MS analysis of the solution showed that the change of colour is accompanied by the disappearance of free PPh₃ and its replacement by Ni-bound PPh₃ as well as by a formation of silylation and reduction products of acetylacetonate. Acetylacetonate reacts, in the absence of catalyst with triethoxysilane, to give MeCO₂CH₂Si(OEt)₃ and MeCO₂Et while in the presence of catalytic amounts of [Ni(acac)₂] MeCH[OSi(OEt)₃]CH₂COMe predominates over these two other products. Detection of MeCH[OSi(OEt)₃]CH₂COMe suggests elimination of acac followed by hydrosilylation. It is interesting that only hydrosilanes having protonic character of hydrogen in the Si^{δ–}–H^{δ+} polarized bond cleave the acac ligand from Ni. Both trimethoxysilane and trichlorosilane also produce red solutions with formation of square planar species under the

same conditions while triethylsilane and methyl-diphenylsilane, silanes with hydridic H character in the Si–H bond, do not react with [Ni(acac)₂] either in the presence or absence of oxygen. In the absence of PPh₃ precipitation of nickel black (especially at elevated temperatures) is observed independent of the nature of the silane used. It is likely that strong protonation of acac is required to abstract it from Ni under the examined conditions.

The red solutions described above are very air-sensitive and turn green immediately on exposure to traces of oxygen with formation of OPPh₃, ethyltriethoxysilane, hexaethoxydisiloxane and pentaethoxyhydrodisiloxane as monitored by GC–MS and ¹H NMR spectroscopy. Addition of further triethoxysilane and PPh₃ leads to reformation of the red colour, its time of reappearance depending on the amount added. Reintroduction of oxygen (air) leads again to a green colouration. A red colouration for nickel complexes is characteristic of square-planar geometry, as opposed to a green–blue colour characteristic of tetrahedral geometry or higher coordination number.¹ We also found that initially a nickel complex with one PPh₃ molecule is formed, but with a large PPh₃ excess, even Ni(PPh₃)₃ was formed. A shift of the complex equilibrium in the presence of an excess of acetylacetonate to the starting material supports our suggestion that one acac ligand is lost in the initial step of [Ni(acac)₂] activation by HSi(OEt)₃ in the presence of PPh₃.

For a solution with [Ni(acac)₂]:PPh₃:HSi(OEt)₃ ratio of 1:1:5, concentration *via* evaporation of benzene and addition of *n*-pentane, led to precipitation of yellow complex **1** (52% yield). All spectroscopic data (IR, ¹H, ¹³C, ³¹P NMR) of isolated **1** indicate its molecular formulation as [Ni(acac)Et(PPh₃)]; the same nickel complex prepared by Yamamoto *et al.*⁵ showing identical NMR spectra. Complex **1** even in the solid state is extremely sensitive to traces of oxygen, yielding irreversibly OPPh₃ and some unidentified white–green ‘Ni(acac)’ species.

The above observations (GC–MS, NMR) allow us to propose the reaction route proposed in Scheme 1. Complex **1** is formed by preliminary protonation of the acetylacetonate ligand by HSi(OEt)₃ followed by elimination of acetylacetonate (with fast hydrosilylation) and simultaneous silylation of the nickel complex. The ethyl substituent is produced as the result of C–O



Scheme 1 i, +PPh₃, –MeCH[OSi(OEt)₃]CH₂C(O)Me; ii, HSi(OEt)₃; iii, –(EtO)₃SiOSiH(OEt)₂

bond cleavage in the ethoxy group of the silane molecule and its transfer to Ni while the remainder of the silyl group can be eliminated from the coordination sphere as a pentaethoxyhydrodisiloxane by reaction with the hydrosilane. A similar type of C–O bond cleavage, in vinylic and allylic trimethylsilyl ethers, to release the corresponding olefins, promoted by cobalt complexes,¹² has been reported previously. Additionally, nickel acetylacetonate and phosphine–nickel complexes are good catalysts for the cross-coupling of silyl enol ethers with Grignard reagents to form olefins at elevated temperatures (90–100 °C). This reaction also involves carbon–oxygen cleavage in R₂C=CR'OSiMe₃ and replacement of the siloxy group at nickel by an alkyl and aryl group.¹³

Our preliminary examination of a nickel(0) complex, [Ni(cod)₂] in an analogous system [HSi(OEt)₃, PPh₃, benzene solution, oxygen-free atmosphere] indicates formation of an analogous square-planar red complex.

A facile synthesis of bidentate nickel phosphine complexes containing the Ni–Et moiety, *via* the reaction of Ni(L–L)₂ complexes with triethoxysilane in the presence of PPh₃ can be of great importance in view of their application in catalysis, such species being active in *e.g.* oligomerization of ethene.^{4,14} Moreover, triethoxysilane can generally replace more hazardous alkylating reagents such as organoaluminum compounds in the formation of transition metal(nickel)–alkyl(ethyl) bonds.

This work was supported by funds from the Polish Committee of Scientific Research, Research Project 2 0681 91 01.

Received, 30th December 1994; Com. 4/07923J

Footnote

† IR (CsBr, cm⁻¹) 3100–3000, 1450–1400, 1590, 1525, 1250, 1190, 1010 and 700–600; ¹H NMR (C₆D₆) δ 0.26(s), 1.53(s), 1.65(s), 5.43(s) and 6.73–7.35(m); ¹³C NMR (C₆D₆) δ 14.22, 22.63, 34.35, 100.46, 127.26, 129.61, 131.62 and 132.97; ³¹P NMR (C₆D₆) δ 32.01.

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