PENTAFLUOROPHENYL DERIVATIVES OF TRANSITION METALS

III[a]. TERTIARY PHOSPHINE COMPLEXES OF NICKEL AND COBALT

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We have recently described[1] some pentafluorophenyl complexes of titanium(IV). Continuing our studies on pentafluorophenyl derivatives of transition metals we now report several nickel(II) complexes and one cobalt(II) compound. As in the case of their titanium analogues, the new nickel compounds and the cobalt complex show a relatively high degree of stability.

Although nickel in the pentafluorophenyl complexes has not attained the electronic structure of krypton, the compounds are diamagnetic, and must have square planar structures similar to those of a large number of organo-derivatives of Group VIII metals of type $(R'_3P)_2MR_2$ (M = Co, Ni and Pt; R, R' = organic radicals) and $(R'_3P)_2M(R)X$ (X = halogen) made by Chatt and Shaw[2-4] and $(R'_3P)_2PdR_2$ and $(R'_3P)_2Pd(R)X$ made by Calvin and Coates[5].

The pentafluorophenyl Grignard reagent reacts rapidly under mild conditions with either bis(triphenylphosphine)nickel dibromide or bis(triethylphosphine)nickel dibromide to give products (Table 1) in which one bromine atom has been replaced by a pentafluorophenyl group. Treatment of [1,2-bis(diphenylphosphino)ethane]-cobalt dibromide with the Grignard reagent afforded a disubstituted product.

Reaction between pentafluorophenyllithium and the square-planar[6] complex bis(triethylphosphine)nickel dichloride affords two products where one or both of the chlorine atoms have been replaced by pentafluorophenyl groups. However, the tetrahedral[6] complexes bis(triphenylphosphine)nickel dichloride and bipyridylnickel dichloride yield only the disubstituted products. Since these reactions involve a change in stereochemistry, they may proceed via a different reaction path from that of the triethylphosphinenickel complex which permits formation of a monosubstituted product.

Bis(triethylphosphine)pentafluorophenylnickel chloride undergoes metathetical replacement of the remaining chlorine atom when an acetone solution is treated with sodium iodide or potassium thiocyanate.

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The new nickel complexes (Table 1) are more stable than their phenyl analogues, being unchanged after storage in air for many months, and in solution for several days. Most of the compounds melt without decomposition and can be solidified and remelted. In contrast, phenyl derivatives of nickel have low stability unless *ortho*-substituents are present in the phenyl ring[3]. The *ortho*-fluorine atoms of the pentafluorophenyl groups may be responsible for some of the enhanced stability of the nickel compounds but a much more powerful stabilising factor is undoubtedly the electronegativity of the C_6F_5 group, which appears to lie between that of chlorine and that of bromine[7,8]. Because of this electronegativity, the organic group would tend to remove charge from nickel, consequently the ionic resonance energy of the pentafluorophenyl–nickel bond would be greater than that of the phenyl–nickel bond. This factor is believed to be responsible for the relatively high stability of σ-bonded fluorocarbon–transition metal complexes in general[9].

The infrared spectra of the new compounds show very strong bands attributable to C_6F_5 absorptions near 1065 and 954 cm^{-1}. A characteristic absorption also occurs near 780 cm^{-1}.

EXPERIMENTAL

Microanalytical determinations were made at the Alfred Bernhardt Mikroanalytisches Laboratorium im Max-Planck-Institut für Kohlenforschung, Mülheim (Ruhr). Pentafluorophenyl bromide was obtained from Imperial Smelting Co., Avonmouth, Bristol, England.

The nickel complexes required as starting materials were prepared by published methods, *viz.* $(Et_3P)_2NiCl_2$ [10], $(Ph_3P)_2NiCl_2$ [11], $(o\text{-}C_5H_4N)_2NiCl_2$ [12]. [1,2-Bis(diphenylphosphino)ethane]cobalt dibromide was obtained by treating cobalt(II) bromide with the diphosphine.

(1) *Reactions between pentafluorophenylmagnesium bromide and halide complexes*

To an ice-cooled Grignard reagent from pentafluorophenyl bromide (2.3 g, 9.3 mmole), magnesium (0.225 g, 9.3 g-atom) and tetrahydrofuran (20 ml) was added bis(triphenylphosphine)nickel dibromide (4.9 g, 6.6 mmole). The green colour of the nickel complex disappeared, and a deep yellow solution resulted. After stirring (10 min) dilute (5 %) aqueous hydrobromic acid (10 ml) was added, and the organic layer worked up to give $[(C_6H_5)_3P]_2Ni(C_6F_5)Br$ (4.4 g, 81 % yield).

Bis(triethylphosphine)pentafluorophenylnickel bromide (Table 1), and [1,2-bis-(diphenylphosphino)ethane]bis(pentafluorophenyl)cobalt were obtained by a similar procedure. The cobalt compound (found: C, 57.6; H, 3.4; F, 25.6. $C_{38}H_{24}CoF_{10}P_2$ calcd.: C, 57.7; H, 3.1; F, 24.0 %), yellow needles (decomp. 186°) recrystallized from benzene–cyclohexane, is less stable than the nickel compounds. Its solutions in organic solvents decompose in air.

(2) *Reactions between pentafluorophenyllithium and halide complexes*

(*a*) *Bis(triethylphosphine)bis(pentafluorophenyl)nickel and bis(triethylphosphine)-pentafluorophenylnickel chloride.* Pentafluorophenyllithium[13] [prepared under nitrogen from C_6F_5Br (543 mg, 2.18 mmole) and a 15 % hexane solution of $n\text{-}C_4H_9Li$ (1.3 ml, 2.2 mmole) in diethyl ether (10 ml) at −78°] was added by means of a syringe to a diethyl ether (20 ml) solution of $[(C_2H_5)_3P]_2NiCl_2$ (398 mg, 1.09 mmole) at room temperature under nitrogen. During addition the colour of the reaction mixture changed from red to yellow, a white solid being deposited. Solvent was removed, and the residue shaken with benzene (75 ml) and water (2 × 10 ml). The organic layer was separated, dried (calcium chloride) and concentrated affording 401 mg (58.5 % yield) of $[(C_2H_5)_3P]_2Ni(C_6F_5)_2$. The mother liquor was taken to dryness and the residue recrystallised to give 100 mg (18.5 % yield) of $[(C_2H_5)_3P]_2Ni(C_6F_5)Cl$.

By increasing the ratio of bis(triethylphosphine)nickel dichloride to pentafluorophenyllithium a higher proportion of the monopentafluorophenylnickel complex can be obtained. Thus $[(C_2H_5)_3P]_2NiCl_2$ (1.0 g, 2.73 mmole) in diethyl ether (50 ml) was treated under nitrogen at −78° with C_6F_5Li [obtained from C_6F_5Br (1.0 g, 4.02 mmole) in diethyl ether (10 ml) and 2.5 ml (4.0 mmole) of the n-C_4H_9Li solution]. After allowing the mixture to come to room temperature separation of products, as described above, afforded 839 mg (62 % yield) of $[(C_2H_5)_3P]_2Ni(C_6F_5)Cl$ and 20 mg (1.2 % yield) of $[(C_2H_5)_3P]_2Ni(C_6F_5)_2$. The latter compound can be made in 80% yield when the $[(C_2H_5)_3P]_2Ni(C_6F_5)Cl$ complex is treated with excess of pentafluorophenyllithium.

(*b*) *Bis(triphenylphosphine)bis(pentafluorophenyl)nickel*. Pentafluorophenyllithium [from C_6F_5Br (185 mg, 0.75 mmole) and 0.45 ml (0.75 mmole) of 15 % n-C_4H_9Li solution in diethyl ether (6 ml) at −78°] was treated with bis(triphenylphosphine)-nickel dichloride (300 mg, 0.46 mmole) under nitrogen. The blue crystals remained until the temperature was raised to −60°, whereupon the solution turned yellow and solid deposited. The mixture was kept (15 h) at 0° under nitrogen, then boiled briefly with a further 50 ml of ether. The mixture was filtered, the filtrate evaporated, and the residue crystallised to give 169 mg (40 % yield) of $[(C_6H_5)_3P]_2Ni(C_6F_5)_2$ (Table 1).

Bis(triphenylphosphine)bis(pentafluorophenyl)nickel was shown to be diamagnetic by the NMR method of Evans[14].

When a solution of $[(C_6H_5)_3P]_2NiCl_2$ in dichloromethane was used, instead of the solid complex, the bis(pentafluoro)nickel compound was formed in about 30 % yield, along with much triphenylphosphine and an insoluble solid (m.p. $\nless$ 300°) having a strong infrared absorption at 950 cm^{-1}. In an attempt to prepare $[(C_6H_5)_3P]_2$-$Ni(C_6F_5)Cl$, pentafluorophenyllithium and bis(triphenylphosphine)nickel dichloride were mixed in a 1:1 ratio. A 3 % yield of $[(C_6H_5)_3P]_2Ni(C_6F_5)_2$ was obtained, and triphenylphosphine recovered accounted for 53 % of this ligand present in the starting material.

(*c*) *Bipyidylbis(pentafluorophenyl)nickel*. Powdered bipyridylnickel dichloride (250 mg, 0.87 mmole) was added to pentafluorophenyllithium [from C_6F_5Br (430 mg, 1.74 mmole) and the hexane solution of n-C_4H_9Li (1.0 ml, 1.74 mmole)] in diethyl ether (20 ml) at −78° under nitrogen. The mixture turned yellow and was stirred at −78° for 15 min and then until it had come to room temperature. Solvent was removed and the residue extracted (benzene) to give 140 mg (29 % yield) of $(o$-$C_5H_4N)_2Ni(C_6F_5)_2$. A further 85 mg of product was obtained from the mother liquor. The bipyridylbis(pentafluorophenyl)nickel complex sometimes decomposes explosively between 255 and 260°.

In an attempt to obtain $(o$-$C_5H_4N)_2Ni(C_6F_5)Cl$, the reactants were mixed in a 1:1 ratio. None of the desired product was formed but the bis(pentafluorophenyl)-nickel complex was formed in 21 % yield (based on C_6F_5Br).

TABLE 1

PENTAFLUOROPHENYLNICKEL COMPLEXES

Compound	M.p. °C	Colour	Recrystallization solvent	Carbon, %		Hydrogen, %		Fluorine, %		Phosphorus, %	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
$[(C_6H_5)_3P]_2Ni(C_6F_5)Br$[a]	199–200 (decomp.)	Yellow	benzene–methanol	60,8	61.3	3,6	3,8	11,4	11,1	—	—
$[(C_2H_5)_3P]_2Ni(C_6F_5)Br$	130–131	Yellow Orange	methanol	39,0	39,8	5,6	5,9	—	—	—	—
$[(C_2H_5)_3P]_2Ni(C_6F_5)Cl$[b]	112–113	Deep Yellow	methanol	43.3	43.4	6.1	5.8	19.1	19.2	12.4	12.3
$[(C_2H_5)_3P]_2Ni(C_6F_5)I$[c]	151–152	Brown	methanol	36.9	36.9	5.1	5.3	16.1	16,3	—	—
$[(C_2H_5)_3P]_2Ni(C_6F_5)SCN$[d]	149–150	Yellow	methanol	43.9	43.7	5.8	5.7	18,3	18.1	—	—
$[(C_2H_5)_3P]_2Ni(C_6F_5)_2$	213–214	Pale Yellow	benzene–methanol	45.8	46.0	4.8	4.8	30.2	30.3	9.8	9.7
$[(C_6H_5)_3P]_2Ni(C_6F_5)_2$	201–204 (decomp.)	Yellow	benzene–methanol	62.8	63.0	3.3	3.4	20,7	20.7	6.7	6.7
$(o\text{-}C_5H_4N)_2Ni(C_6F_5)_2$[e]	255 (decomp.)	Dark Yellow	benzene	48.1	48.3	1.5	1.6	34.6	34.8	—	—

[a] Nickel: calcd. 7.1, found, 6.6%. [b] Chlorine: calcd. 7.1, found 7.0%. [c] Iodine: calcd. 21.5, found 21.6%. [d] Nitrogen: calcd. 2.7, found 2.8%. [e] Nitrogen: calcd. 5.1, found 5.2%.

(3) *Metathetical replacement of chloride in bis(triethylphosphine)pentafluorophenylnickel chloride*

(*a*) *Bis(triethylphosphine)pentafluorophenylnickel iodide.* $[(C_2H_5)_3P]_2Ni(C_6F_5)Cl$ (215 mg, 0.43 mmole) and NaI (73 mg, 0.49 mmole) dissolved in acetone (20 ml) gave a brown solution and a white solid. The mixture was boiled briefly, solvent removed and the residue extracted with warm water (2 × 25 ml). The brown solid remaining was crystallized (yield 180 mg). A further 49 mg was obtained from the mother liquor giving $[(C_2H_5)_3P]_2Ni(C_6F_5)I$ in a total yield of 90%.

(*b*) *Bis(triethylphosphine)pentafluorophenylnickel thiocyanate.* In an analogous way, $[(C_2H_5)_3P]_2Ni(C_6F_5)Cl$ with KSCN (7.5% excess) gave $[(C_2H_5)_3P]_2Ni(C_6F_5)SCN$ in 73% yield.

(4) *Infrared spectra*

These were recorded in carbon disulphide solution using a Perkin-Elmer model 237 spectrophotometer.

$[(C_2H_5)_3P]_2Ni(C_6F_5)_2$: 2960(m), 2930(m), 2905(m), 2870(m), 1336(w), 1319(vw), 1271(w), 1250(w), 1230(vw), 1099(w), 1057(s), 1044(s), 1031(s), 998(w), 954(vs), 845(w, br), 773(s), 763(s), 734(vw), 719(s), 709(sh).

$[(C_2H_5)_3P]_2Ni(C_6F_5)Cl$: 2960(s), 2930(s), 2905(s), 2870(s), 1378(m), 1362(sh), 1350(w), 1275(m), 1250(m), 1240(sh), 1118(w), 1102(w), 1065(sh), 1057(s), 1047(s), 1034(s), 1003(m), 954(vs), 850(w, br), 787(s), 761(s), 736(m), 724(s), 712(sh), 705(sh)

$[(C_2H_5)_3P]_2Ni(C_6F_5)I$: 2960(s), 2924(s), 2900(s), 2868(s), 2815(vw), 2720(vw), 1373(m), 1357(sh), 1345(m), 1269(m), 1245(m), 1232(m), 1113(vw), 1097(w), 1060(sh), 1054(s), 1044(s), 1030(s), 997(m), 951(vs), 850 (w, br), 779(s), 754(s), 729(w), 715(s), 706(sh).

$[(C_2H_5)_3P]_2Ni(C_6F_5)SCN)$: 2960(s), 2930(s), 2905(s), 2870(s), 2820(vw), 2730(vw), 2075(vs), 1375(m), 1360(w), 1349(w), 1323(vw), 1270(w), 1248(m), 1233(w), 1113(vw), 1099(w), 1065(sh), 1053(s), 1043(s), 1028(s), 997(w), 952(vs), 850 (w, br), 841(m), 783(s), 757(s), 731(m), 720(s), 708(sh), 700(sh).

$[(C_6H_5)_3P]_2Ni(C_6F_5)_2$: 3070(w), 3050(m), 3010(vw), 2990(vw), 1335(w), 1319(vw), 1271(vw), 1250(vw), 1095(m), 1084(sh), 1055(sh), 1045(m), 1024(w), 997(vw), 954(vs), 840(w, br), 771(m), 742(m), 735(sh), 689(m).

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SUMMARY

Several new complexes in which pentafluorophenyl groups are σ-bonded to nickel have been prepared by treating bis(tertiaryphosphine)nickel dihalides, or bipyridylnickel dichloride, with pentafluorophenylmagnesium bromide and pentafluorophenyllithium. The synthesis of [1,2-bis(diphenylphosphino)ethane]bis(pentafluorophenyl)cobalt is also reported. Bis(triethylphosphine)pentafluorophenylnickel chloride can be converted to $[(C_2H_5)_3P]_2Ni(C_6F_5)I$ and $[(C_2H_5)_3P]_2Ni(C_6F_5)SCN$ by metathetical reactions.

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