

Nickel σ -sydnonyl complexes, stabilized by tertiary phosphines

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(Received August 1st, 1989)

Abstract

The first nickel(II) complexes bearing the mesoionic radical have been synthesized by the oxidative addition of either 4-bromo-3-phenylsydnone or (3-phenylsydnone-4-yl)mercury chloride to nickel(0) phosphine complexes. Chemical properties of the σ -sydnonyl compounds obtained have been studied in the reaction of carbonylation as an example.

Introduction

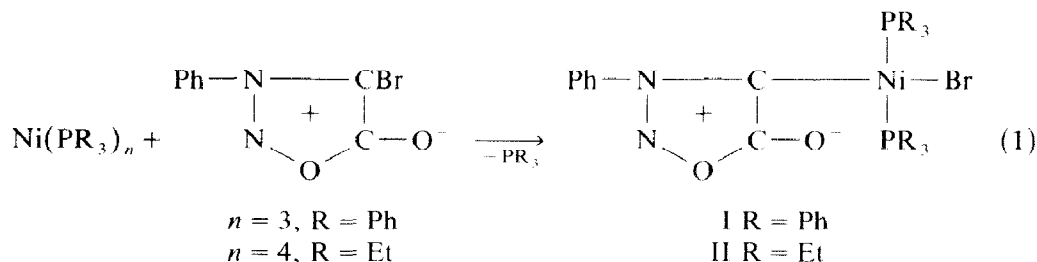
Derivatives of organometallic compounds containing metal-nickel σ -bonds in the heterocycle have been scarcely studied. Recently the σ -sydnonyl complexes of iron obtained from the reaction of 4-lithium- or 4-copper derivatives of sydnone with bromocyclopentadienyldicarbonyliron have been described [1,2]. The ability of 4-copper-3-phenylsydnone to enter cross-coupling reactions with aryl and vinyl halides, under conditions of palladium catalysis, which are thought to proceed by the intermediate formation of palladium σ -sydnonyl complexes, has been described [2].

Oxidative additions of organic halides to compounds of zero-valent metals is a widely applied method for the synthesis of σ -derivatives of nickel subgroup metals [3]. This reaction has been used to make nickel(II), palladium(II), and platinum(II) complexes having heterocyclic ligands [4–8]. Thus, for nickel(II), the complexes $[\text{NiX}(\text{R})(\text{PR}'_3)_2]_n$ ($n = 1$, $\text{X} = \text{Cl}$, $\text{R} = \text{C}_9\text{H}_6\text{N}-\text{C}^8$; $n = 2$, $\text{X} = \text{Cl}$, Br , I , $\text{R} = \mu\text{-C}_5\text{H}_4\text{N}-\text{C}^2$) containing the derivatives of quinoline and pyridine are known [4,5].

As exemplified by sydnones, the first representatives of nickel(II) organometallic compounds with mesoionic heterocyclic radical have been prepared, and the behaviour of these compounds during carbonylation is described here.

Results and discussion

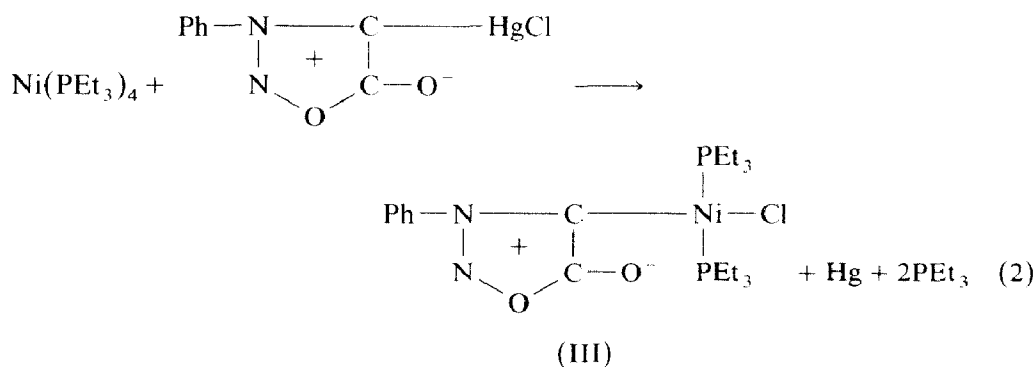
First the reactions of oxidative addition of 4-bromo-3-phenylsydnone to phosphine complexes of zero-valent nickel were studied. It was found that 4-bromo-3-phenylsydnone reacts either with tris(triphenylphosphine)- or tetrakis(triethylphosphine)nickel at room temperature to give σ -sydnonyl compounds of nickel in high yields:



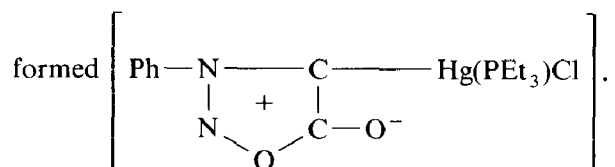
The nickel(0) complex with triethylphosphine was found to be the most reactive in reaction (1). The addition 4-bromo-3-phenylsydnone in benzene solution to $\text{Ni}(\text{PEt}_3)_4$ results in an immediate colour change of the reaction mixture and the reaction is complete after 2 hours. For $\text{Ni}(\text{PPh}_3)_3$ the reaction proceeds more slowly (20 hours) and complex I is formed in lower yield.

Compounds I and II are brightly coloured crystalline substances, stable in air in the solid state, and soluble in conventional organic solvents. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of I and II recorded in chloroform show single narrow singlets at δ 20.76 and 13.93 ppm, respectively. The absence of signal splitting indicates the *trans*-configuration of the phosphine ligands around the nickel atom.

The possibility of using the redox-demercuration for the synthesis of σ -sydnonyl compounds of nickel was also studied. It was found that reaction of benzene solution of tetrakis(triethylphosphine)nickel with (3-phenylsydnon-4-yl)mercury chloride gives in chlorobis(triethylphosphine)(3-phenylsydnon-4-yl)nickel (III) in 57% yield:



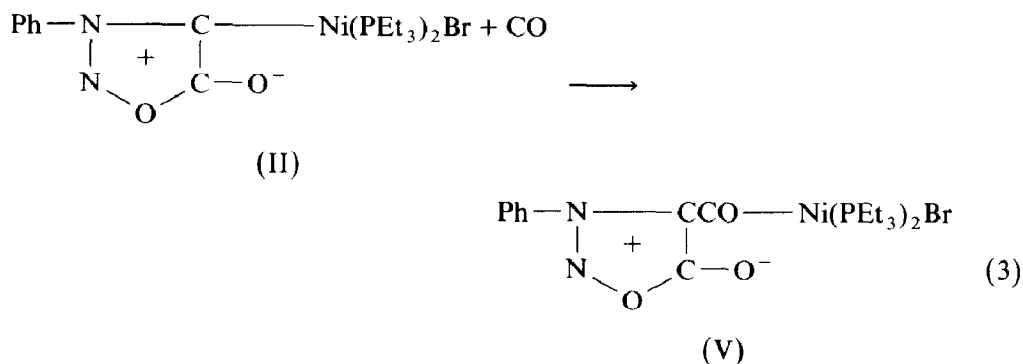
A by-product, $\text{HgCl}_2(\text{PEt}_3)_2$ (IV), was also isolated in 16% yield. Compound IV seems to be the product of disproportionation of the intermediary



A similar reaction is known for $\text{HgCl}(\text{Me})(\text{PEt}_3)$ which yields IV and dimethyl mercury upon standing [9].

Compound III has properties similar to those of the bromides I and II described above. The $^{31}\text{P}\{^1\text{H}\}$ NMR of III shows one singlet signal, its chemical shift coinciding with that of II.

The reaction of the novel σ -sydnonyl compounds with CO was examined. It was found that if carbon monoxide was bubbled through a suspension of compound II in hexane for two hours at 25°C the substance changes colour from orange to the dark-yellow of bromobis(triethylphosphine)(3-phenylsydnone-4-ylcarbonyl)nickel (V), isolated 75% yields:



The structure of V was confirmed from the elemental analysis data and from its IR spectrum which shows an absorption band at 1770 cm^{-1} which can be assigned to the carbonyl group and which is absent in the spectrum of original compound II.

The lability of compound V is similar to that of the nickel σ -benzoyl complexes $\text{NiCl}(\text{COC}_6\text{H}_5)(\text{PEt}_3)_2$ and $\text{NiCl}(\text{COC}_6\text{H}_4\text{Cl-3})(\text{PEt}_3)_2$ described in the literature [10]. V is readily decarbonylated both in solution and in the solid state, hence attempts to recrystallize it are unsuccessful.

Experimental

The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a Bruker WP-200SY spectrometer (81.01 MHz)-external reference: 85% H_3PO_4 . The IR spectra were recorded on an UR-20 spectrophotometer in KBr tablets.

$\text{Ni}(\text{PPh}_3)_3$, $\text{Ni}(\text{PEt}_3)_4$ and PEt_3 were prepared by procedures previously described [11–13]; as was (3-phenylsydnone-4-yl)mercury chloride [14]. The synthesis and isolation of the nickel complexes was performed under argon in absolute solvents that had been distilled in argon beforehand.

Bromobis(triphenylphosphine)(3-phenylsydnone-4-yl)nickel (I). A suspension of 4-bromo-3-phenylsydnone (2.74 mmol) in 10 ml of toluene was added to a suspen-

sion of $\text{Ni}(\text{PPh}_3)_3$ (2.68 mmol) in 20 ml of toluene at -40°C . The reaction mixture was stirred for 4 hours at 25°C and evaporated to half of its volume. The resulting brown substance was filtered off, washed with ether and dried in vacuo, to give 1.27 g (58%) of $\text{NiBr}(3\text{-phenylsydnnon-4-yl})(\text{PPh}_3)_2$, m.p. $135\text{--}137^\circ\text{C}$ (dec.) (from benzene). Analysis. Found: C, 63.48; H, 4.34; N, 3.63. $\text{C}_{44}\text{H}_{35}\text{BrN}_2\text{NiO}_2\text{P}_2$ calcd.: C, 64.07; H, 4.24; N, 3.40%.

Bromobis(triethylphosphine)(3-phenylsydnnon-4-yl)nickel (II). A suspension of 4-bromo-3-phenylsydnnon (5.20 mmol) in 10 ml of benzene was added to a suspension of $\text{Ni}(\text{PEt}_3)_4$ (5.17 mmol) in 20 ml of benzene. The reaction mixture was stirred for 2 hours at 25°C . The resulting solution was evaporated to dryness, and 20 ml of ether was added to the residue. The orange substance obtained was filtered off, washed with ether and dried in vacuo, to give 1.72 g (69%) of $\text{NiBr}(3\text{-phenylsydnnon-4-yl})(\text{PEt}_3)_2$, m.p. $129\text{--}131^\circ\text{C}$ (from ether). Analysis. Found: Br, 14.58; N, 5.27; P, 11.50. $\text{C}_{20}\text{H}_{35}\text{BrN}_2\text{NiO}_2\text{P}_2$ calcd.: Br, 14.58; N, 5.11; P, 11.30%.

Bromobis(triethylphosphine)(3-phenylsydnnon-4-ylcarbonyl)nickel (V). CO * gas was bubbled through a suspension of $\text{NiBr}(3\text{-phenylsydnnon-4-yl})(\text{PEt}_3)_2$ (1 mmol) in 30 ml of hexane for 2 hours at 25°C . The resulting dark-yellow substance was filtered off, washed with pentane and dried in a stream of argon, to give 0.43 g (75%) of $\text{NiBr}(3\text{-phenylsydnnon-4-ylcarbonyl})(\text{PEt}_3)_2$. Analysis. Found: C, 44.55; H, 6.04; P, 10.69. $\text{C}_{21}\text{H}_{35}\text{BrN}_2\text{NiO}_3\text{P}_2$ calcd.: C, 44.02; H, 6.13; P, 10.80%.

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* Carbon monoxide was obtained by dehydration of formic acid.