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PREPARATIONS OF σ-BONDED ALKYL-, ARYL- AND ALKYNYLNICKEL COMPOUNDS

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Recent rapid progress in the field of the chemistry of organometallic compound has included preparation of many σ-bonded alkyl derivatives of most of the transition metals. There are many examples in which they were thought to be an intermediate in catalytic processes, such as alkyltitanium compounds[1,2] in Ziegler–Natta polymerization and alkylcobalt compounds[3] in carbonylation reactions. In this connection, we intended to prepare σ-bonded alkylnickel derivatives in order to elucidate the catalytic process of the dimerization of ethylene[4] in which an alkylnickel compound possibly plays the main role. There are many compounds in which an aryl[5], ethynyl[6] and perfluoroalkyl[7,8] group is attached to nickel by means of a σ-bond. However, simple alkyl derivatives have not been isolated because of their instability, though evidence has been obtained about their formation[8,9].

We had succeeded in preparing stable σ-bonded alkyl, aryl and alkynyl derivatives of nickel which have a cyclopentadienyl group and phosphine, arsine or stibine in a molecule as ligands and have briefly described such compounds previously[10]. Now we wish to report on the compounds in detail.

RESULTS AND DISCUSSION

Recently the reaction of nickelocene with bis(triphenylphosphine)nickel dichloride was claimed to yield triphenylphosphine-π-cyclopentadienylnickel chloride, π-$C_5H_5Ni(PPh_3)Cl$[11]. Another method of preparation of analogous iodine compound[12] from cyclopentadienylnickel dicarbonyl, triphenylphosphine and iodine was also known. The former method is superior to the latter in terms of its high yield and convenience. The former method was employed and improved for the preparation of related compounds. Preparation by dropwise addition of an iodine solution to the mixture of nickelocene, nickel carbonyl and triphenylphosphine (or the phosphite, arsine and stibine) in tetrahydrofuran was widely employed. The compounds thus prepared are summarized in Table 1.

Derivatives having phosphines and phosphite as the ligand are stable in air, both in solid state and in solution. Arsine- and stibine-substituted compounds are less stable than their phosphine analogues. They are all soluble in benzene and tetrahydrofuran but less soluble in aliphatic solvents, except for the tributylphosphine substituted compound.

TABLE 1

π-$C_5H_5Ni(L)X$ COMPOUNDS

Method[a]	*Compound*	*Colour*	*M.p.* (°C)	*Yield* (%)	*Analyses found (calcd.) (%)* C	H
1	π-$C_5H_5Ni(PPh_3)Cl$	dark red	138–139[b]	90	65.53 (65.53)	4.82 (4.78)
1	π-$C_5H_5Ni(PBu_3)Cl$	dark brown	59–59.5	67	56.47 (56.31)	8.92 (8.98)
1	π-$C_5H_5Ni(PPh_2Me)Br$	dark brown red	118–120	79	53.86 (53.52)	4.51 (4.49)
2	π-$C_5H_5Ni(P(OPh)_3)I$	dark brown red	132–133[b]	39	49.45 (49.24)	3.69 (3.59)
3	π-$C_5H_5Ni(AsPh_3)Br$	dark red violet	109–110[b]	66	54.20 (54.17)	4.01 (3.95)
2	π-$C_5H_5Ni(AsPh_3)I$	dark red violet	118–119[b]	53	49.65 (49.60)	3.68 (3.62)
2	π-$C_5H_5Ni(SbPh_3)I$	dark red violet	101–102[b]	52	45.82 (45.75)	3.36 (3.34)

[a] Method 1: $(\pi$-$C_5H_5)_2Ni + L_2NiX_2$; method 2: $(\pi$-$C_5H_5)_2Ni + Ni(CO)_4 + 2\ L + I_2$; method 3: $(\pi$-$C_5H_5)_2Ni + NiX_2 + 2\ L$. [b] Decomposing.

Treatment of these halides in benzene at ice temperature with Grignard reagents affords π-$C_5H_5Ni(L)R$ compounds in good yields.

π-$C_5H_5Ni(L)X + RMgX \longrightarrow \pi$-$C_5H_5Ni(L)R$
R = CH_3, C_2H_5, *n*-C_3H_7, *n*-C_4H_9, *sec.*-C_4H_9, $CH_2C_6H_5$, C_6H_5, *p*-ClC_6H_4, *o*-$CH_3C_6H_4$, *m*-$CH_3C_6H_4$, *p*-$CH_3C_6H_4$, 2,4,6-$(CH_3)_3C_6H_2$, $C{\equiv}CH$ and $C{\equiv}CC_6H_5$. X = Cl, Br and I. L = $(C_6H_5)_3P$, $(CH_3)(C_6H_5)_2P$, $(n$-$C_4H_9)_3P$, $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$.

The compounds thus prepared are summarized in Table 2.

TABLE 2

π-$C_5H_5Ni(L)R$ COMPOUNDS

Compound	*Colour*	*M.p.*[a] (°C)	*Yield* (%)	*Analyses found (calcd.) (%)* C	H
π-$C_5H_5Ni(PPh_3)CH_3$	green	(126–129)	67	71.64 (71.86)	5.99 (5.78)
π-$C_5H_5Ni(PPh_3)C_2H_5$	green	(118–120)	61	72.64 (72.33)	6.15 (6.07)
π-$C_5H_5Ni(PPh_3)$-*n*-C_3H_7	green	(75–77)	71	72.89 (72.76)	6.30 (6.34)
π-$C_5H_5Ni(PPh_3)$-*n*-C_4H_9	green	(88–91)	50	73.33 (73.17)	6.63 (6.60)
π-$C_5H_5Ni(PPh_3)$-*sec*-C_4H_9	green	(111–112)	27	73.37 (73.17)	6.65 (6.60)
π-$C_5H_5Ni(PPh_3)CH_2C_6H_5$	green brown	(129–131)	79	75.22 (75.50)	5.70 (5.70)
π-$C_5H_5Ni(PPh_3)C_6H_5$	green	137–139	77	75.03 (75.20)	5.53 (5.44)
π-$C_5H_5Ni(PPh_3)C_6H_4Cl$-*p*	green brown	140–143	28	70.31 (69.99)	4.86 (4.86)
π-$C_5H_5Ni(PPh_3)C_6H_4CH_3$-*o*	green	164–165	18	75.06 (75.50)	5.82 (5.70)
π-$C_5H_5Ni(PPh_3)C_6H_4CH_3$-*m*	green	106–107	42	75.24 (75.50)	5.60 (5.70)
π-$C_5H_5Ni(PPh_3)C_6H_4CH_3$-*p*	green brown	139–142	65	75.04 (75.50)	5.69 (5.70)
π-$C_5H_5Ni(PPh_3)C_6H_2(CH_3)_3$-2,4,6	green	190–191	57	76.03 (76.07)	6.34 (6.19)
π-$C_5H_5Ni(PPh_3)C{\equiv}CH$	green	111.5–112.5	75	72.96 (73.03)	5.30 (5.15)
π-$C_5H_5Ni(PPh_3)C{\equiv}CC_6H_5$	green	135	65	76.71 (76.42)	5.26 (5.17)
π-$C_5H_5Ni(PBu_3)CH_3$	green brown	29–30	53	63.52 (63.37)	10.39 (10.34)
π-$C_5H_5Ni(PPh_2Me)CH_3$	green	97–100	53	67.15 (67.30)	6.37 (6.24)
π-$C_5H_5Ni(AsPh_3)CH_3$	green	(101–104)	50	65.24 (64.77)	5.32 (5.21)
π-$C_5H_5Ni(AsPh_3)C_6H_5$	green	(126–127)	36	68.56 (68.68)	5.09 (4.97)
π-$C_5H_5Ni(SbPh_3)C_6H_5$	green	(96–98)	32	62.82 (62.87)	4.55 (4.71)
π-$C_5H_5Ni(SbPh_3)C_6H_2(CH_3)_3$-2,4,6	yellow green	134–135	42	64.85 (64.48)	5.45 (5.24)

[a] Melting points given in parentheses were measured in nitrogen filled capillary tube. All compounds melt with decomposition except π-$C_5H_5Ni(PBu_3)CH_3$.

They were mostly dark green crystals soluble in most organic solvents. Triphenylphosphine-π-cyclopentadienylmethylnickel is diamagnetic, monomeric in benzene and very stable, especially in solid state, which permits handling in air. The nuclear magnetic resonance (NMR) spectrum of the compound showed a singlet at 2.56 τ (C_6H_5), a singlet at 4.94 τ (C_5H_5), and a doublet centered at 10.82 τ (CH_3). The coupling constant J between the methyl protons and the ^{31}P nucleus is 6.0 cps. Alkyl derivatives are less stable in air when dissolved in organic solvents than are the aryl and ethynyl derivatives; the methyl derivative is the most stable of the alkyl analogs.

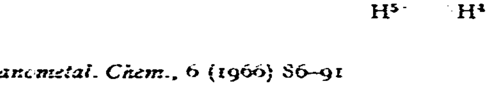
Attempts to obtain analytically pure triphenylstibine-π-cyclopentadienylmethylnickel was unsuccessful, although green crystals were obtained. In general, replacement of the ligand on nickel from phosphine to arsine and to stibine depressed the stability of the compounds in this order. The reaction between triphenylphosphite-π-cyclopentadienylnickel iodide and mesityl Grignard reagent in tetrahydrofuran did not afford the expected mesitylnickel compound. σ-Bonded nickel–carbon compounds having only weakly donating ligands seem to be unstable.

In an attempt to obtain the σ-allylnickel derivative, π-$C_5H_5Ni(PPh_3)CH_2CH=CH_2$, the reaction of the chloride and allylmagnesium bromide at room temperature affords π-cyclopentadienyl-π-allylnickel[13,14] in 40 % yield. Transient formation of the desired compound was suggested by the initial development of green color which was followed by the change to red-violet. This change of color possibly corresponds to the isomerization of σ-bonded allyl group to a π-bonded structure by replacement of phosphine.

In an attempt to prepare the triphenylphosphine-π-cyclopentadienylnickel hydride, the chloride was treated with lithium aluminum hydride in tetrahydrofuran at Dry Ice temperature. Di-μ-(diphenylphosphido)-π-cyclopentadienyldinickel[15] was obtained in 38 % yield instead of the desired hydride.

Reaction between the methyl derivative and halogens resulted in cleavage of methyl–nickel bond. Thus, the reaction of triphenylphosphine-π-cyclopentadienylmethylnickel with bromine in ether at Dry Ice temperature afforded triphenylphosphine-π-cyclopentadienylnickel bromide (16 %) and with iodine at ice temperature gave the iodide (70 %). In a later case, 40 % of methyl group from the nickel compound employed was detected as ethane and 17 % as methyl iodide by vapor phase chromatographic analysis, suggesting that the reaction did not proceed in a simple way.

There are many examples of insertion of carbon monoxide into an alkyl–transition metal bond. The reaction of the methyl and phenyl derivatives of nickel with carbon monoxide were carried out to examine the possibility of such insertion. The reaction with carbon monoxide at high pressure proceeded at room temperature without formation of the expected acetyl and benzoyl derivatives. The main product was triphenylphosphinenickel tricarbonyl. Another product obtained from the reaction of the phenyl derivative was an air-unstable white crystalline solid which melted at 65° in a nitrogen filled capillary tube. Based on elemental analysis, the electronic spectrum indicating the presence of conjugate band (λ_{max} 298 mμ; ε 14400) and the NMR spectrum, its structure was assigned as 1-phenyl-1,3-cyclopentadiene[16].



NMR: 6.74 τ (2, doublet, H^1 and H^2), 3.66 τ (1, doublet, H^5), 3.53 τ (1, sextet, H^3), 3.24 τ (1, triplet, H^4), 2.77 τ (5, complex, C_6H_5). Tetramethylsilane was employed as internal standard in CS_2 solution. Separation of components are 0.1 cps. Relative intensities, multiplicities and assignments are given in parentheses.

EXPERIMENTAL

Apparatus and instruments

The reactions were all carried out in nitrogen atmosphere with apparatus of conventional design. Melting points were determined on a Yanagimoto hotstage apparatus unless otherwise mentioned. Infrared spectra were obtained by using a Hitachi EPI-I spectrophotometer. Proton magnetic resonance spectra were made on a Varian A-60 spectrometer.

Preparations of cyclopentadienylnickel halides

Melting points, yields and analyses of all compounds prepared in this section are summarized in Table 1.

(*a*) *Triphenylphosphine-π-cyclopentadienylnickel chloride*. This compound was prepared according to the method described in ref. 11. It was diamagnetic, χ_{mol} -164×10^{-6}. The same method was employed for the preparation of methyldiphenylphosphine-π-cyclopentadienylnickel bromide and tri-*n*-butylphosphine-π-cyclopentadienylnickel chloride, although the reactions were carried out at room temperature and with equimolar amounts of the corresponding bis(phosphine)nickel dihalide and nickelocene.

(*b*) *Triphenylarsine-π-cyclopentadienylnickel iodide*. To the solution of triphenylarsine (4.6 g, 15 mmole) in tetrahydrofuran (30 ml) was added nickel carbonyl (1.3 g, 7.5 mmole) in tetrahydrofuran (10 ml) at room temperature. After the gas evolution had ceased, the solution was refluxed for one hour. To an ice-cooled solution was added nickelocene (1.5 g) and then iodine (1.9 g) in tetrahydrofuran (40 ml) dropwise. The solution was stirred for 30 min at room temperature and 30 min more at reflux temperature. After concentration of the solution, *n*-hexane was added to precipitate red-violet crystals. Recrystallization from cyclohexane gave dark red-violet crystals (6.9 g, 53 %). The same method was employed to prepare triphenylstibine-π-cyclopentadienylnickel iodide and triphenylphosphite-π-cyclopentadienylnickel iodide.

(*c*) *Triphenylarsine-π-cyclopentadienylnickel bromide*. The mixture of nickel bromide (2.4 g), triphenylarsine (6.2 g) and nickelocene (2.0 g) in tetrahydrofuran (50 ml) was stirred for 3 h at 50°. A procedure similar to that in (*b*) above for isolation of title compound gave dark red-violet crystals (6.7 g, 66 %).

Preparation of alkyl, aryl and alkynyl derivatives of nickel

Melting points, yield and analyses of the compounds prepared in this section are summarized in Table 2.

To an ice cooled Grignard reagent from methyl iodide (5.8 g), magnesium (1 g) and ether (70 ml) was added triphenylphosphine-π-cyclopentadienylnickel chloride (4.22 g, 10 mmole) in benzene (100 ml). A deep green solution resulted. After stirring for 2 h, aqueous ammonium chloride was added and the green-colored organic layer was dried with sodium sulfate. After the solvent was removed under reduced pressure, the residue was resolved in benzene and chromatographed on alumina, benzene/*n*-hexane (1 : 1) being used as eluant. The dark green fraction was collected and solvent was evaporated almost to dryness. After addition of *n*-hexane (20 ml), it was kept in the refrigerator to give dark green crystals (2.68 g, 67 %) of triphenylphosphine-π-cyclopentadienylmethylnickel. The molecular weight was measured cryoscopically in benzene (found 387; calcd. for $C_{24}H_{23}PNi$ 401). The NMR spectrum was obtained in CS_2 with tetramethylsilane as internal standard. The magnetic susceptibility was measured (χ_{mol} -149×10^{-6}).

All other compounds were prepared according to procedures similar to that described above. In the case of the mesityl derivative, tetrahydrofuran was employed as solvent instead of ether. The IR spectrum of the ethynyl derivative, $\pi\text{-}C_5H_5Ni(PPh_3)C{\equiv}CH$, showed the presence of an acetylenic proton (3290 cm^{-1}) and a triple bond (1968 cm^{-1}), and that of phenylethynyl derivative, $\pi\text{-}C_5H_5Ni(PPh_3)C{\equiv}CPh$, also showed the presence of a triple bond (2090 cm^{-1}).

Reduction of triphenylphosphine-π-cyclopentadienylnickel chloride by lithium aluminum hydride

To a Dry Ice-cooled solution of lithium aluminum hydride (0.5 g) in tetrahydrofuran (20 ml) was added dropwise triphenylphosphine-π-cyclopentadienylnickel chloride (2 g) in tetrahydrofuran (30 ml) during 15 minutes and the mixture kept for one hour under stirring. To the resulting brown solution was added methanol (10 ml) dropwise and then water (30 ml). The brown-red colored organic layer was separated and dried with calcium chloride. After removal of the solvent, the residue was chromatographed on alumina with benzene as eluant. The eluent was concentrated and kept in the refrigerator to give dark brown crystals. They were recrystallized from a mixture of benzene and *n*-hexane to give 0.55 g of air-stable, dark brown crystals, m.p. 275–277°. (Found: C, 66.10; H, 5.10. $C_{34}H_{30}Ni_2P_2$ calcd.: C, 66.08; H, 4.89 %.) The absorption maxima of IR spectrum of these crystals were fully identical with those of already known di-μ-(diphenylphosphido)-π-cyclopentadienyldinickel.

Reactions of triphenylphosphine-π-cyclopentadienylmethylnickel with halogens

To an ice-cooled solution of triphenylphosphine-π-cyclopentadienylmethylnickel (2.0 g) in ether (50 ml) was added dropwise a solution of iodine (0.63 g) in ether (50 ml) during 20 minutes under stirring. After completion of addition, the solvent was evaporated at reduced pressure. The residue was dissolved in a small amount of benzene, followed by the addition of a large amount of *n*-hexane to give red-brown solid. This was recrystallised from cyclohexane to give dark red-violet crystals, m.p. 140–141° (decomp.) (1.8 g). It was identified by analysis as triphenylphosphine-π-cyclopentadienylnickel iodide which had been reported in literature[12]. (Found: C, 54.17; H, 4.04. $C_{23}H_{20}INiP$ calcd.: C, 53.85; H, 3.93 %.)

From an experiment similar to that above, triphenylphosphine-π-cyclopentadienylmethylnickel (1.2 g) and bromine (0.24 g) at Dry Ice temperature yielded red crystals. Recrystallization from cyclohexane and drying at 100° under reduced pressure gave red crystals, m.p. 118–120° (decomp.) (0.2 g). These were identified by analysis as triphenylphosphine-π-cyclopentadienylnickel bromide. (Found: C, 59.18; H, 4.26. $C_{23}H_{20}BrNiP$ calcd.: C, 59.28; H, 4.33 %.)

The IR spectra of these halides are quite similar to that of the chloride.

Reaction of triphenylphosphine-π-cyclopentadienylphenylnickel with carbon monoxide

In a stainless steel autoclave containing triphenylphosphine-π-cyclopentadienylphenylnickel (2.32 g) and benzene (30 ml) was introduced carbon monoxide (80 atm). The autoclave was allowed to stand several days. The orange-red solution was concentrated almost to dryness under reduced pressure (5 mm Hg, room temperature). The residue was treated with methanol (10 ml) and filtered to give white crystals (1.5 g) which were identified as triphenylphosphinenickeltricarbonyl by comparison with authentic compound. The orange-red filtrate was concentrated to dryness under reduced pressure without heating, and the residue sublimed under reduced pressure (5 mm Hg, 70°) to give slightly purple colored crystals (0.42 g). Resublimation of the crystals gave white crystals, m.p. 60.5–61.5° (in air); 65° (in a nitrogen filled capillary tube). (Found: C, 93.30; H, 7.01. $C_{11}H_{10}$ calcd.: C, 92.91; H, 7.09%.) The crystals were polymerized gradually in air. The electronic spectrum of the compound was measured in ethanol.

SUMMARY

The preparations and some properties of π-$C_5H_5Ni(L)X$ and π-$C_5H_5Ni(L)R$ [X = halogens; $L = (C_6H_5)_3P$, $(CH_3)(C_6H_5)_2P$, $(n\text{-}C_4H_9)_3P$, $(C_6H_5)_3As$ and $(C_6H_5)_3Sb$; $R = CH_3$, C_2H_5, n-C_3H_7, n-C_4H_9, *sec*-C_4H_9, $CH_2C_6H_5$, C_6H_5, p-ClC_6H_4, o-$CH_3C_6H_4$, m-$CH_3C_6H_4$, p-$CH_3C_6H_4$, 2,4,6-$(CH_3)_3C_6H_2$, $C{\equiv}CH$ and $C{\equiv}CC_6H_5$] are described.

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