ARYL- AND ACETYLENE-NICKEL(I) COMPLEXES

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Summary

Reduction of various pentafluorophenylnickel(II) complexes in the presence of phosphines gives unstable nickel(I) compounds but $Ni(C_6F_5)(CO)_2(PPh_3)_2$ is isolated in the presence of CO. Similar $NiR(CO)_2(PPh_3)_2$ ($R = C_6F_5$, C_6Cl_5, 2,3,5,6-C_6Cl_4H) are obtained by reaction of the halogenonickel(I) complex with MgRBr or LiR. Reduction of NiX_2L_2 in the presence of acetylenes gives $[NiXL_2]_2(\mu\text{-}PhC{\equiv}CR)$ ($R = H$, $X = Cl$ and $R = Ph$, $X = Cl$, Br) when $L = P\text{-}n\text{-}Bu_3$ but only $NiX(PPh_3)_3$ are recovered when $L = PPh_3$. No reaction with the alkyne is observed for $[NiX(PPh_3)_2]_n$ but $[NiCl(PPh_3)]_n$ reacts with $RC{\equiv}CR'$ to give paramagnetic $NiCl(PPh_3)(CR{\equiv}CR')$ ($R = Ph$, $R' = H$, COOEt), diamagnetic $[NiCl(PPh_3)]_2(\mu\text{-}PhC{\equiv}CPh)$ and cyclotrimerization when $R = R' = COOMe$. Chemical and structural behaviour of the new nickel(I) complexes is described.

Introduction

Organonickel(I) complexes have been frequently invoked as intermediates in many different catalytic processes and reaction sequences [1] but few have been isolated. Arylnickel(I) derivatives have been detected in electrochemical studies [2]. Acetylene nickel(I) complexes are extensively known for η^5-cyclopentadienyl derivatives [3,4], but no halide complexes are known.
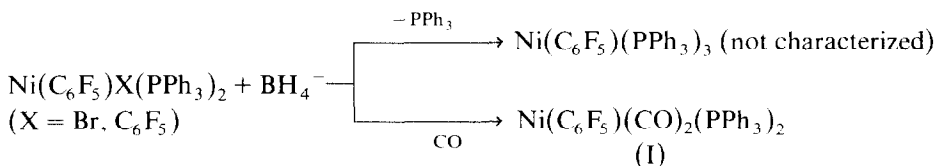
We report below the results of a study of the reduction of various nickel(II) complexes and of the reactions of halogenonickel(I) derivatives with either arylating agents or alkynes.

Results and discussion

Two methods of making the aryl and acetylene nickel(I) complexes were tried, namely (a) reduction of halo-organo nickel(II) derivatives and (b) the reaction of halogenonickel(I) compounds with arylating agents and alkynes.

Reduction of nickel(II) complexes

Aryl compounds. Reduction of an ethanolic suspension of $Ni(C_6F_5)Br(PPh_3)_2$ with $NaBH_4$ in the presence of PPh_3 gives a brown suspension which after filtration yields a crystalline compound, presumably $Ni(C_6F_5)(PPh_3)_3$, which is highly reactive, and decomposes even in the solid state under N_2. Washing and manipulation of the sample always results in a change of colour and any attempts at purification results in formation of disproportionation products, from which $Ni(C_6F_5)_2(PPh_3)_2$ is readily separated. Similar reactions with other alkylphosphines or arsines give compounds which are even less stable since they are more soluble.

$$Ni(C_6F_5)X(PPh_3)_2 + BH_4^- \begin{cases} \xrightarrow{-PPh_3} Ni(C_6F_5)(PPh_3)_3 \text{ (not characterized)} \\ \xrightarrow{CO} Ni(C_6F_5)(CO)_2(PPh_3)_2 \end{cases}$$
$$(X = Br, C_6F_5) \qquad\qquad\qquad\qquad\qquad\qquad (I)$$

When the same reduction is carried out under CO a suspension of a crystalline pale yellow solid is obtained. When the solid is filtered off, repeatedly washed with ethanol, and dried under vacuum it can be identified as $Ni(C_6F_5)(CO)_2(PPh_3)_2$ (I), (see analytical data in Table 1). Complex I is also isolated by a similar procedure following reduction with $NaBH_4$ of a suspension of $Ni(C_6F_5)_2(PPh_3)_2$ under CO. Reactions with other phosphine nickel(II) complexes give more soluble products, which disproportionate readily, preventing isolation of the nickel(I) derivatives.

Acetylene complexes. Reduction of THF solutions of NiX_2 $(P-n-Bu_3)_2$ with Na/Hg 10% in the presence of 0.5 mol of $PhC\equiv CR$ (R = H, Ph) gives red solutions which after filtration and evaporation of the solvent yield oils. These crystallize when kept at $-60°C$ to give red crystals, identified as $[NiX(P-n-Bu_3)_2]_2(\mu-PhC\equiv CR)$ (R = H, X = Cl (V); R = Ph, X = Cl (VI), Br (VII)). (The analytical data are shown in Table 1.)

$$NiX_2(P-n-Bu_3)_2 + Na/Hg + 0.5 \ PhC\equiv CR \rightarrow [NiX(P-n-Bu_3)_2]_2(\mu-PhC\equiv CR)$$
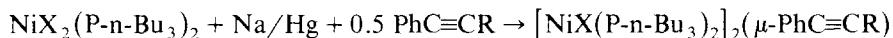
The same compounds are also obtained if the alkyne is added to the previously reduced brown solution, but because of the low stability of the resulting nickel(I) complex it is advisable to have the alkyne present initially.

Complexes V–VII are liquids at room temperature and are stable under nitrogen. They are fairly stable in solution and can be recrystallized, but cannot be purified by chromatography as they decompose slowly.

When the reduction is carried out with $NiX_2(PPh_3)_2$ brown-yellow solutions are obtained, from which only $NiX(PPh_3)_3$ can be recovered. Probably steric and electronic effects prevent the coordination of the alkyne when PPh_3 is the ligand. In this case, reduction with an excess of Na/Hg provides the Ni^0 derivative $Ni(PPh_3)_2(PhC\equiv CPh)$, previously isolated by a different method [5].

Complexes V–VII are diamagnetic at room temperature. The IR spectra show the characteristic absorptions for $P-n-Bu_3$, and a $\nu(C\equiv C)$ band at 1740 (R = H) and 1790 cm^{-1} (R = Ph) typical of a coordinated acetylene. These frequencies are lower by 370 and 430 cm^{-1}, respectively, relative to those for the free alkyne (2223 cm^{-1} (Raman) for $PhC\equiv CPh$).

The ^1H NMR spectra show typical resonances due to $P-n-Bu_3$ at δ 1.72 and 1.08 ppm, and to the phenyl groups as multiplets between 7.19 and 7.55 ppm. Recording

of ^{13}C NMR spectra is prevented by the instability in solution over long periods.

The results are consistent with a formulation of the complexes as dimeric species containing a nickel-nickel bond and with the acetylene bridging the two metal atoms:
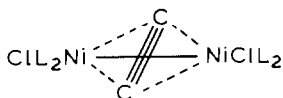
Reactions with halonickel(I) complexes

Aryl compounds Another way of making the aryl compounds involves the alkylation of NiCl(CO)$_2$(PPh$_3$)$_2$ [6]. Addition of a THF solution of Mg(C$_6$F$_5$)Br to a hexane suspension of NiCl(CO)$_2$(PPh$_3$)$_2$ gives a solid, which can be recrystallized from chloroform ethanol and identified as complex I. Organolithium reagents are better alkylating agents, since they react at lower temperatures and permit introduction of various organic substituents. Thus reactions of NiCl(CO)$_2$(PPh$_3$)$_2$ with THF solutions of LiR (R = C$_6$F$_5$, C$_6$Cl$_5$, 2,3,5,6-HC$_6$Cl$_4$) give the corresponding nickel(I) complexes I–III.

All these compounds are stable as solids under N$_2$, but are oxidized in air and also rapidly in solution. Hexane suspensions of I are stable under UV irradiation at $-70°$C, but disproportionate at room temperature to give crystalline Ni(C$_6$F$_5$)$_2$(PPh$_3$)$_2$ and a solution from which Ni(CO)$_2$(PPh$_3$)$_2$ can be obtained.

Complex I is readily oxidized. Addition of a benzene solution of Tl(C$_6$F$_5$)$_2$Br leads to evolution of CO and precipitation of TlBr, giving a solution from which Ni(C$_6$F$_5$)$_2$(PPh$_3$)$_2$ can be isolated. Similarly addition of I to a CCl$_4$ solution of chlorine displaces CO, and NiCl(C$_6$F$_5$)(PPh$_3$)$_2$ can be crystallized from the resulting solution.

Reaction of complex I with a CH$_2$Cl$_2$ solution of AgBF$_4$ gives metallic silver and a solution which shows an IR absorption at 2090 cm^{-1}, probably due to the ν(CO) stretching vibration of the resulting cationic Ni(C$_6$F$_5$)CO(PPh$_3$)$_2{}^+$ complex. This compound cannot be isolated because the solution gives off CO even at low temperature. Addition of ligands gives cationic Ni(C$_6$F$_5$)L$_3{}^+$ complexes of the type previously described [7].

The study of substitution reactions of complex I is limited by its ready decomposition in solution, but the following observations are relevant.

The CO ligands are not displaced by PPh$_3$ and the starting complex remains unaltered, whereas P(OMe)$_3$ undergoes both substitution and disproportionation to give crystals of Ni(C$_6$F$_5$)$_2$[P(OMe$_3$)]$_2$ (IV), as indicated by the analysis shown in Table 1. This complex is similar to those previously reported [8].

Bubbling CO through solutions of I produces a new IR absorption at 2065 cm^{-1}, probably due to the presence of a tricarbonylnickel complex, which cannot be isolated.

The nickel(I) complexes are paramagnetic at room temperature with μ_{eff} between 1.87 and 1.92 BM as expected for mononuclear Ni^I (d^9) derivatives. The observed molecular weight of complex I in benzene is 816 (Theor. 807).

The IR spectra show the characteristic absorptions for PPh$_3$ and the organic substituent at 1490, 1045 and 955 cm^{-1} for C$_6$F$_5$ [9], 1325, 1285 cm^{-1} for C$_6$Cl$_5$ and 1340, 1290 cm^{-1} for 2,3,5,6-HC$_6$Cl$_4$ [10]. The three complexes show two absorption

TABLE 1

COLOURS AND ANALYTICAL DATA FOR NICKEL(I) COMPLEXES

Complex	Colour	Analyses (Found (calcd.) (%))	
		C	H
$Ni(C_6F_5)(CO)_2(PPh_3)_2$ (I)	Pale yellow	65.31 (65.50)	4.49 (3.72)
$Ni(C_6Cl_5)(CO)_2(PPh_3)_2$ (II)	orange	58.39 (59.41)	3.93 (3.37)
$Ni(C_6Cl_4H)(CO)_2(PPh_3)_2$ (III)	orange	60.68 (61.80)	3.68 (3.63)
$Ni(C_6F_5)_2[P(OMe)_3]_2$ (IV)	red	32.35 (33.81)	2.41 (2.80)
$[NiCl(P-n-Bu_3)_2]_2(\mu\text{-}PhC{\equiv}CH)$ (V)	red	58.87 (61.15)	10.60 (10.43)
$[NiCl(P-n-Bu_3)_2]_2(\mu\text{-}PhC{\equiv}CPh)$ (VI)	red	62.55 (63.30)	9.95 (10.03)
$[NiBr(P-n-Bu_3)_2]_2(\mu\text{-}PhC{\equiv}CPh)$ (VII)	red	57.56 (58.87)	10.02 (9.32)
$NiCl(PPh_3)(PhC{\equiv}CH)$ (VIII)	brown	68.05 (68.12)	4.23 (4.61)
$NiCl(PPh_3)(PhC{\equiv}CCOOEt)$ (IX)	brown-green	62.98 (65.62)	5.01 (4.74)
$[NiCl(PPh_3)]_2(\mu\text{-}PhC{\equiv}CPh)$ (X)	brown-black	68.33 (67.43)	4.86 (4.52)

bands due to $\nu(CO)$ stretching vibrations at 1990–2000 and 1930–1940 cm^{-1}. The ratio of the intensities of the antisymmetric and symmetric $\nu(CO)$ frequencies, I(as)/I(s) points to CO–Ni–CO bond angles between 103 and 107° [11]. From the available data (NMR studies being prevented by the paramagnetic character) the only structure that can be ruled out is that with both CO occupying axial positions in a trigonal bypiramid.

Acetylene complexes. We know that dimeric or polymeric $[NiX(PPh_3)_2]_n$ and

TABLE 2

MAGNETIC AND IR DATA (cm^{-1}) FOR NICKEL(I) COMPLEXES

Complex	$\mu_{eff.}$ (BM) (300 K)	$\nu(CO)$	Angle CO–M–CO (°)	$\nu(C{\equiv}C)$
I	1.87	1997, 1937	107	–
II	1.91	2000, 1940	103	–
III	1.92	1998, 1938	105	–
V	a	–	–	1740
VI	a	–	–	1790
VII	a	–	–	1790
VIII	1.68	–	–	–
IX	1.84	–	–	–
XI	a	–	–	1630

a Diamagnetic.

[NiX(PPh$_3$)]$_n$ compounds react with CO to give the corresponding mononuclear carbonyl derivatives NiX(CO)$_2$(PPh$_3$)$_2$ [12] and it seems reasonable that a similar cleavage could be brought about by acetylenes. However, we find that [NiX(PPh$_3$)$_2$]$_n$ derivatives do not react with alkynes, NiX(PPh$_3$)$_3$ being recovered in all the experiments. This behaviour is consistent with that observed before in reduction of NiX$_2$(PPh$_3$)$_2$, in which no coordination of the alkynes occurs. Such coordination does take place with the more reactive [NiX(PPh$_3$)]$_n$ species, as shown below.

When toluene solutions of [NiX(PPh$_3$)]$_n$ are treated at $-20°C$ with RC≡CR′ (R = R′ = Ph, COOCH$_3$ and R = Ph, R′ = H, COOEt) dark brown solutions are obtained. These behave differently, depending on the alkyne.

When R = Ph, R′ = H the solution crystallizes upon evaporation of the solvent to give NiCl(PPh$_3$)(PhC≡CH) (VIII), as shown by analytical data in Table 1. The same compound is obtained even in the presence of a 2/1 Ni/acetylene molar ratio.

An analogous complex NiCl(PPh$_3$)(PhC≡CCOOEt) (IX) is formed when R′ = COOEt, but this compound is insoluble in benzene and precipitates out directly from the reaction solution. Pure samples of IX can be obtained by mixing two previously filtered solutions of both reagents at $-20°C$. The mixture becomes brown-green, and IX can be filtered off from the suspension.

When R = R′ = COOMe, the brown solution becomes red and evaporation of the solvent gives crystals of hexamethyl mellitate. No metal complex is isolated in this case.

The complexes VIII–IX are paramagnetic with μ_{eff} 1.68 and 1.84 BM, respectively, at room temperature (see Table 2).

The IR spectra show the characteristic bands for PPh$_3$, but there is no absorption due to the ν(C≡C) stretching vibration in the region between 1600 and 2000 cm^{-1}. Complex IX exhibits the typical absorptions of the COOEt group at 1715 cm^{-1} (ν(C=O)), unshifted with respect to the free ligand, and 1234 (ν(COC) antisymmetric) and 1120 cm^{-1} (ν(COC) symmetric) displaced to lower frequencies with respect to the free ligand.

These compounds are stable in the solid under nitrogen but decompose slowly in solution, which prevents recrystallization and NMR studies. Gas chromatography of the solutions after addition of HCl shows the presence of the free acetylene.

This behaviour is consistent with either a monomeric or dimeric structure, containing the alkyne as terminal group acting as a two or four electron donor, respectively.
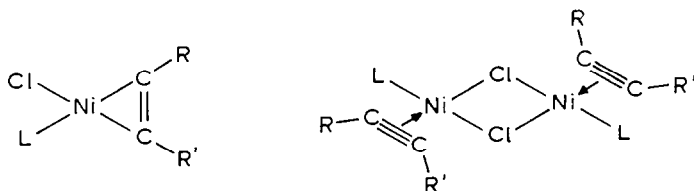
The absence of ν(C≡C) absorption bands suggest that the acetylene acts as a four electron donor, but no definite assignment can be made.

The reaction can be understood by assuming that chlorine bridges in the polymeric [NiCl(PPh$_3$)]$_n$ are cleaved by the alkyne, probably through intermediate formation of a dimer containing a bridging μ-acetylene group with a nickel–nickel bond. An excess of the alkyne would give the monomeric species, and further

coordination of the alkyne would account for the trimerization observed with dimethylacetylene dicarboxylate. Electronic and steric effects would account for the different behaviours observed for different alkynes.
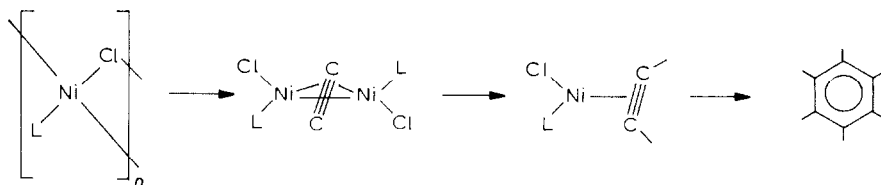
The reaction of $[NiCl(PPh_3)]_n$ with $PhC{\equiv}CPh$ gives black crystals of a diamagnetic complex analysing as the dimer $[NiCl(PPh_3)]_2(\mu\text{-}PhC{\equiv}CPh)$ (X), even in the presence of an excess of the acetylene, which remains unaltered. This complex is scarcely stable in air in the solid state and decomposes very slowly in solution, so that recrystallization is easy. The IR spectrum shows an absorption at 1630 cm^{-1} which must be assigned to the $\nu(C{\equiv}C)$ stretching vibration. The ^1H NMR spectrum shows a multiplet due to the Ph groups, but the solution is not stable for a sufficiently long period to permit recording of the ^{13}C NMR spectrum.

Further structural studies are being carried out on crystals of complex X.

Experimental

All experiments were performed under dry N_2 in Schlenk-type glassware. Solvents were previously distilled under N_2, dried by standard methods, and degassed before use. Halogeno and pentafluorophenyl Ni^{II} complexes were prepared as previously described [8,13,14] as were Ni^I complexes [6,15]. Acetylenes were obtained from Alfa, and used without further purification.

The C,H analyses carried out with a Perkin–Elmer 240 B microanalyzer and molecular weight measurements with a Knauer vapour pressure osmometer. Magnetic measurements were carried out by the Faraday method, with a Bruker magnet system at room temperature. Melting points were determined with a Reichert Thermopan microscope. IR spectra were recorded on a Perkin–Elmer 599 spectrophotometer between 4000–250 cm^{-1} using Nujol mulls or KBr pellets. NMR spectra were recorded on a Varian FT 80 A spectrometer. Gas chromatography was carried out with a Perkin–Elmer Sigma 3B chromatograph.

$Ni(C_6F_5)(CO)_2(PPh_3)_2$ (I)

This complex was made by the following methods.

(a) A suspension of 0.995 g (1.2 mmol) of $Ni(C_6F_5)Br(PPh_3)_2$ in 20 ml of ethanol was treated dropwise with a solution of 0.0227 g of $NaBH_4$ in 15 ml of ethanol as dry CO was bubbled through the solution at room pressure and temperature. The solid was filtered off, recrystallized from chloroform ethanol, and dried under vacuum. Yield 73%.

(b) $Ni(C_6F_5)_2(PPh_3)_2$ is reduced by the same method. Yield 90%.

(c) A suspension of 2.9 g (4.29 mmol) of $NiCl(CO)_2(PPh_3)_2$ in 20 ml of hexane was treated at $-20°C$ with 35 ml of THF containing 4.29 g of $Mg(C_6F_5)Br$. The mixture was stirred for 3 h as it was allowed to warm to room temperature. After filtration the yellow-red solution was evaporated to dryness, and the residue was recrystallized from chloroform ethanol. Yield 80%.

NiR(CO)₂(PPh₃)₂ (R = C₆Cl₅ (II), 2,3,5,6-C₆Cl₄H (III)

A suspension of 1.01 g (1.5 mmol) of $NiCl(CO)_2(PPh_3)_2$ in 15 ml of hexane was treated with 35 ml of THF containing 1.5 mmol of LiR at −78°C. The mixture was stirred for 5 h as it was allowed to warm slowly to room temperature. After filtration, the solution was evaporated to dryness, and the residue recrystallized from chloroform ethanol. Yields 65–80%.

Oxidation of complex I

Tl(C₆F₅)₂Br. 1.00 g (1.2 mmol) of I was added to a suspension of 0.37 g (0.6 mmol) of $Tl(C_6F_5)_2Br$ in 60 ml of benzene. After 2 h stirring the white precipitate of TlBr was filtered off, the solution evaporated to dryness, and the residue was recrystallized from chloroform/ethanol and shown to be $Ni(C_6F_5)_2(PPh_3)_2$. Yield 90%.

Cl₂. A solution of chlorine (excess) in CCl_4 was added to a solution of 1.00 g (1.2 mmol) of I in 25 ml of chloroform and the mixture was stirred for 0.5 h. After filtration and evaporation to dryness, yellow crystals of $Ni(C_6F_5)Cl(PPh_3)_2$ were obtained by recrystallization of the residue from chloroform/ethanol. Yield 80%.

AgBF₄. 20 ml of CH_2Cl_2 were added to a solid mixture of 0.635 g (0.79 mmol) of $Ni(C_6F_5)(CO)_2(PPh_3)_2$ and 0.135 g (0.79 mmol) of $AgBF_4$. Then mixture was stirred for 1 h then filtered. The orange filtrate gave the reported $Ni(C_6F_5)(PPh_3)_2L^+$ complexes [13] upon addition of L followed by the usual work up.

[NiX(P-n-Bu₃)₂]₂(μ-PhC≡CR) (V–VII)

A mixture of 1.89 mmol of $NiX_2(P-n-Bu_3)_2$ (X = Cl, Br), 0.94 mmol of PhC≡CR (R = H, Ph) and 2.17 mmol of Na/Hg 10% was treated with 20 ml of THF. After 3 h stirring the red solution was filtered and evaporated, to give a red oil, which was extracted with hexane. The extract was filtered then cooled to −60°C to give brown crystals of $[NiX(P-n-Bu_3)_2]_2(\mu$-PhC≡CR). Yield ca. 50%.

The same compounds were obtained when an excess of the alkyne was used. Similar reduction of $NiX_2(PPh_3)_2$ gave solutions from which $NiX(PPh_3)_3$ were crystallized.

When the reduction of $NiBr_2(PPh_3)_2$ was carried out with an excess of Na/Hg 10%, a yellow orange solution was obtained. This was filtered and evaporated to dryness and the residue was extracted with pentane, from which it was crystallized. It was identified as $Ni(PPh_3)_2(PhC≡CPh)$ [5]. Yield 60%.

NiCl(PPh₃)(PhC≡CH) (VIII)

A mixture of 0.671 g (1.88 mmol) of $[NiCl(PPh_3)]_n$ and 0.21 g (1.88 mmol) of PhC≡CH in 20 ml of toluene was kept at −20°C for 8 h. The solution was filtered and evaporated and hexane was added to give brown crystals of VIII. Yield 30%.

NiCl(PPh₃)(PhC≡CCOOEt) (IX)

A toluene solution (25 ml) of 0.376 g (1.055 mmol) of $[NiCl(PPh_3)]_n$ was added to a toluene (10 ml) solution of 0.17 g (1.055 mmol) of PhC≡CCOOEt at room temperature. After 10 min a brown-green solid appeared. The mixture was stirred for 6 h then the solid was filtered off, repeatedly washed with toluene and hexane, dried under vacuum, and identified as IX. Yield 60%.

[NiCl(PPh₃)]₂(PhC≡CPh) (X)

A toluene solution (30 ml) containing 1.067 g (3.00 mmol) of $[NiCl(PPh_3)]_n$ and

0.530 g (3.00 mmol) of PhC≡CPh was stirred for 5 h at −20°C. After filtration and concentration of the solvent, hexane was added and the solution was kept at −30°C for 12 h. The brown-black crystals of diamagnetic X were filtered off, and recrystallized from toluene/hexane. Yield 40%.

Reaction with MeOOCC≡COOMe

A toluene solution (40 ml) of 0.674 g (1.89 mmol) of [NiCl(PPh$_3$)]$_n$ and 0.23 ml (1.89 mmol) of acetylenedicarboxylic acid was stirred at 5°C for 6 h. The red solution was filtered, concentrated, and treated with 1 ml of hexane to give crystals of hexamethyl mellitate which were recrystallized from toluene/hexane. Yield 25%. Better yields were obtained by using an excess of the alkyne. The red mother liquors contained unidentified phosphine nickel derivatives.

Acknowledgement

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