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Reactions of Cyclopentadienylnickel(II) Complexes

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The compounds π-$C_5H_5NiPPh_3X$ (X = $SnMe_3$, $GePh_3$, $SnPh_3$, $PbPh_3$, CN, NCS, NCO, NO_2 and CH_2CMe_3) and $(\pi$-$C_5H_5)_2NiFe(CO)_2PPh_3 . C_6H_6$ have been prepared and characterized. The metal-metal bond of π-$C_5H_5NiPPh_3SnPh_3$ is readily cleaved by iodine to give π-$C_5H_5NiPPh_3I$ and Ph_3SnI, while the germanium and lead analogues rearrange in solution to give π-$C_5H_5NiPPh_3Ph$ and, apparently diphenylgermanium and lead.

The compound π-$C_5H_5NiPPh_3Cl$ disproportionates reversibly in aqueous acetone to give the cation, $[\pi$-$C_5H_5Ni(PPh_3)_2]^+$, and, a paramagnetic nickel species, probably $[\pi$-$C_5H_5Ni(solvent)_n]^+$ (n = 2 or 3). The reversible nature of this reaction permits the ready substitution of the chloride by various pseudohalides.

Introduction

We have recently discussed the thermal stabilities,[1] ^{31}P chemical shifts[2] and preferred conformations[3] of the series of nickel alkyl compounds, π-$C_5H_5NiPPh_3R$, prepared by substituting the chloride of π-$C_5H_5NiPPh_3Cl$ by various carbanions. In the course of this work, it became necessary to extend the series somewhat, and it seemed of interest to prepare compounds containing the other group IVa elements as well as new pseudo-halide complexes. This paper describes the preparation and properties of the new organonickel compounds π-$C_5H_5NiPPh_3R$ (R = CH_2CMe_3, $CHPhSiMe_3$), the bimetallic compounds π-$C_5H_5NiPPh_3MR_3$ (MR_3 = $SnMe_3$, $GePh_3$, $SnPh_3$, $PbPh_3$) and $(\pi$-$C_5H_5)_2NiFe(CO)_2PPh_3 . C_6H_6$, as well as the pseudohalide compounds π-$C_5H_5NiPPh_3X$ (X = CN, NCS, NCO, NO_2).

Experimental Section

Preparation of the complexes π-$C_5H_5NiPPh_3MR_3$ (MR_3 = $SnMe_3$, $GePh_3$, $SnPh_3$, $PbPh_3$). A filtered solution of the appropriate lithium salt, $LiMR_3$[4] (0.03 mole) was added over a period of one hour under nitrogen to a stirred solution of π-$C_5H_5NiPPh_3Cl$[5] (0.04 mole) in THF (200 ml) cooled to −70° in a dry ice-acetone bath. During the addition the colour changed from dark red to green or brown, and after two hours methyl alcohol (5.0 ml) was added to the reaction mixture in order to destroy any unreacted lithium salt. The solvent was removed under reduced pressure at room temperature and the residue was extracted with benzene (75 ml). Chromatography of the extract on an oxygen-free activated alumina column using benzene-hexane (1:1) as eluant yielded a dark green or green brown fraction, which was collected and concentrated under reduced pressure. n-Hexane (40 ml) was added and the solution was cooled over-night. The crystals which formed (20-40% yields) were filtered off, recrystallized from carbon disulphide-hexane and dried for several hours at room temperature and 1 mm pressure.

The analyses and physical properties are summarized in Table I.

An attempted preparation of the complex π-$C_5H_5NiPPh_3SiPh_3$ resulted in brown pyrophoric crystals.

Reaction of π-$C_5H_5NiPPh_3SnPh_3$ with iodine. π-$C_5H_5NiPPh_3SnPh_3$ (1.23 g, 1.7 mmole) was dissolved in dry THF (30 ml) in an atmosphere of nitrogen and was cooled to −70°C in a dry ice-acetone bath. Iodine (0.42 g, 1.7 mmole) in dry THF (40 ml) was added dropwise over a period of thirty minutes, during which time the colour of the solution changed from dark green to red. The solution was stirred for a further thirty minutes, was extracted twice with diethyl ether (30 ml) and the combined extracts were cooled overnight. The red crystals which formed were filtered off, washed with cold diethyl ether and recrystallized from cyclohexane, and were identified by melting point and analysis as π-$C_5H_5NiPPh_3I$ (m. p. 139-140°, lit.[6] 140-141°). The yield was 0.4 g (65%). Analytical data are listed in Table I.

The solvent was removed from the original filtrate under reduced pressure and the residue was recrystallized from heptane using activated charcoal as decolouriser. The white crystals that were obtained were dried under vacuum and identified as triphenyltin iodide by mixed melting point (119°C) with an authentic sample.

Yield = 0.40 g = 65% Theoretical.

Pyrolysis of π-$C_5H_5NiPPh_3PbPh_3$. π-$C_5H_5NiPPh_3$-

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Table I. Analyses and Physical Properties of the Compounds π-$C_5H_5NiPPh_3R$ (MR_3, X).

R, MR_3 or X	Colour	M.P. (°C)	Calculated %C	Calculated H%	Found %C	Found H%
$SnMe_3$	Red-brown	—	56.17	6.35	55.57	5.16
$GePh_3$	Green-brown	*	71.37	5.11	68.88	4.93
$SnPh_3$	Green	163°	66.90	4.79	66.63	5.50
$PbPh_3$	Green	*	59.72	4.38	59.47	4.35
CN	Green	167°	69.95	4.89	69.95	4.87
NCS	Red-brown	140°	64.89	4.54	64.94	4.43
NCO	Red-brown	135°	67.33	4.71	67.27	4.67
NO_2	Gold	147°	63.93	4.66	64.31	5.06
I	Red	139-140°	53.85	3.93	53.46	3.83
CH_2CMe_3	Green	126°	73.55	6.83	73.32	7.72
Ph	Green	138°	75.20	5.44	74.71	5.05

* These compounds rearrange in the solid state. See discussion.

$PbPh_3$ (1.5 g, 1.8 mmole) was refluxed in cyclohexane (100 ml) for two hours under nitrogen, during which time the colour remained green and a dark metallic precipitate formed. The precipitate was filtered off, washed with cyclohexane and identified as lead metal (0.35 g, 93%).

The filtrate was concentrated under reduced pressure to approximately 30 ml and was cooled overnight. The dark green crystals which formed were filtered off, washed with hexane and recrystallized from cyclohexane. The solvent was removed from the filtrate under reduced pressure and the residue was extracted with acetone (25 ml). The addition of water to the extract yielded whitish crystals which were purified by sublimation (0.1 mm, 56°C) and identified by their melting point (69-70°) and their mass spectrum as biphenyl (yield 0.12 g, 43%).

The green crystals were identified by melting point (138°(lit.[6] 139°) and analysis (Table I) as π-$C_5H_5NiPPh_3Ph$ (yield 0.41 g, 49%).

A similar rearrangement was found to occur on heating the triphenylgermyl complex, but not the triphenyltin complex (in toluene at 115°C).

Preparation of π-$C_5H_5Ni(CO)Fe(CO)(PPh_3)$(π-$C_5H_5$). A solution of sodium cyclopentadienylirondicarbonylate, prepared from [π-$C_5H_5Fe(CO)_2]_2$ (5.0 g, 14 mmole) and sodium amalgam in dry THF, was added dropwise under nitrogen to a stirred solution of π-$C_5H_5NiPPh_3Cl$ (14.0 g, 30 mmole) in THF (250 ml) cooled to –70°C in a dry ice-acetone bath. After two hours the mixture was treated with methanol (5 ml) and worked up as above. Chromatography resulted in a dark brown fraction which yielded dark brown air-sensitive crystals. These were recrystallized from benzene-hexane and dried under vacuum at room temperature to give 10.4 g of product, m.p. 146-147 °C.

Calculated for $(C_5H_5)_2NiFe(CO)_2PPh_3$-$C_6H_6$: C, 67.67%; H, 4.87%. Found: C, 68.70%; H, 4.84%.

Preparation of the Complexes π-$C_5H_5NiPPh_3X$, *where X = CN, OCN, SCN,* NO_2. π-$C_5H_5NiPPh_3Cl$ (2.0 g, 4.8 mmole) was dissolved in hot methanol (60 ml) and a large excess of potassium cyanide (4.0 g, 0.06 mole) was added. The mixture was stirred for ten minutes, during which time the colour changed from red to green. The green solution was allowed to cool and was filtered. Benzene (60 ml) was added to the filtrate and the solution was again filtered. The solvent was removed from the filtrate under reduced pressure at room temperature and the residue was extracted with hot benzene (2×50 ml). Concentration of the extract and addition of n-hexane (60 ml) resulted in the formation of green crystals (71% yield), which were filtered off, recrystallized from benzene-hexane and dried at 56°C at 1 mm pressure.

The isothiocyanato, isocyanato and nitrito complexes were prepared in 50-70% yields in a similar fashion using the appropriate potassium salt. The analyses and physical properties are shown in Table I, and the infrared-active modes of the coordinated anions, X, are listed in Table II.

Table II. Infrared data on the compounds π-$C_5H_5NiPPh_3X$.

X	Bands attributable to X (cm^{-1})	
CN	2110 $\nu(CN)$	($CHCl_3$)
NCO	2240 $\nu_{as}(NCO)$	($CHCl_3$)
	1332 $\nu_s(NCO)$	(Hexachlorobutadiene mull)
	582 $\delta(NCO)$	(Nujol mull)
NCS	2108 $\nu(CN)$	($CHCl_3$)
NO_2	1375 $\nu_{as}(NO_2)$	(Hexachlorobutadiene mull)
	1320 $\nu_s(NO_2)$	(Hexachlorobutadiene mull)
	833 $\delta(ONO)$	(Nujol mull)
	539 $\rho_w(NO_2)$	(Nujol mull)

Preparation of the Complexes π-$C_5H_5NiPPh_3R$, *R* = CH_2Ph, $CH_2C(CH_3)_3$, $CH_2Si(CH_3)_3$ *and* $CH(Ph)Si(CH_3)_3$. The method of preparation was similar to that described by us for similar nickel-alkyl complexes.[1] The preparation of the silicon-containing compounds[3] and the benzyl compound[5] has been mentioned previously, but physical properties such as their n.m.r. spectra have not been described. Yields of these compounds were 35-70%. Analytical data are shown in Table I.

Physical Measurements. Infrared spectra were run on a Beckman IR10, n.m.r. spectra on a Bruker HX 60 spectrometer. The n.m.r. spectra are listed in Table III. Melting points were obtained on samples scaled in capillaries under nitrogen. Chemical analyses were done by Schwarzkopf Microanalytical La-

Table III. N.m.r. spectra of the complexes.

X, R, MR_3	$\tau(C_5H_5)$*	(Solvent)	$\tau(PPh_3, MPh_3)$*	Other resonances*
$SnMe_3$	5.22 (s)	(CS_2)	2.88 (m)	τ10.36 ($SnMe_3$)
$GePh_3$	5.22 (s)	(CS_2)	2.88 (m)	
$SnPh_3$	5.05 (s)	(CS_2)	2.88 (m)	
$PbPh_3$	5.00 (s)	(CS_2)	2.88 (m)	
CN	4.78 (s)	($CDCl_3$)	2.45 (m)	
NCS	4.85 (s)	($CDCl_3$)	2.42 (m)	
NCO	4.88 (s)	($CDCl_3$)	2.42 (m)	
NO_2	4.78 (s)	($CDCl_3$)	2.42 (m)	
CH_2CMe_3	5.03 (s)	(CS_2)	2.58 (m)	~τ9.46 (m) CH_2, CH_3
CH_2SiMe_3	5.04 (s)	(CS_2)	2.58 (m)	τ11.31 (d, J = 9.8 Hz) CH_2 τ10.19 (s) CH_3
$CHPhSiMe_3$	5.11 (s)	(CS_2)	2.76 (m)	τ10.22 (s) CH_3 τ9.51 (d, J = 16.8 Hz) CH τ3.46 (m) Ph
CH_2Ph	5.42 (s)	(CS_2)	2.74 (m)	τ8.65 (d, J = 8.8 Hz) CH_2 τ3.47 (m) Ph

* s = singlet, d = doublet, m = multiplet.

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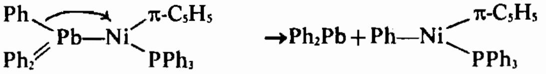
Results and Discussion

Although a variety of compounds containing transition metals bonded to the group IVa metals has been reported,[7] complexes of nickel were, until 1967, conspicuous for their absence. Recently compounds of π-C_5H_5NiL- (L = neutral ligand) with the groups $SiCl_3$,[8,9] $GeCl_3$,[9] $SnCl_3$,[10] and $GeEt_3$[11] have been characterized, but their chemistry has been little studied.

The triphenylgermanium, -tin and -lead complexes reported here are similar to the analogous alkyl complexes,[1] decomposing rapidly in soluton but to a lesser degree in the solid state in air. The reaction of the triphenyltin complex with electrophilic reagents such as the halogens and hydrogen chloride resulted in cleavage of the metal-metal bond in the case of iodine to give π-$C_5H_5NiPPh_3I$ and Ph_3SnI, and complete decomposition with other halogens and hydrogen chloride. The nickel-tin bond in the complex would therefore appear to be considerably more reactive than the metal-tin bonds in the complexes $Ph_3SnMn(CO)_5$[12] and π-$C_5H_5Fe(CO)_2SnPh_3$.[12] Chlorine and bromine cleave the tin-carbon bonds of the former to yield $X_3SnMn(CO)_5$ (X = Cl, Br), and while the iron-tin bond of the latter is cleaved by chlorine, it is inert to hydrogen chloride.

Thermal decomposition of the triphenyllead complex resulted in a rearrangement to give π-C_5H_5Ni-PPh_3Ph, lead metal and biphenyl, possibly by a mechanism resembling the well known, 1,2 shifts in organic chemistry.[13] Thus the reaction may proceed by migration of the phenyl group from the lead to the nickel, followed by breaking of the nickel-lead bond to yield diphenyllead.



Attempts to trap the extremely reactive diphenyllead by using cyclo-hexene as solvent in a similar fashion to that described for carbenes[14] failed to yield the expected product. This result does not necessarily rule out the proposed mechanism, since diphenyllead is known to disproportionate to form tetraphenyllead and lead metal,[15] and tetraphenyllead is known to decompose in the presence of nickel catalysts[16] to yield biphenyl and lead metal.

Thermal decomposition of π-$C_5H_5NiPPh_3GePh_3$ to the phenyl complex also readily occurs, and the germanium compound could not be satisfactorily purified. The triphenyltin compound, in contrast, is quite stable in cyclohexene both to refluxing and to ultraviolet irradiation. Rearrangements similar to those discussed here have been reported previously for the complexes $PtCl(MPh_3)(PPh_3)_2$ (M = Sn, Pb).[17]

The attempted preparation of the metal-metal bonded complex π-$C_5H_5PPh_3NiFe(CO)_2$(π-C_5H_5) by a similar method to that described for the group IVa metal-metal bonded complexes, resulted in a brown crystalline product which analyzed as a benzene solvate and whose infrared spectrum showed two carbonyl stretching bands at 1763 cm^{-1} (s) and 1813 cm^{-1} (2), in the region usually attributed to bridging carbonyls.[18]

The n.m.r. spectrum contained a broad band of approximate intensity twenty at τ 2.5, attributable to phenyl protons, and a singlet at τ 5.14 and a doublet at τ 5.72 (J = 1.4 Hz), each of relative intensity five, which may be attributed to the two cyclopentadienyl groups. Since coupling of the cyclopentadienyl protons to the phosphorus

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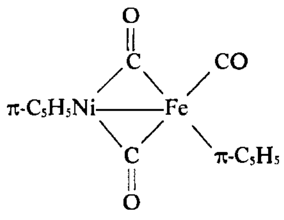
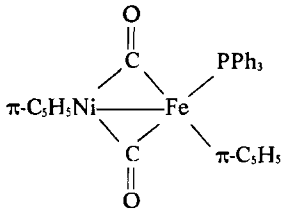
has been noted for complexes of the type $[\pi\text{-}C_5H_5Fe(CO)_2PPh_3]X$,[19] but not for any of the cyclopentadienyltriphenylphosphinenickel complexes prepared by us, it would therefore appear that the product has the triphenylphosphine directly bonded to the iron rather than the nickel. Tilney-Bassett[20] has reported the preparation of the tricarbonylcyclopentadienyliron-cyclopentadienylnickel complex, I.



I

This complex exhibited two bridging carbonyl absorptions in the infrared at 1806 cm^{-1} (s) and 1836 cm^{-1} (w). It would therefore appear that the triphenylphosphine derivative has a similar structure to the above complex (II).



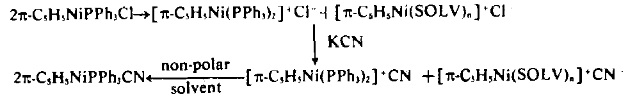
II

The calculated carbon and hydrogen content for a complex having the above structure was found to be lower than the analysis values for the products, but since the n.m.r. integration showed a higher phenyl content than expected, it seems likely that one molecule of benzene is present as a solvate. Taking this into account, the calculated carbon and hydrogen content show good agreement with the analysis values.

Cyclopentadienyltriphenylphosphinenickel chloride has been known to ionize with rearrangement in polar solvents to yield the diamagnetic cation, $[\pi\text{-}C_5H_5Ni(PPh_3)_2]^+$, which has been isolated as the tetraphenylborate[21] and trichlorostannate[10,22] salts. We have found that addition of water to a solution of $\pi\text{-}C_5H_5NiPPh_3Cl$ in acetone causes a reversible change in colour from red to yellow, and that addition of an aqueous solution of potassium hexafluorophosphate to the yellow solution result in precipitation of up to fifty per cent of the nickel present as $[\pi\text{-}C_5H_5Ni(PPh_3)_2]PF_6$. Although we were unable to isolate a second nickel complex, the reversibility of the colour changes suggests that the cyclopentadienyl group remained bonded to the metal ion, which presumably exists in solution as a solvated complex, i.e. $[\pi\text{-}C_5H_5Ni(H_2O)_n]^+$ ($n = 2, 3$).

Magnetic susceptibility measurements using the Evans[23] method showed that the second species is paramagnetic, with a magnetic moment of approximatel 2.3 B.M. This is somewhat less than the expected value for two unpaired electrons expected for complexes of nickel(II), possibly because of incomplete ionization of the $\pi\text{-}C_5H_5NiPPh_3Cl$. However, it seems clear that species in solution is a paramagnetic complex of the type suggested above.

The lability of the complex $\pi\text{-}C_5H_5NiPPh_3Cl$ and the reversibility of the substitution of the chloride by other ligands suggested that displacement of the chloride by other anions might occur in polar solvents, for instance by the addition of potassium cyanide or other appropriate potassium salt to a hot ethanolic solution of $\pi\text{-}C_5H_5NiPPh_3Cl$.



$$2\pi\text{-}C_5H_5NiPPh_3Cl \rightarrow [\pi\text{-}C_5H_5Ni(PPh_3)_2]^+Cl^- + [\pi\text{-}C_5H_5Ni(SOLV)_n]^+Cl^-$$
$$\Big\downarrow \text{KCN}$$
$$2\pi\text{-}C_5H_5NiPPh_3CN \xleftarrow[\text{solvent}]{\text{non-polar}} [\pi\text{-}C_5H_5Ni(PPh_3)_2]^+CN^- + [\pi\text{-}C_5H_5Ni(SOLV)_n]^+CN^-$$

Since potassium cyanide is much more soluble in ethanol than potassium chloride, the potassium chloride precipitated and could be filtered off. The addition of a non-polar solvent had the effect of shifting the equilibrium towards the non-ionized species, resulting in the formation of the substituted complexes. The n.m.r. and infrared spectra and the analyses were consistent with covalent complexes of the type $\pi\text{-}C_5H_5NiPPh_3X$. A recent publication by Sato *et al.*[24] has reported the preparation of a similar complex, $\pi\text{-}C_5H_5NiPBu_3CN$, from the reaction of sodium cyanide and $[\pi\text{-}C_5H_5Ni(PBu_3)_2]Cl$.

In order to determine whether the thiocyanate anion was bonded to the nickel through the sulphur or nitrogen atom, a calculation of the extinction coefficient of the band at 2108 cm^{-1} was carried out. The molar extinction co-efficient was found to be 1190 cm^{-1} $mole^{-1}$, in the region expected for N-bonded complexes,[25] and is therefore consistent with the general belief[26] that most first row transition metals form isothiocyanate complexes.

Considerable interest has been focused in recent years on the stability of metal alkyl complexes. It is generally believed the decomposition of such complexes proceeds by either homolytic cleavage of the metal carbon bond or by a low energy β-elimination mechanism,[27] and that by blocking the latter route by using alkyl ligands which contain no β-hydrogens, the stability of the complexes will be enhanced.[28,29]

We have recently[1] reported on the relative stabilities of the series of nickel alkyl compounds $\pi\text{-}C_5H_5NiPPh_3R$; those which contained no β-hydrogens were indeed unusually stable. In this paper, we report some of the physical properties of four additio-

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nal compounds in this series which do not contain β-hydrogen atoms. Although data on quantitative stability studies will be deferred to a later publication, we note that the neopentyl, trimethylsilyl-methyl and benzyl compounds all have decomposition points (126°, 130-131°,[3] 129-131°,[6] respectively) which are comparable with that of the methyl complex,[1] and significantly greater than those of the ethyl, n-propyl,[1] et cetera.

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