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INSERTION REACTIONS OF ISOCYANIDES INTO NICKEL-TO-CARBON SIGMA BONDS

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SUMMARY

The treatment of isocyanides with π-$C_5H_5Ni(PPh_3)R$ in benzene at room temperature gave the complexes, π-$C_5H_5Ni(CNR')[C(R)=NR]$ (I), the products of isocyanide insertion into nickel–alkyl sigma bonds. The reactions of isocyanides with π-$C_5H_5(PR_3)I$ ($R = Ph$, Et, OPh) produced the salt-like complexes (II), formulated as $[\pi\text{-}C_5H_5Ni(CNR')(PR_3)]I$ and $[\pi\text{-}C_5H_5Ni(CNR')_2]I$ ($R' = Ph$, Et). Based on the formation of (I) from the reactions of (II) with phenylmagnesium bromide, the mechanism of the insertion reaction of isocyanides into nickel-to-carbon bonds has been considered.

INTRODUCTION

Isocyanides are among the very few substances with a lone electron pair on a carbon atom and this enables isocyanides to act as carbon-ligands in coordination compounds. Although there exists a close similarity between an isocyanide and carbon monoxide based on the electronic structure, the characteristic property of isocyanides as ligands is the capacity to function as a stronger sigma donor and a weaker pi acceptor than carbon monoxide. We intended to obtain more information about the interaction of isocyanides with various transition metal complexes of organic compounds.

Many examples of the insertions of carbon monoxide and olefins into transition metal complexes are known. Such insertion reactions are thought to be an intermediate step in catalytic processes, such as carbonylation reactions[1] and Ziegler–Natta polymerization[2]. On the other hand, there exists as yet no example of the insertion of an isocyanide into transition metal complexes. Recently, evidence for the insertion of hydrogen isocyanide into a cobalt–carbon bond was obtained in the course of the study of the acid-catalyzed decomposition of 2-, 3-, and 4-pyridylmethylpentacyanocobaltate ion[3], but a stable isocyanide insertion product was not isolated. We have studied the interaction of isocyanides with transition metal alkyls in connection with a study of the coordination polymerization of isocyanides by various transition metal complexes, which we had already reported[4], and have found that isocyanides are inserted into alkyl–nickel sigma bonds to give stable complexes. The

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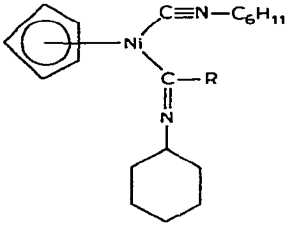
results were briefly described previously[5]. In this paper, we wish to report more fully on this subject, and about some considerations of the mechanism of isocyanide insertion reactions.

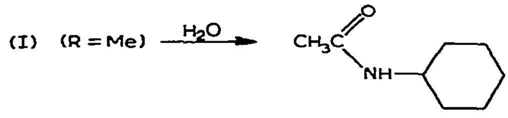
RESULTS AND DISCUSSION

(Triphenylphosphine)-π-cyclopentadienylalkylnickel compounds, π-$C_5H_5Ni(PPh_3)R$, such as methyl, n-butyl, phenyl and *para*-substituted phenyl derivatives, have been treated with cyclohexyl isocyanide in benzene at room temperature to give reddisch brown compounds (I). These compounds (I) were soluble in most organic solvents and stable in the solid state, except in the case of methyl derivative. The compounds (I) were formulated as π-$C_5H_5Ni(CNC_6H_{11})_2R$, based on their elemental analyses and their NMR spectra. Evidence concerning their structures was obtained from their IR and NMR spectra and from their decomposition with moist air. Thus, the IR spectra of each compound (I) showed two characteristic bands in the range from 2130 to 2140 cm^{-1}, and from 1580 to 1620 cm^{-1}; the former band is attributable to the coordinated isocyanide group and the latter to a carbon–nitrogen double bond, suggesting the insertion of isocyanides into alkyl–nickel sigma bonds. In these complexes, the frequency of a nitrogen–carbon triple bond of the coordinated isocyanide groups was almost analogous to that of uncoordinated isocyanides. The NMR spectra indicated the presence of a cyclopentadienyl and an alkyl group in addition to cyclohexyl groups. It was concluded from these results that the compounds (I) were π-cyclopentadienyl(cyclohexyl isocyanide)[alkyl(cyclohexylimino)methyl]nickel.

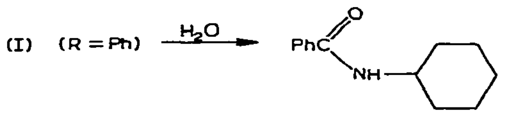


(I)

These structures were supported by the degradation of these compounds with moist air to give *N*-cyclohexylamides:



(1)

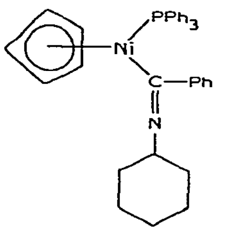


(2)

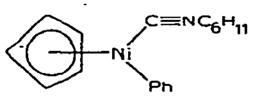
The reaction of the 1-butynylnickel derivative with cyclohexyl isocyanide gave π-cyclopentadienyl(cyclohexyl isocyanide)[(1-butynyl)(cyclohexylimino)methyl]nickel. However, no insertion reactions of carbon monoxide into alkynyl–metal sigma bonds have been reported to date, and this behavior may be one of the characteristic differences between the reactivities of isocyanide and carbon monoxide.

Steric effects were observed in insertion reactions of isocyanides into nickel-to-carbon bonds. Cyclohexyl isocyanide failed to react with arylnickel complexes having *o*-methyl substituents (*o*-tolyl and mesityl), an observation explicable in terms of steric hindrance. In addition, reactions of (triphenylphosphine)-π-cyclopentadienylphenylnickel with hindered isocyanides, such as tert-butyl and 2,6-dimethylphenyl isocyanide were also carried out. The operation of a steric effect was indicated by the finding that treatment of the phenylnickel derivative with tert-butyl isocyanide at room temperature gave tris(tert-butyl isocyanide)(triphenylphosphine)nickel and biphenyl as main products and only a small amount of π-cyclopentadienyl(tert-butyl isocyanide)[phenyl(tert-butylimino)methyl]nickel. The reaction with 2,6-dimethylphenyl isocyanide gave tetrakis(2,6-dimethylphenyl isocyanide)nickel, biphenyl and a small amount of π-cyclopentadienyl(2,6-dimethylphenyl isocyanide){phenyl[(2,6-dimethylphenyl)imino]methyl}nickel.

In an attempt to prepare the complexes of the types (II) and (III), which might be intermediates in the formation of (I), we examined the reaction of (triphenylphosphine)-π-cyclopentadienylphenylnickel with cyclohexyl isocyanide in 1/1 molar ratio in benzene at room temperature. The only product isolated was already mentioned π-cyclopentadienyl(cyclohexyl isocyanide)[phenyl(cyclohexylimino)methyl]nickel and some unconverted starting nickel compound was recovered. The result is interesting in connection with the insertion mechanism of isocyanides into alkyl–nickel sigma bonds.



(II)

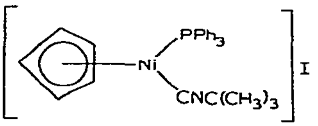


(III)

In addition, extensive studies of insertion reactions of isocyanides into nickel–halogen bonds in connection with those of isocyanides into alkyl–nickel sigma bonds were also carried out.

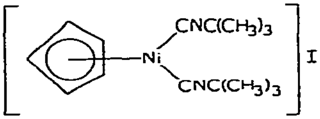
There are several examples of the insertion reactions into transition metal to halogen bonds. $PtF_2(PEt_3)_2$ reacted with C_2F_4 in HF at 150° to give $(C_2F_5)_2Pt(PEt_3)_2$[6]. It has been reported by Mango and Dvoretzky that methylene was inserted into iridium–chlorine bond to give $Ir(CH_2Cl)CO(PPh_3)$ from the reaction of $IrCl(CO)(PPh_3)$ with diazomethane[7]. It has been also established that the reaction of $(PhCN)_2PdCl_2$ with butadiene gave a product in which butadiene was formally inserted into a palladium–chlorine bond[8]. In the case of our reactions, new complexes of isocyanides were isolated, although the expected compounds were not obtained.

Thus, (triphenylphosphine)-π-cyclopentadienylnickel iodide was treated with tert-butyl isocyanide to give green needles (IV) in quantitative yield. The IR spectrum of the complex (IV) showed a carbon–nitrogen stretching frequency at 2190 cm^{-1}, attributable to the presence of a coordinated isocyanide group and a characteristic absorption for a cyclopentadienyl group near 800 cm^{-1}. The NMR spectrum showed three resonances at τ 2.48–2.58 (broad, 15 H), 4.58 (singlet, 5 H) and 8.96 ppm (singlet, 9 H), corresponding to the phenyl, cyclopentadienyl and methyl protons, respectively. The spectroscopic studies and the analytical data suggested that the compound (IV) could be formulated as π-$C_5H_5Ni(PPh_3)[CNC(CH_3)_3]I$. The structure of compound (IV) may best be represented by the ionic structure, $\{\pi$-$C_5H_5Ni(PPh_3)[CNC(CH_3)_3]\}I$, in order to attain the krypton configuration for the nickel atom. An analogous complex, π-$C_5H_5Ni(PPh_3)_2SnCl_3$, has been recently prepared by Van den Akker and Jellinek[9], and McArdle and Manning[10] by treatment of (triphenylphosphine)-π-cyclopentadienylnickel chloride with tin(II) chloride. The ionic nature of (IV) was confirmed by a molecular weight measurement in methylene chloride and nitrobenzene, in which a lower value than the theoretical one for $\{\pi$-$C_5H_5Ni(PPh_3)$-$[CNC(CH_3)_3]\}I$ was obtained. This structure also was supported by formation of $\{\pi$-$C_5H_5Ni(PPh_3)[CNC(CH_3)_3]\}BPh_4$ from the reaction of (IV) with sodium tetraphenylborate in acetone. The reaction with cyclohexyl isocyanide also gave the similar result, *i.e.*, $[\pi$-$C_5H_5Ni(PPh_3)(CNC_6H_{11})]I$ was produced.



(IV)

Reactions with complexes containing ligands other than triphenylphosphine coordinated were also carried out. The treatment of tert-butyl isocyanide with triethylphosphine-coordinated complex gave a compound of the type (IV). However, when π-C_5H_5NiLI $[L = P(OPh)_3, AsPh_3]$ was treated with tert-butyl isocyanide, π-cyclopentadienylbis(tert-butyl isocyanide)nickel iodide (V) was obtained, rather than complexes of type (IV). The formation of (IV) or (V) depending on the ligand L might relate to the pi-acceptor ability of the ligands and it may be that the formation of (V) proceeds through the complex of the type (IV).

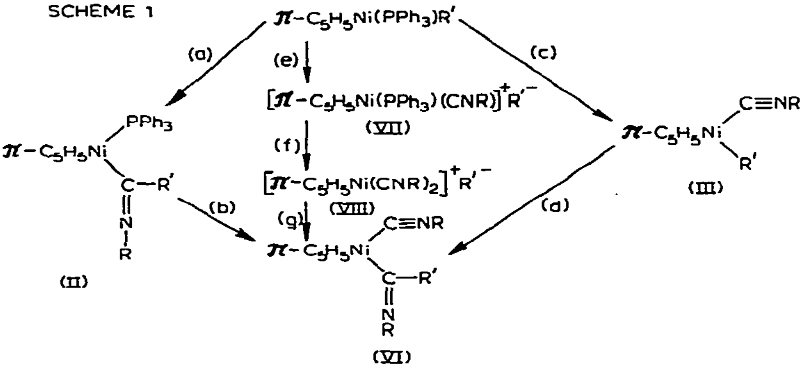


(V)

The mechanism on the insertion reactions of isocyanides into nickel-to-carbon bonds has been now considered from the results presented here.

Three simple mechanisms may be accounted for the isocyanide insertion reaction, as shown in Scheme 1. The first [(a)–(b)] involves a direct attack of RNC on nickel, accompanied, or immediately followed, by migration of R to the isocyanide ligand, and the replacement of PPh_3 with RNC. The second path [(c)–(d)] consists of an initial replacement of PPh_3 with RNC, followed by an attack of the second isocyanide on nickel and a rapid transfer of R to the isocyanide ligand or by a rearrangement of (III) to a coordinately unsaturated (or solvated) $C_5H_5Ni(CR'{=}NR)$ and then an addition of another isocyanide. The third route [(e)–(f)–(g)] is the extensive application to alkyl derivatives, based on the complexes obtained from the reaction of isocyanides with iodide, although there are differences between iodide and alkyl derivatives. In an attempt to possibly resolve among the three suggested mechanisms, experiments were conducted with the objective of trapping the intermediates. Accordingly, the attempt of conducting from the iodide to the corresponding alkyl derivatives has been carried out.

SCHEME 1



Treatment of (triphenylphosphine)-π-cyclopentadienyl(cyclohexyl isocyanide)nickel iodide with phenylmagnesium bromide in 1/2 molar ratio in ether/benzene at ice temperature gave π-cyclopentadienyl(cyclohexyl isocyanide)[phenyl(cyclohexylimino)methyl]nickel (VI) and (triphenylphosphine)-π-cyclopentadienylphenylnickel (IX) without forming any compound of (II) or (III). In addition, the treatment

$$2\,[\pi\text{-}C_5H_5Ni(PPh_3)(CNC_6H_{11})]I \xrightarrow{2\,PhMgBr} \{2\,[\pi\text{-}C_5H_5Ni(PPh_3)(CNC_6H_{11})]^+Ph^-\}$$

$$\rightarrow \underset{(VI)}{\pi\text{-}C_5H_5Ni(CNC_6H_{11})[C(Ph){=}NC_6H_{11}]} + \underset{(IX)}{\pi\text{-}C_5H_5Ni(PPh_3)Ph} + PPh_3 \qquad (3)$$

of π-cyclopentadienylbis(cyclohexyl isocyanide)nickel iodide with phenylmagnesium bromide gave complex (VI) only. These reactions may be suggestive of the formation of the intermediates (VII) and (VIII).

$$[\pi\text{-}C_5H_5Ni(CNC_6H_{11})_2]I + PhMgBr \rightarrow (VI) \qquad (4)$$

Failure to isolate (II) in the reaction of $\pi\text{-}C_5H_5Ni(PPh_3)Ph$ with cyclohexyl isocyanide in 1 : 1 molar ratio and in the reaction of $[\pi\text{-}C_5H_5Ni(PPh_3)(CNC_6H_{11})]I$ with phenylmagnesium bromide [eqn. (3)] may rule out the possibility of the first path [(a)–(b)].

Although an analogous mechanism to the second route is the most widely accepted one in the case of carbon monoxide insertion reaction, we could not obtain any

TABLE 1

PRODUCTS OF THE REACTIONS OF ISOCYANIDES WITH (TRIPHENYLPHOSPHINE)-π-CYCLOPENTADIENYLALKYL-NICKEL

Compound[a]	Yield (%)	M.p.[b] (°C)	Analyses: found (calcd.) (%)			IR (cm^{-1})	NMR[c], τ (ppm)
			C	H	N		
CpNi(CNC$_6$H$_{11}$)- [C(CH$_3$)=NC$_6$H$_{11}$]	85	72.5–73.5	67.08 (67.24)	8.88 (8.47)	7.70 (7.84)	2146(N≡C) 1618(C=N)	4.72(s, C$_5$H$_5$), 6.37(b, m), 7.73(s, CH$_3$), 7.00–9.00(b,o)
CpNi(CNC$_6$H$_{11}$)- [C(C$_4$H$_8$)=NC$_6$H$_{11}$]	68	51–53	68.68 (69.19)	9.14 (9.09)	7.31 (7.02)	2140(N≡C) 1618(C=N)	4.73(s, C$_5$H$_5$), 6.20–6.60(b, m), 7.56(t, CH$_3$), 8.00–8.90(b,o+C$_3$H$_6$)
CpNi(CNC$_6$H$_{11}$)- [C(Ph)=NC$_6$H$_{11}$]	85	113–114	71.46 (71.62)	7.72 (7.69)	6.70 (6.68)	2140(N≡C) 1589(C=N)	2.10–3.00(c, C$_6$H$_5$), 4.77(s, C$_5$H$_5$), 5.70–6.20(b, d), 6.20–6.70(b, e), 7.70–9.10(b,o)
CpNi(CNC$_6$H$_{11}$)- [C(C$_6$H$_4$CH$_3$-*p*)=NC$_6$H$_{11}$]	72	99–101.5	71.92 (72.07)	8.00 (7.91)	6.19 (6.47)	2140(N≡C) 1589(C=N)	
CpNi(CNC$_6$H$_{11}$)- [C(C$_6$H$_4$Cl-*p*)=NC$_6$H$_{11}$]	89	126–128	66.17 (66.18)	7.14 (6.89)	6.39 (6.17)	2135(N≡C) 1589(C=N)	2.10–2.90(c, C$_6$H$_5$), 4.73(s, C$_5$H$_5$) 5.80–6.20(b, d), 6.25–6.67(b, e), 7.80–9.10(b,o)
CpNi[CNC$_6$H$_3$(CH$_3$)$_2$-2,6]- [C(Ph)=NC$_6$H$_3$(CH$_3$)$_2$-2,6]	15	103	74.83 (75.19)	5.73 (6.09)	5.93 (6.05)	2129(N≡C) 1618(C=N)	2.60–3.15(c, C$_6$H$_3$), 4.95(s, C$_5$H$_5$), 7.85(s, CH$_3$), 8.01(s, CH$_3$)
CpNi(CNC$_6$H$_{11}$)- [C(C≡CC$_2$H$_5$)=NC$_6$H$_{11}$]	31	83–86	72.52 (72.23)	7.38 (7.46)	6.63 (6.48)	2163(N≡C, 2155 C≡C) 1564(C=N)	4.70(s, C$_5$H$_5$), 6.06–6.65(b, m), 7.65(s, CH$_3$), 7.80–9.10(b, o)
CpNi[CNC(CH$_3$)$_3$]- [C(Ph)=NC(CH$_3$)$_3$]	11	82–84	68.48 (68.69)	7.57 (7.69)	7.34 (7.63)	2135(N≡C) 1599(C=N)	

[a] Cp = π-C$_5$H$_5$. [b] Melting points were measured in nitrogen filled capillary tube. All compounds melt with decomposition. [c] s = singlet, t = triplet, b = broad, c = complex, o = methylene protons of cyclohexyl group, m = methine proton of cyclohexyl group, d = methine proton of the inserted isocyanide group, e = methine proton of the coordinated isocyanide group.

evidence to support the second route. At present, we suggest the third path, although the second one cannot be ruled out.

EXPERIMENTAL

Apparatus and instruments

The reactions were all carried out under a nitrogen atmosphere with apparatus of conventional design. All melting points are uncorrected; they were measured by a micro melting point apparatus Yanagimoto Model MP-S2. The IR spectra were obtained by a Jasco Model DS-402G grating spectrometer. The NMR spectra were recorded by a Varian Model A-60 instrument in $CDCl_3$ using tetramethylsilane as an internal standard. Melting points, yields and analyses of all compounds prepared are summerized in Tables 1 and 2.

TABLE 2

PRODUCTS OF THE REACTIONS OF ISOCYANIDES WITH (TRIPHENYLPHOSPHINE)-π-CYCLOPENTADIENYLNICKEL HALIDES

Compound[a]	M.p.[b] (°C)	Analyses: found (calcd.) (%)			ν(N≡C) (cm⁻¹)
		C	H	N	
$\{CpNi(PPh_3)[CNC(CH_3)_3]\}I$[c]	137–139	57.55 (57.38)	4.84 (4.99)	2.15 (2.39)	2163
$[CpNi(PPh_3)(CNC_6H_{11})]I$	138–141	58.05 (57.91)	4.99 (5.02)	2.06 (2.25)	2189
$\{CpNi(PPh_3)[CNC(CH_3)_3]\}BPh_4$	161–162	79.03 (79.21)	6.16 (6.26)	1.69 (1.78)	2208
$[CpNi(PPh_3)(CNC_6H_{11})]BPh_4$	98–101	79.68 (79.83)	6.39 (6.08)	1.61 (1.72)	2193
$\{CpNi(PEt_3)[CNC(CH_3)_3]\}I$	117–119	42.09 (42.52)	6.31 (6.47)	3.03 (3.10)	2172
$\{CpNi[CNC(CH_3)_3]_2\}I$[d]	124	43.36 (43.27)	5.58 (5.56)	5.79 (5.72)	2192
$\{CpNi[CNC(CH_3)_3]_2\}Br$	118–119	48.55 (48.53)	6.04 (6.27)	7.37 (7.57)	2190
$\{CpNi[CNC(CH_3)_3]_2\}BPh_4$	145–149	76.34 (76.88)	7.07 (7.11)	4.68 (4.60)	2193

[a] Cp = π-C_5H_5. [b] All compounds melt with decomposition. [c] NMR spectrum (τ): 2.49, 2.59 (complex, C_6H_5); 4.58 (singlet, C_5H_5); 8.96 (singlet, CH_3). Mol.wt. found: 491 by vapour pressure osmometer (in CH_2Cl_2), 314 by the cryoscopic nitrobenzene method; calcd.: 586. [d] NMR spectrum (τ): 4.18 (singlet, C_5H_5), 8.40 (singlet, CH_3).

Reaction of (triphenylphosphine)-π-cyclopentadienylphenylnickel with cyclohexyl isocyanide

To a solution of π-$C_5H_5Ni(PPh_3)Ph$[11] (2.0 g, 4.32 mmoles) in benzene was added cyclohexyl isocyanide (1.5 g, 13.7 mmoles) at room temperature. After stirring for 2 h, the reaction mixture was evaporated to about 5 ml under reduced pressure and chromatographed on alumina, benzene being used as eluant. The reddish-brown fraction was collected and solvent was evaporated almost to dryness. Its recrystallization from hexane/benzene (10/1) gave reddish-brown crystals (1.55 g, 85%) of π-cyclopentadienyl(cyclohexyl isocyanide)[phenyl(cyclohexylimino)methyl]nickel.

By procedures similar to those described above, the other isocyanide insertion complexes were obtained from the reaction of cyclohexyl isocyanide with the other alkylnickel derivatives.

Reaction of (triphenylphosphine)-π-cyclopentadienylphenylnickel with tert-butyl isocyanide

A solution of 2.0 g (4.32 mmoles) of π-$C_5H_5Ni(PPh_3)Ph$ in 20 ml of benzene was treated with 1.2 g (14.5 mmoles) of tert-butyl isocyanide at room temperature and then stirred for 3.5 h. The reaction mixture was evaporated to about 10 ml under reduced pressure and chromatographed on alumina. Yellow and reddish-brown bands were observed. They were eluted with benzene and collected separately. Evaporation of the eluates and crystallization of the residues from hexane/benzene gave $Ni(PPh_3)[CNC(CH_3)_3]_3$ (1.3 g) and π-cyclopentadienyl(tert-butyl isocyanide)-[phenyl(tert-butylimino)methyl] nickel (0.18 g) in the order of their elution. Concentration and sublimation of mother liquors gave biphenyl (0.41 g).

Reaction of (triphenylphosphine)-π-cyclopentadienylphenylnickel with 2,6-dimethylphenyl isocyanide

By procedures similar to those described above, π-cyclopentadienyl(2,6-dimethylphenyl isocyanide){phenyl[(2,6-dimethylphenyl)imino]methyl}nickel (0.2 g), tetrakis(2,6-dimethylphenyl isocyanide)nickel (0.45 g) and biphenyl (0.13 g) were obtained from 0.65 g of 2,6-dimethylphenyl isocyanide and 0.93 g of (triphenylphosphine)-π-cyclopentadienylphenylnickel.

Reaction of tert-butyl isocyanide with (triphenylphosphine)-π-cyclopentadienylnickel iodide

To a solution of π-$C_5H_5Ni(PPh_3)I$ (1.5 g, 3.4 mmoles) in 20 ml of benzene was added tert-butyl isocyanide (0.7 g, 8.4 mmoles) at room temperature. The mixture was stirred for 3 h. After the reaction period was over, the resulting green solid was removed by filtration and recrystallized from acetone/benzene. The green needles were identified as {π-$C_5H_5Ni(PPh_3)[CNC(CH_3)_3]$}I by means of their IR spectrum, analysis and NMR spectrum.

Reaction of {π-$C_5H_5Ni(PPh_3)[CNC(CH_3)_3]$}I with sodium tetraphenyl borate

To a solution of {π-$C_5H_5Ni(PPh_3)[CNC(CH_3)_3]$}I (0.3 g, 0.5 mmole) in 10 ml of acetone was added sodium tetraphenylborate at room temperature and kept for 3 h. Water was added to the reaction mixture after the reaction period was over. The resultant pale green precipitate was removed by filtration. Crystallization from acetone/water gave 0.35 g of {π-$C_5H_5Ni(PPh_3)[CNC(CH_3)_3]$}$BPh_4$.

Reaction of tert-butyl isocyanide with (triphenylphosphine)-π-cyclopentadienylnickel iodide

To a solution of π-$C_5H_5NiP(OPh)_3I$ (0.6 g, 1.07 mmoles) in 15 ml of benzene was added tert-butyl isocyanide (0.3 g, 3.6 mmoles) at room temperature and kept for 2 h. The resultant green crystals were removed by filtration. Recrystallization from acetone/benzene gave 0.5 g of {π-$C_5H_5Ni[CNC(CH_3)_3]_2$}I as green crystals.

Reaction of $\{\pi\text{-}C_5H_5Ni[CNC(CH_3)_3]_2\}I$ *with sodium tetraphenylborate*

The procedure was similar to the reaction described above. The work-up of the reaction mixture gave $\{\pi\text{-}C_5H_5Ni[CNC(CH_3)_3]_2\}BPh_4$.

Reaction of $[\pi\text{-}C_5H_5Ni(PPh_3)(CNC_6H_{11})]I$ *with phenylmagnesium bromide*

To a slurry of $[\pi\text{-}C_5H_5Ni(PPh_3)(CNC_6H_{11})]I$ (1.5 g, 2.6 mmoles) in 10 ml of benzene were added 3.75 mmoles of phenylmagnesium bromide in ether with ice cooling. After stirring for 80 min at room temperature, aqueous ammonium chloride was added and the greenish-brown-colored organic layer was dried with sodium sulfate. The reaction mixture was evaporated to about 5 ml under reduced pressure and chromatographed on alumina with benzene as eluant. Two bands (red brown and yellow green) were observed and collected. The product from these bands were identified as π-cyclopentadienyl(cyclohexyl isocyanide)[phenyl(cyclohexylimino)-methyl]nickel [0.5 g, m.p. 113–114° (decompn.)] and (triphenylphosphine)-π-cyclopentadienylphenylnickel [0.39 g, m.p. 136–138° (decompn.)] in the order of their elution.

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