INTERACTION OF A ZEROVALENT NICKEL COMPLEX WITH ORGANOMERCURIALS

L.S. ISAEVA*, L.N. MOROZOVA, V.V. BASHILOV, P.V. PETROVSKII, V.I. SOKOLOV *
and O.A. REUTOV

A.N. Nesmeyanov Institute of Organo-Element Compounds of the Academy of Sciences, Vavilov Street 28, Moscow B-234 (U.S.S.R.)

Summary

The oxidative addition of ArHgX (Ar = Ph, X = Cl; Ar = C_6F_5, X = Br) to the nickel complex $(Ph_3P)_4Ni$ resulting in formation of σ-aryl derivatives of bivalent nickel, $(Ph_3P)_2Ni(Ar)X$, has been performed. It was found that the reaction between $(Ph_3P)_4Ni$ and $(C_6F_5)_2Hg$ yields the bimetallic compound $(Ph_3P)_2Ni(C_6F_5)HgC_6F_5$. Similarly, the reaction between $[(C_6F_5)_3Ge]_3Hg$ and $(Ph_3P)_4Ni$ gives $(Ph_3P)_2$-$Ni[Ge(C_6F_5)_3]HgGe(C_6F_5)_3$, containing a Ge–Ni–Hg–Ge chain. A five-membered metallocycle with a N → Ni chelate bond was obtained from the reaction of $(Ph_3P)_4Ni$ with 8-(α-bromomercuriethyl)quinoline.

Introduction

In recent years the redox reactions of zerovalent complexes of platinum and palladium with organomercurials have been studied extensively [1]. In this paper it is shown that a complex of nickel(0) can undergo a similar reaction.

We have studied the reaction of $(Ph_3P)_4Ni$ with some non-symmetrical and symmetrical organomercurials chosen, using our previous experience in the chemistry of Pt and Pd [2,3], to obtain the following results:

1) to synthesize a σ-aryl derivative of Ni^{II}, starting from phenylmercuric chloride and pentafluorophenylmercuric bromide;

2) to synthesize a chelate metallocycle with a N → Ni–C fragment and a chiral centre, starting from 8-(α-bromomercuriethyl)quinoline;

3) to synthesize a bimetallic compound with a Ni–Hg bond, starting from bis(pentafluorophenyl)mercury;

4) to synthesize a compound containing an oligometallic chain of four atoms, M–Ni–Hg–M, starting from bis[tris(pentafluorophenyl)germyl]mercury.

Results and discussion

The reaction of tetrakis(triphenylphosphine)nickel and phenylmercuric chloride proceeds readily at room temperature in a benzene solution, with liberation of metallic mercury:

$$(Ph_3P)_4Ni + PhHgCl \rightarrow (Ph_3P)_2Ni(Ph)Cl + Hg + 2PPh_3 \qquad (1)$$
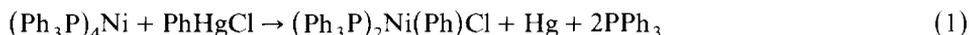
Phenylbis(triphenylphosphine)nickel chloride was purified by recrystallization and is stable only in an argon atmosphere.

A more stable σ-aryl derivative of nickel is formed in the reaction of pentafluoro-phenylmercuric bromide with tetrakis(triphenylphosphine)nickel. In this case, however, along with pentafluorophenylbis(triphenylphosphine)nickel bromide, bis(triphenylphosphine)nickel dibromide was also isolated from the reaction mixture. In some oxidative addition reactions of RBr to zerovalent nickel complexes studied previously, the formation of $(Ph_3P)_2NiBr_2$ was also observed [4].

Contrary to the reaction with C_6F_5HgBr described above, interaction of tetrakis(triphenylphosphine)nickel with the symmetrical organomercurial $(C_6F_5)_2Hg$, containing two electron-accepting C_6F_5 groups, leads to the formation of a bimetallic compound with a Ni–Hg σ-bond:

$$(Ph_3P)_4Ni + (C_6F_5)_2Hg \rightarrow (Ph_3P)_2Ni(C_6F_5)HgC_6F_5 + 2PPh_3 \qquad (2)$$
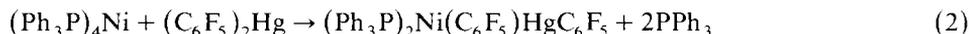
The complex $(Ph_3P)_2Ni(C_6F_5)HgC_6F_5$ is a yellow crystalline compound, readily soluble in benzene and stable under argon. The $^{31}P-\{^1H\}$ NMR spectrum of this compound recorded in toluene at $-70°C$ reveals two signals at δ 25.38 and -8.20 ppm with an integral intensity ratio 8 : 1. The singlet at 25.38 ppm indicates a *trans*-disposition of the coordinated triphenylphosphine ligands at the nickel atom and, consequently, to *trans* addition of $(C_6F_5)_2Hg$ to $(Ph_3P)_4Ni$. The signal at -8.20 ppm corresponds to free triphenylphosphine, which may be formed as a result of partial dissociation of the complex in solution (cf. $\delta - 9.4$ ppm in toluene at $-80°C$ [5]).

The interaction of $Ni(PPh_3)_4$ with $[(C_6F_5)_2Ge]_2Hg$ * proceeds similarly and yields a polymetallic compound containing a Ge–Ni–Hg–Ge chain of the atoms:

$$(Ph_3P)_4Ni + [(C_6F_5)_3Ge]_2Hg \rightarrow (Ph_3P)_2Ni[Ge(C_6F_5)_3]Hg–Ge(C_6F_5)_3 + 2PPh_3 \quad (3)$$

The compound $(Ph_3P)_2Ni[Ge(C_6F_5)_3]HgGe(C_6F_5)_3$ forms white crystals readily soluble in THF and moderately soluble in ether. In the solid state the compound is air-stable. Recently, the formation of a phenyl analog has been reported [6].

Further, we have applied redox-demercuration to the synthesis of metallocycles containing a chelate N → Ni bond. A five-membered metallocycle is formed when a benzene solution of $Ni(PPh_3)_4$ is treated with 8-(α-bromomercuriethyl)quinoline:
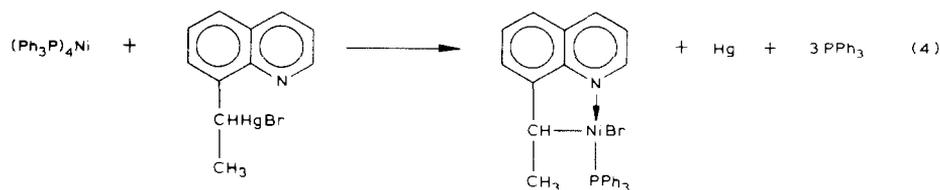
The chelate complex is a red-brown crystalline compound, stable in an argon atmosphere, readily soluble in benzene and moderately soluble in ether. The PMR spectrum of triphenylphosphine-(8-ethylquinoline-α-C, N)nickel bromide (in C_6D_6) shows, in addition to the broad complex multiplet of PPh_3 and quinoline ligands at δ 7.0–8.0 ppm, a doublet of methyl group protons at δ 1.12 ppm and a quintet of the methine proton at δ 2.22 ppm. The spin-spin coupling constants ^3J(H–H) and ^3J(H–P) are similar, approximately 7 Hz.

The starting material $(Ph_3P)_4Ni$ was prepared by reductive elimination from $(Ph_3P)Ni(Et)(acac)$ under the action of triphenylphosphine:

$$(Ph_3P)Ni(Et)(acac) + 3PPh_3 \rightarrow (Ph_3P)_4Ni + C_2H_4 + Hacac \tag{5}$$

The formation of the zerovalent nickel complex is presumably preceded by a nickel hydride β-elimination from the σ-ethyl nickel compound. Apparently, in this reaction hydride acts as a reducing agent. For comparison it should be noted that similar reductive elimination of dialkyl derivatives of the type $RR'Ni(PR''_3)_2$ also takes place under the action of tertiary phosphines and phosphites and leads to the reduction of nickel from the +2 to the zero oxidation state and to the formation of the coupling products of the hydrocarbon radicals [7].

Experimental

^1H NMR spectra were recorded on a 'Hitachi-Perkin-Elmer R-20' instrument with an operating frequency of 60 MHz and using hexamethyldisiloxane as an internal standard. ^{31}P-$\{^1H\}$ NMR spectra were recorded on 'Bruker HX-90' spectrometer (with 85% H_3PO_4 as an external standard).

All the experiments on the synthesis and isolation of nickel complexes were carried out under an argon atmosphere using absolute solvents distilled under argon.

1. Tetrakis(triphenylphosphine)nickel

A mixture of 3.80 g (8.45 mmol) $(Ph_3P)Ni(Et)(acac)$ and 7.68 g (29.6 mmol) triphenylphosphine in 60 ml of ether was stirred for 16 hours at 22°C. The precipitate formed was filtered off washed with ether and dried in vacuo. 4.21 g (45%) of $(Ph_3P)_4Ni$, m.p. 120–123°C, was obtained. Found: C, 78.10; H, 5.24; Ni, 5.31. $C_{72}H_{60}NiP_4$ calcd.: C, 78.07; H, 5.45; Ni, 5.30%. The ^{31}P-$\{^1H\}$ NMR spectrum of $Ni(PPh_3)_4$ recorded in toluene at -50°C contained a sharp singlet at δ 23.78 ppm (lit. [5] δ 24.10 ppm; -80°C).

A mother liquor after separation of $(Ph_3P)_4Ni$ was concentrated to a minimum volume and analyzed by GLC; it contains acetylacetone.

2. Phenylbis(triphenylphosphine)nickel chloride

A mixture of 4.31 g (3.9 mmol) $(Ph_3P)_4Ni$ and 1.22 g (3.9 mmol) phenylmercuric chloride in 50 ml of benzene was stirred for 10 min at 22°C. Metallic mercury (0.76 g) was isolated, the benzene solution evaporated to a minimum volume and treated with pentane. The yellow precipitate was crystallized from ether to yield 2.09 g (76%) of $(Ph_3P)_2Ni(Ph)Cl$, m.p. 134–136°C (Lit. [8], 122–123°C). Found: C, 73.01; H, 5.31; Cl, 5.37. $C_{42}H_{35}ClNiP_2$ calcd.: C, 72.70; H, 5.03; Cl, 5.05%.

3. Pentafluorophenylbis(triphenylphosphine)nickel bromide

A mixture of 0.76 g (0.68 mmol) $(Ph_3P)_4Ni$ and 0.33 g (0.68 mmol) C_6F_5HgBr in

30 ml of benzene was stirred for 10 min at 22°C. Metallic mercury was isolated, the benzene solution was evaporated to a minimum volume and treated with pentane. A mixture of yellow and dark green compounds was precipitated. The yellow compound was dissolved in ether to yield 0.25 g (44%) of $(Ph_3P)_2Ni(C_6F_5)Br$, m.p. 197–199°C (from a benzene-methanol mixture) (Lit. [9] 199–200°C. Found: C, 60.30; H, 3.73; F, 11.50. $C_{42}H_{30}BrF_5NiP_2$ calcd.: C, 60.61; H, 3.63; F, 11.39%. The dark green compound, which was insoluble in ether was recrystallized from acetone to yield 0.15 g (30%) of $(Ph_3P)_2NiBr_2$, m.p. 214–218°C. (Lit. [10], 222–225°C).

4. $(Ph_3P)_2Ni(C_6F_5)HgC_6F_5$

1.27 g (1.15 mmol) of $(Ph_3P)_4Ni$ and 0.61 g (1.15 mmol) of $(C_6F_5)_2Hg$ were dissolved in benzene at 5°C. After 24 hours the benzene solution was evaporated to a minimum volume; yellow crystals were filtered off, washed with hexane, and dried in vacuo: 1.04 g (76%) of $(Ph_3P)_2Ni(C_6F_5)Hg(C_6F_5)$, m.p. 140–142°C (from benzene), was obtained. Found: C, 51.50; H, 2.68; Hg, 17.93; F, 17.38. $C_{48}H_{30}HgF_{10}NiP_2$ calcd.: C, 51.58; H, 2.71; Hg, 17.95; F, 17.00%.

5. $(Ph_3P)_2Ni[(C_6F_5)_3Ge]HgGe(C_6F_5)_3$

A mixture of 0.78 g (0.71 mmol) $(Ph_3P)_4Ni$ and 0.95 g (0.71 mmol) $[(C_6F_5)_3Ge]_2Hg$ in 30 ml THF was kept for 24 hours at 22°C. The solution was evaporated to dryness and a small amount of ether was added to the residue. A white crystalline compound was filtered off and recrystallized from ether: 0.69 g (50%) of $(Ph_3P)_2Ni[(C_6F_5)_3Ge]HgGe(C_6F_5)_3$, m.p. 154–156°C (from hexane) was obtained. Found: C, 45.55; H, 1.75; F, 29.18. $C_{72}H_{30}HgF_{30}Ge_2NiP_2$ calcd.: C, 44.75; H, 1.57; F, 29.50%.

6. Triphenylphosphine-(8-ethylquinoline-α-C,N)nickel bromide

A mixture of 1.70 g (1.54 mmol) $(Ph_3P)_4Ni$ and 0.67 g (1.54 mmol) 8-(α-bromomercuriethyl)quinoline in 30 ml of benzene was stirred for 1 hour at 22°C. Metallic mercury was removed and benzene solution was evaporated to dryness. A small amount of ether was added to the tarry residue. Red-brown crystals were filtered off and recrystallized from ether: 0.70 g (54%) of triphenylphosphine-(8-ethylquinoline-α-C, N)nickel bromide, m.p. 135–136°C, was obtained. Found: C, 62.60, H, 4.71; Br, 14.20. $C_{29}H_{25}BrNNiP$ calcd.: C, 62.53; H, 4.52; Br, 14.34%.

References

1 V.I. Sokolov and O.A. Reutov, Coord. Chem. Rev., 27 (1978) 89.
2 V.I. Sokolov, V.V. Bashilov and O.A. Reutov, J. Organometal. Chem., 111 (1976) C13.
3 V.I. Sokolov, V.V. Bashilov, A.A. Musaev and O.A. Reutov, J. Organometal. Chem., 225 (1982) 57.
4 T.R. Tsou and J.K. Kochi, J. Amer. Chem. Soc., 101 (1979) 6319.
5 R. Mynott, A. Mollbach, G. Wilke, J. Organometal. Chem., 199 (1980) 107.
6 G.A. Razuvaev, J. Organometal. Chem., 200 (1980) 243.
7 G. Wilke and G. Hermann, Angew. Chem., Int. Ed., 5 (1966) 581; D.R. Fahey, J. Organometal. Chem. Rev. Ser. A, 7 (1972) 245; H.F. Klein and H.H. Karsh, Chem. Ber., 105 (1972) 2628; B. Bogdanovič, H. Bönnenman and G. Wilke, Angew. Chem. Int. Ed., 5 (1966) 582.
8 M. Hidai, T. Kashiwagi, T. Ikeuchi and Y. Uchida, J. Organometal. Chem., 30 (1971) 279.
9 J.R. Phillips, D.T. Rosevear and F.G.A. Stone, J. Organometal. Chem., 2 (1964) 455.
10 L.M. Venanzi, J. Chem. Soc., (1958) 719.