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PREPARATION OF PHENYL(ACETYLACETONATO)NICKEL(II) COMPLEXES WITH TERTIARY PHOSPHINE LIGANDS AND THEIR REACTIONS WITH ORGANIC HALOGEN COMPOUNDS AND OLEFINS

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Summary

Treatment of Ni(acac)$_2$ (acac = acetylacetonato ligand) with AlPh$_3$·Et$_2$O in the presence of PR$_3$ gave PhNi(acac)(PR$_3$)$_n$ (n = 1; R = Ph(1), cyclo-C$_6$H$_{11}$(2), Et(3); n = 2; R = Et(4)). The pyrolysis of 1 in toluene gave one equivalent of biphenyl indicating that oxidative addition of PPh$_3$ to Ni involving the P-C bond cleavage took place. Reactions of 1 - 3 with organic halogen compounds (R'-X) afforded cross coupling products, Ph-R'. Complexes 1 - 3 reacted with olefinic compounds such as CH$_2$=CH$_2$, CH$_3$CH=CH$_2$, CH$_3$COOCH=CH$_2$, CH$_3$OCOCH=CH$_2$, C$_6$H$_5$CH=CH$_2$, and CH$_2$=CHCH$_2$X (X = OCOCH$_3$, OCOH, Br, OH, OC$_6$H$_5$, and OCH$_2$CH=CH$_2$) to give phenyl-substituted organic compounds. Examination of the reaction products suggests that these substitution reactions may proceed mainly through (i) olefin coordination to Ni, (ii) insertion of olefin into Ph-Ni bond, and (iii) β-elimination reactions to yield olefinic products. In the arylation of vinyl acetate and allylic compounds, phenyl-substituted hydrocarbon products were obtained in fairly high yields suggesting that the C-O or C-X bond cleavage reaction is taking place.

Introduction

In various catalytic reactions involving olefinic compounds promoted by transition metal compounds, a species having a metal-to-carbon σ-bond is often believed to play an important role as a key intermediate. In this respect, the study of the reactions between isolated alkyl, aryl or hydrido transition metal complexes and olefinic compounds is expected to afford a clue for understanding the mechanism of catalysis [1]. This paper concerns firstly the preparation of a series of a new type of phenylnickel complexes and secondly their reactions with various olefinic compounds to give, mainly, phenylated olefins.

Arylnickel complexes stabilized with tertiary phosphine ligands have been prepared by two routes: one is arylation of nickel halides with aryl Grignard reagents [2] and another is oxidative addition of an aryl or aroyl halogen compound to zero valent nickel complexes [3-8]. As an extension of our studies on the preparation of transition metal alkyl complexes using alkylaluminums as alkylating agents [9], triarylaluminums were employed to prepare arylnickel complexes. In contrast to the alkylaluminums which have been successfully used in the preparation of a variety of new alkyl-transition metal complexes, surprisingly little has been reported on the application of arylaluminums to the syntheses of aryl-transition metal complexes [10]. Several of a new series of phenylnickel complexes of the type $PhNi(acac)(PR_3)_n$ (acac = the chelated acetylacetonato ligand) were isolated from the system consisting of triphenylaluminum etherate, nickel acetylacetonate, and tertiary phosphine, PR_3. This has been briefly communicated [11]. These phenyl complexes are more stable than the previously reported complexes of the type $PhNiX(PR_3)_2$ with monodentate halogen or pseudohalogen ligands, X, and react with carbon monoxide to give new isolable benzoylnickel complexes, which will be the subject of a separate report [12].

Recently attention has been focused on the utilization of transition metal compounds for organic synthesis under mild conditions. With this view, aryl substitution of olefinic compounds, for instance, has been extensively studied using palladium compounds [1, 13-20]. Sources of the aryl group used in these studies are arylmercurials [14], aryl halides [15-18], aromatic hydrocarbons [19], or arylamines [20], and mechanisms of arylation proceeding through processes involving the formation of arylpalladium intermediates have been postulated for these reactions. Arylation of olefins using isolated aryltransition metal complexes, on the other hand, has been limited only to a brief study with $PhMBr(PPh_3)_2$ (M = Ni and Pd) [6]. The phenylnickel complexes, $PhNi(acac)(PR_3)_n$, prepared in the present study were found to react with various olefins at ambient conditions to yield phenyl-substituted organic compounds in which the phenyl group is attached predominantly to the terminal olefinic carbon.

Results and discussion

Preparation and properties of $PhNi(acac)(PR_3)_n$

Treatment of nickel acetylacetonate with triphenylaluminum etherate in diethyl ether in the presence of a tertiary phosphine at or below room temperature afforded phenylnickel complexes, $PhNi(acac)(PR_3)_n$.

$$Ni(acac)_2 + mAlPh_3{\cdot}Et_2O + nPR_3 \xrightarrow{Et_2O} PhNi(acac)(PR_3)_n \qquad (1)$$

$R = Ph,\ m = 1/2,\ n = 1$ — **1** $R = Ph\ (n = 1)$

$R = cyclo\text{-}C_6H_{11},\ m = n = 1$ — **2** $R = cyclo\text{-}C_6H_{11}\ (n = 1)$

$R = Et,\ m = 1,\ n = 2$ — **3** $R = Et\ (n = 2)$

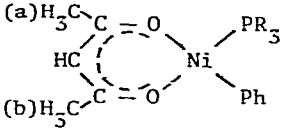
In order to obtain the best yields of the phenylnickel complexes, the use of molar ratios of the reagents as shown in equation (1) seems to be most suitable. It is noted that only one-half mole of triphenylaluminum per mol of nickel acetylacetonate was necessary when triphenylphosphine was used, while an equimolar amount of aluminum was needed in the case of cyclohexylphosphine (hereafter denoted as PCy_3) and triethylphosphine (PEt_3) complexes. In the case of PEt_3, complex **3** coordinated with two phosphine ligands was obtained only when two mol of PEt_3 per $Ni(acac)_2$ was used, otherwise an intractable, oily material resulted. Complex **3** was recrystallized from a mixture of dichloromethane and diethyl ether in the presence of excess of triethylphosphine. Crystallization of **3** in the absence of added triethylphosphine afforded a phenyl complex containing only one PEt_3 ligand, $PhNi(acac)PEt_3$, **4**. Analytical data and physical properties of complexes **1**-**4** are summarized in Table 1. Treatment of complexes **1**-**3** with an excess of gaseous HCl in diethyl ether (**1** and **3**) or hexane (**2**) afforded one mol of benzene per mol of the complex.

Similar reactions using alkylaluminums in place of $AlPh_3 \cdot Et_2O$ in equation (1) have been reported to afford analogous alkylnickel complexes, $RNi(acac)L_n$, where R = Me, Et, and iso-Bu, L = PCy_3 (n=1)[21]; R = Me, L = PPh_3 (n=2) and R = Et, L = PPh_3 (n=1)[22]; and R = $PhCH_2$, L = PPh_3, $P(CH_2Ph)_3$, and PCy_3 (n=1)[23]. Preparation of an analogous p-tolylnickel complex also was attempted using tri-p-tolylaluminum in place of triphenylaluminum for each phosphine ligand. Although some products containing a nickel-bonded p-tolyl group were obtained, their purification so far has been unsuccessful.

IR and ^1H-NMR spectra of $PhNi(acac)(PR_3)_n$

Infrared spectra of the phenylnickel complexes **1**, **2**, and **4** resemble each other except for the bands assignable to the phosphine ligands. As a typical example, the characteristic bands of complex **2** were assigned as follows: 3025 cm^{-1}, ν(C-H) of the phenyl group; 2900 and 2825 cm^{-1}, $\nu_{as}(CH_2)$ and $\nu_s(CH_2)$ of PCy_3; 1580, 1560, 1513, 1444, and 1395 cm^{-1}, ν(C=O) and ν(C=C) of the acac ligand, ν(C=C) of phenyl, or δ(C-H) of PCy_3. The detailed assignments of the IR bands of this type of complex have been carried out on $MeNi(acac)PMe_3$, in which the band at 533 cm^{-1} was assigned to the stretching of Ni-C σ-bond [24]. In the present phenylnickel complexes, many bands due to the phosphine ligands around this area prevented the assignment of the bands of Ni-C σ-bond.

^{1}H-NMR spectral data of 1-4 are summarized in Table 2. The assignment of the signals due to the phenyl ligand attached to nickel was performed with reference to those of arylcopper(I) compounds [25]. Protons of the two acac-methyl groups appeared as a pair of singlets in the cases of 1 and 2 at room temperature indicating that these complexes have a square-planar configuration in solution. The singlets at higher field were assigned to the protons of the methyl group (a) and the lower ones to (b) as the chemical shifts of the acac methyl protons are known to be sensitive to the nature of the ligand at their cis position in the complexes of the type Pd(acac)XL [26].



The ^{1}H-NMR signals of the PPh_3-coordinated complex 1 broadened only slightly on raising the temperature to 60°C, indicating that the exchange of the acac methyl protons is very slow at room temperature and accelerated only slightly at higher temperatures. The ^{31}P-NMR spectrum of 1 in toluene at -70°C shows a singlet of half width 12 Hz at 42.7 ppm downfield from the external PPh_3 reference. The signal shifts to a higher field of 36.1 ppm with broadening to a half width of 65 Hz on raising the temperature to 25°C. These results, together with the experimentally determined molecular weight of 1 in benzene, show that the triphenylphosphine ligand in 1 is dissociated only to a minor extent and that the exchange takes place between the coordinated and uncoordinated PPh_3 ligand without affecting the square planar configuration of the nickel complex. Similar dissociation behavior of the coordinated ligands, acac and PPh_3, dissociating and exchanging in different rates independently of each other, has

(Continued on p. 366)

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES OF $PhNi(acac)(PR_3)_n$

Complex		Appearance	M.p. (°C)	Anal.found(calcd)(%)			M.w.[b]
				C	H	Ni[a]	found(calcd)
$PhNi(acac)PPh_3$	**1**	yellow powder	148-149.5[c]	69.9(70.0)	5.5(5.5)	11.9(11.8)	464±30(497)
$PhNi(acac)PCy_3$	**2**	yellow powder	155.5-158[c]	68.0(67.6)	8.3(8.8)	11.7(11.4)	345±30(515)
$PhNi(acac)(PEt_3)_2$	**3**	red columns	63-63.5	57.2(58.6)	9.2(9.0)	12.8(12.5)	
$PhNi(acac)PEt_3$	**4**	yellow powder		57.8(57.8)	8.1(7.7)		

a) Ni content was measured by the chelate titration. b) Molecular weight was measured cryoscopically in benzene under nitrogen. c) With decomposition.

TABLE 2

^{1}H-NMR DATA FOR PhNi(acac)$(PR_3)_n$

Complex	Solvent	acac ligand		Ph-Ni		PR_3
		CH_3	CH	ortho	meta and para	
1	C_6D_6	1.72(3 s)	5.30(1 s)	7.4-7.8[b)]	6.8-6.9(3 m)	7.4-7.8(o-)[b)]
		1.50(3 s)				6.9-7.1(m,p-)
1	$(CD_3)_2CO$	1.78(3 s)	5.44(1 s)	7.0-7.7[b)]	6.44-6.62(3 m)	7.0-7.7[b)]
		1.40(3 s)				
2	C_6D_6	1.75(s)	5.40(1 s)	8.0-8.2(2 m)	7.1-7.4(3 m)	0.9-2.3(m)
		1.70(s)				
2	$(CD_3)_2CO$	1.74(s)	5.38(1 s)	7.42-7.56(2 m)	6.6-6.8(3 m)	0.8-2.2
		1.68(s)				
3	C_6D_6	1.89(s)	5.28(1 s)	7.68-7.78(2 m)	6.88-7.20(m)	$PCH_2\underline{CH}_3$ 1.00(18 t[c)])
						$P\underline{CH}_2CH_3$ 1.62(q[c)])
4	C_6D_6	1.86(6 s)	5.30(1 s)	7.90-7.96(2 m)	6.92-7.28(m)	$PCH_2\underline{CH}_3$ 0.97(9 t[d)])
						$P\underline{CH}_2CH_3$ 1.16-1.60(6 m)

a) 100 MHz at 25°C, tetramethylsilane as an internal standard. Chemical shifts are in δ values. Figures in parentheses are peak intensities. Multiplicity abbreviations are as follows: s, singlet, t, triplet; q, quartet; and m, multiplet.

b) *ortho*-Protons of PhNi and PPh_3 are not distinguishable.

c) ^3J(H-H) = 8 Hz.

d) ^3J(H-H) = 7 Hz.

been observed in EtNi(acac)PPh_3 [27] and PhCONi(acac)PPh_3 [12]. Pd(acac)(γ-acac)py (γ-acac denotes the acac ligand bonded to the metal through its central carbon) also is known to behave similarly [28].

The ^{1}H-NMR spectra of the PEt_3-coordinated complexes 3 and 4 show only a sharp singlet signal for the acac methyl protons in a temperature range between -80°C and +60°C. The ^{31}P-NMR spectrum of 3 in toluene at -70°C showed a broad singlet (half width = 72 Hz) at 8.3 ppm (downfield from the external PPh_3 reference) which shifted to the higher field with broadening on raising the temperature with eventual disappearance of the signal at 25°C. These ^{31}P-NMR spectral observations suggest that PEt_3 ligand in 3 is exchanging on the NMR time scale evan at -70°C and very rapidly at room temperature. The fact that the ^{1}H-NMR spectrum of 3 in benzene at room temperature shows a triplet-quartet pattern which is typical for the PEt_3-coordinated complex in which the PEt_3 ligand is rapidly exchanging further supplements the observation made in the ^{31}P-NMR spectrum. The reason for the appearance of the acac methyl proton of 3 as a sharp singlet may be due either to the equivalence of the acac methyl protons in the five-coordinated configuration of 3 or to accidental coincidence of the chemical shifts of the two acac methyl protons. Regarding the four-coordinated complex 4 the latter explanation is more reasonable.

Pyrolysis of the phenylnickel complexes

Pyrolyses of PhNi(acac)PPh_3 1 and PhNi(acac)$(PEt_3)_2$ 3, either in the solid state or in toluene solution, gave benzene and biphenyl (Table 3). The amount of biphenyl produced by the pyrolysis of 1 was much more than the expected value accounting for the presence of one phenyl group per nickel especially when the pyrolysis was conducted in toluene. It is natural to assume that the phenyl group of triphenylphosphine also is involved in the decomposition of 1. Taking into account that there is some precedent for the oxidative addition of triphenylphosphine involving P-C bond

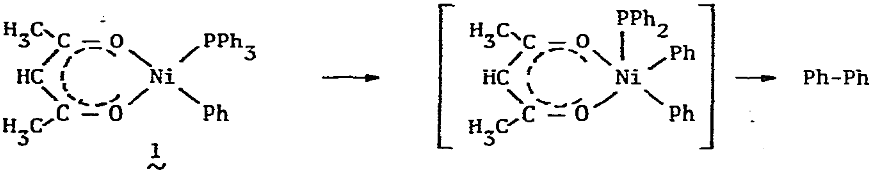
TABLE 3

PYROLYSIS OF PhNi(acac)$(PR_3)_n$

Complex	Solvent	Temp.(°C)	Time(hr)	Products(mol/mol of complex)	
				Ph-H	Ph-Ph
1	none	170	0.33	0.03	0.60
1	toluene	95	3	0.04	0.97
3	none	r.t.~160	—	0.19	0.32
3	toluene	95	50	— a)	0.14

a) Not measured.

cleavage [29], we consider it reasonable to assume the following reaction scheme involving the oxidative addition of the PPh_3 ligand to nickel for the present system.



(2)

In order to obtain further support for the participation of PPh_3 in the pyrolysis of 1, MeNi(acac)$(PPh_3)_2$ and EtNi(acac)PPh_3 [22] were heated at 95°C in ethylbenzene and toluene, respectively, and, albeit in low yield, toluene (3 %) and ethylbenzene (4 %), respectively, were detected in the pyrolyzed solution by GLC analyses.

Reactions of PhNi(acac)$(PR_3)_n$ with organic halogen compounds

Phenyl complexes 1, 2, and 3 reacted with organic halogen compounds (R'X) at room temperature to yield cross-coupled products Ph-R'.

$$\mathrm{PhNi(acac)(PR_3)_n + R'X \longrightarrow Ph\text{-}R' + NiX(acac)(PR_3)_n} \qquad (3)$$

The IR spectrum of the residual solid of the reaction mixture indicated the absence of the starting phenyl complex and the presence of the species formulated as NiX(acac)$(PR_3)_n$. In these reactions biphenyl was formed as the main by-product other than the cross-coupling products. However, the yields of the coupling products were not so high (Table 4). The remaining phenyl group may have been converted into biphenyl and benzene as in the thermolysis. In one case these byproducts were in fact identified.

Reactions of PhNi(acac)$(PR_3)_n$ with olefins

Reaction with ethylene and propylene

The phenylnickel complex containing the triphenylphosphine ligand, 1, reacted with ethylene and propylene at atmospheric pressure at room temperature in diethyl ether suspension to give a series of phenylated organic compounds. Table 5 lists the product distribution of these reactions. Although about one-half of the phenyl complex seems to have been decomposed to give benzene and biphenyl in the reaction of ethylene, the rest of the phenyl complex was converted into styrene, ethylbenzene, trans-stilbene, and 1,2-diphenylethane.

TABLE 4

REACTIONS OF PhNi(acac)$(PR_3)_n$ WITH ORGANIC HALOGEN COMPOUNDS (R'-X)[a)]

Complex		R'-X	Product Ph-R'[b)] (mol/mol of complex)
PhNi(acac)PPh_3	1	CH_3I	0.14
PhNi(acac)PPh_3	1	CH_3COCl[c)]	0.15
PhNi(acac)PPh_3	1	C_6H_5COCl[c)]	trace
PhNi(acac)PCy_3	2	CH_3I	0.20
PhNi(acac)PCy_3	2	CH_3I	0.37[d)]
PhNi(acac)PCy_3	2	CH_3CH_2Br	0.21
PhNi(acac)PCy_3	2	CH_3CH_2I	0.25
PhNi(acac)$(PEt_3)_2$	3	CH_3I	0.20

a) Reactions with R'-X were carried out at room temperature for one day. b) In addition to Ph-R', biphenyl was produced as well. c) In diethyl ether as solvent. d) Reaction temperature was elevated slowly from -30°C to room temperature. Other products were biphenyl (0.28 mol/mol of complex) and benzene (0.01).

TABLE 5

REACTIONS OF ETHYLENE AND PROPYLENE WITH PHENYLNICKEL COMPLEXES[a)]

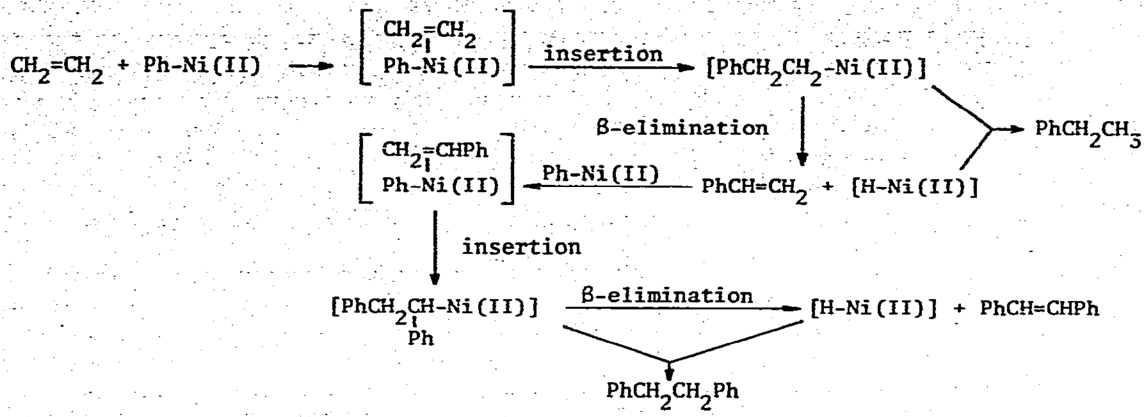
Olefin	Complex		Organic products (mol/mol of complex)					
$CH_2=CH_2$			$PhCH=CH_2$	$PhCH_2CH_3$	*trans*-$PhCH=CHPh$	$PhCH_2CH_2Ph$	PhH	Ph-Ph
	PhNi(acac)PPh_3	1	0.19	0.11	0.05	0.06	0.05	0.21
	PhNi(acac)PCy_3	2	0	0.01	0	0.07	0.06	0.17
	PhNi(acac)$(PEt_3)_2$	3	0	0	0	0	0.05	0.04[b)]
$CH_2=CHCH_3$			$PhCH=CHCH_3$ cis	 trans	$PhCH_2CH_2CH_3$	$Ph(CH_3)C=CH_2$	PhH	Ph-Ph
	PhNi(acac)PPh_3	1	0.02	0.55	0.03	0.06	0.08	0.04
	PhNi(acac)PCy_3	2	0	0.02	0	0	0	0
	PhNi(acac)$(PEt_3)_2$	3	0	0.02	0	0	0.05	0.12[b)]

a) Reactions were carried out under 1 atm of olefin at room temperature for 2 days either in Et_2O suspension (1 and 2) or solution (3). b) In order to avoid the contribution from the unreacted phenyl complex, the system was treated with HCl prior to the measurement of this value.

Formation of these products can be explained by assuming the following reaction paths consisting of conventional insertion and β-elimination steps (Scheme). Ethylene coordinates to the phenylnickel complex and is inserted into the phenyl-nickel bond to give a β-phenylethylnickel intermediate, from which styrene and ethylbenzene are formed by β-elimination and disproportionation. A portion of the styrene thus formed reacts further with the phenylnickel complex in fashion similar to that suggested for ethylene to give stilbene and 1,2-diphenylethane (vide infra). In the case of propylene, similar results in terms of product distribution have been obtained by Heck [14] in the arylation of propylene with the "arylpalladium salt" which was prepared in situ from $ArHgOCOCH_3$ and $Pd(OCOCH_3)_2$. A slightly higher selectivity for the direction of phenyl addition in the present system (terminal addition/internal addition = 10.0) than in the Heck's system (5.3) was observed.

In contrast to complex 1, phenyl complexes containing alkylphosphines, 2 and 3, are reluctant to react with ethylene

Scheme



(In the scheme Ph-Ni(II) stands for $PhNi(acac)PPh_3$)

and propylene, as shown in Table 5. This fact suggests that the coordination of olefin to nickel is important in initiating the reaction. Complex 1, which contains a less electron-donating phosphine ligand than 2 and 3 and is more electron deficient, may be more susceptible to coordination with olefin as a base than the other alkylphosphine-coordinated complexes.

Reactions with other substituted olefins The results of the reactions of $PhNi(acac)PPh_3$, 1, with styrene, methyl acrylate, and vinyl acetate are summarized in Table 6.

trans-Stiblene was the sole phenylated product of the reaction with styrene, although nearly one-half of a mole of phenylnickel complex was decomposed to give benzene and biphenyl concurrently with the phenylation of styrene. Similar results have been reported by Heck [14] and Otsuka *et al.* [6] using a mixture of $PhHgOCOCH_3$ and $Pd(OCOCH_3)_2$, and $MBr(Ph)(PPh_3)_2$ (M = Ni and Pd), respectively. The mechanism involving the insertion of styrene into phenyl-nickel bond followed by β-elimination may also be operative in this reaction.

Methyl acrylate was phenylated and hydrogenated on reaction with 1 to give 1-phenyl-2-methoxycarbonylethane. The yield was

TABLE 6

REACTIONS OF SUBSTITUTED OLEFINS R-CH=CH_2 WITH PhNi(acac)$PPh_3$$^{a)}$

Substituted Olefin R = Substitutent	Reaction time (days)	Organic products (mol/mol of complex)				
		RCH=CHPh	RCH_2CH_2Ph	others	PhH	Ph-Ph
Styrene (Ph)	4	0.56(trans)	0	0	0.08	0.20
Methyl acrylate ($COOCH_3$)	2	0	0.45	0	trace	trace
Vinyl acetate ($OCOCH_3$)	7	0.12(trans) 0.19(cis)	0	PhCH=CH_2 0.08	0.02	0

a) Reactions were carried out in neat olefins at room temperature.

only 0.45 mol per mol of phenyl complex used and the fate of the rest of the phenyl group is uncertain. The result differs from those reported using $PhHgOCOCH_3/Pd(OCOCH_3)_2$ [14] or $PhNiBr(PPh_3)_2$ [6] where methyl cinnamate was the sole product. Although the source of the proton to afford the hydrogenated product in the present system is uncertain, the mechanism of terminal addition of the phenyl group which is common to the other phenylation reaction may also be operative in this reaction.

The formation of cis- and trans-phenyl-2-acetoxyethene in the reaction of vinyl acetate with 1 may be accounted for by a conventional insertion-β-H abstraction mechanism, while the formation of styrene can be rationalized by assuming the β-acetoxy abstraction process as postulated by Heck [30]. As in the reaction of ethylene and propylene, phenyl complexes 2 and 3 were unreactive to vinyl acetate indicating, again, the importance of coordination of vinyl acetate to nickel at the initial stage of the reaction.

Reactions with allylic compounds

As shown in Table 7, 1 reacted with CH_2=$CHCH_2X$ (X = HCOO, CH_3COO, Br, OH, OPh, and OCH_2CH=CH_2) to afford allylbenzene generally in high yields. Although the similar reactions of allyl halides with "phenylpalladium" to give allylbenzene have been reported by Heck [31], the present results of the reactions of

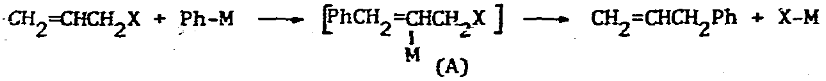
TABLE 7

REACTIONS OF ALLYL COMPOUNDS WITH $PhNi(acac)PPh_3$ [a)]

Allyl compound	Reaction time (days)	Products (mol/mol of complex)	
		$PhCH_2CH=CH_2$	others
$CH_2=CHCH_2OCOCH_3$	3	0.89	—
$CH_2=CHCH_2OCOH$	1	0.82	—
$CH_2=CHCH_2Br$	1	0.75	—
$CH_2=CHCH_2OH$	1	0.76	0.07 ($PhCH_2CH_2CHO$)
$CH_2=CHCH_2OPh$	1	0.72	—
$(CH_2=CHCH_2)_2O$	1	0.23	0.80 (PhH)

a) Reactions were carried out in neat allyl compounds at room temperature.

allyl carboxylates and alcohol are strikingly different from those of Heck who obtained phenyl-substituted allyl compounds which may be accounted for by the insertion-β-hydride elimination mechanism [14, 31, 32]. The present allylbenzene formation in the reaction of **1** with various allylic compounds may have all proceeded through the common reaction path as postulated by Heck for the reaction of allyl halide with "arylpalladium", which involves the insertion of the allyl group into the phenyl-nickel bond followed by β-elimination of X from an intermediate A (eq. 4).



$$CH_2=CHCH_2X + Ph\text{-}M \longrightarrow \underset{(A)}{[PhCH_2=\underset{M}{C}HCH_2X]} \longrightarrow CH_2=CHCH_2Ph + X\text{-}M \qquad (4)$$

The β-elimination involving the abstraction of alkoxy group (when X = OPh and $OCH_2CH=CH_2$) has precedent for the reaction of α,α-dimethylallyl benzyl ether with $RuCl_2(PPh_3)_3$ to give PhCHO and $(CH_3)_2C=CHCH_3$ [33]. In support of this mechanism, a yellow complex, which was proven to contain a PhO-Ni moiety on the basis of production of anisole on its treatment with methyl iodide, was isolated in the present reaction system with X = OPh.

The presence of a by-product of phenylpropionaldehyde in the reaction of allyl alcohol with 1 (Table 7) indicates a partial occurrence of the β-hydride elimination of intermediate A in Eq.4 in addition to the main path of β-hydroxy abstraction.

Experimental

1) General

All reactions and manipulations were carried out under dry, oxygen-free nitrogen or *in vacuo* using Schlenk type flasks. Filtrations were carried out through siphons with sintered-glass disks under positive pressure of nitrogen.

Solvents such as diethyl ether, hexane, tetrahydrofuran (THF) and toluene were dried and purified by distilling over sodium wire and stored under nitrogen

Organic halogen compounds, and olefins were purified by distilling over calcium hydride under reduced pressure. Triphenylaluminum etherate, $AlPh_3 \cdot Et_2O$, was prepared from PhMgBr and $AlCl_3$ according to the reported method [34]. Anal., Found: Al, 8.37, $C_{22}H_{25}OAl$ calcd.: Al, 8.12 %. On acidolysis, benzene (104 % on the basis of the formula) and diethyl ether (79 %) were detected.

The micro analyses of carbon and hydrogen were performed by Mr. T. Saito of our Laboratory using Yanagimoto CHN Autocorder Type MT-2.

Infra-red spectra were recorded on a Hitachi model 295 spectrometer using KBr disks prepared under inert atmosphere. NMR spectra were measured on a JNM-PS-100 spectrometer by Mr. Y. Nakamura of our Laboratory.

The organic products by various reactions of $PhNi(acac)(PR_3)_n$ were quantitatively analyzed by GLC using toluene, ethylbenzene or anisole as an internal standard. Authentic samples for identification of reaction products such as $PhCH{=}CH_2$, $PhCH_2CH{=}CH_2$, *trans*-PhCH=CHPh, etc., were used as purchased and the other samples such as <u>cis</u> and <u>trans</u>-PhCH=CHCH$_3$, <u>cis</u> and <u>trans</u>-CH$_3$COOCH=CHPh, and CH$_3$COOC(Ph)=CH$_2$ were prepared according to the methods described in the literature [35-37]. GLC was recorded on a Shimadzu GC-3BT or GC-6A gas chromatography using SDC-550, TCP and/or PEG-20M columns and hydrogen or helium as a carrier gas. Molecular weights of PhNi(acac)PPh$_3$ and PhNi(acac)PCy$_3$ were measured cryoscopically in benzene under nitrogen.

2) <u>Preparation of PhNi(acac)PPh$_3$</u>

To the mixture of Ni(acac)$_2$ (20.5 g, 8.0 mmol), PPh$_3$ (2.2 g, 8.4 mmol) and diethyl ether (50 ml) cooled at -30°C, AlPh$_3$·Et$_2$O (1.4 g, 4.2 mmol) was added. The initial light green suspension immediately turned to a yellowish green suspension. On raising the temperature to room temperature, the system changed to a brown suspension in 20 min. The system was further stirred for 2 hr. at room temperature to complete the reaction. The precipitate was filtered off, washed with a mixture of diethyl ether and hexane (1:1 in volume). The lemon yellow powder thus obtained weighed 2.0 g (50 % of the theoretical amount based on Ni(acac)$_2$ used), and was analyzed as PhNi(acac)PPh$_3$. The product was soluble in THF, benzene, chloroform, and toluene, and recrystallized from diethyl ether-THF (1:1 in volume) to give yellow crystalline powder. Analytical data and physical properties are listed in Table 1.

3) <u>Preparation of PhNi(acac)PCy$_3$</u>

In a 100 ml Schlenk apparatus were placed Ni(acac)$_2$ (5.14 g, 20 mmol), tricyclohexylphosphine (5.60 g, 20 mmol) and diethyl ether (100 ml). Solid AlPh$_3$·Et$_2$O (7.80 g, 25 mmol) was added portionwise to the mixture cooled at -30°C with stirring. On raising the temperature of the system gradually to -20°C, the initial greenish yellow suspension darkened and finally a dark brown solution with a yellow precipitate resulted. The system was further stirred at -10°C for 2 hrs. The yellow precipitate was filtered, washed with diethyl ether, and dried *in vacuo*. The yellow powder thus obtained, weighed 3.45 g. The second crop of the yellow complex was obtained by further evaporation of the solvent from the mother liquor followed by cooling at -78°C. The total yield of PhNi(acac)(PCy$_3$) was 5.65 g (55 % of the theoretical amount based on Ni(acac)$_2$ used). The product was recrystallized from THF to give a yellow crystalline powder. Analytical data and physical properties are listed in Table 1.

4) Preparation of PhNi(acac)(PEt$_3$)$_2$.

In a 100 ml Schlenk apparatus were placed Ni(acac)$_2$ (5.14 g, 20 mmol), triethylphosphine (6.5 ml, 45 mmol) and diethyl ether (100 ml). The light green precipitate of nickel acetylacetonate turned to blue in a minute after mixing, indicating the formation of an adduct [Ni(acac)$_2$(PEt$_3$)$_2$]. After the mixture was cooled to -40°C, the solid AlPh$_3$·Et$_2$O (6.8 g, 21 mmol) was added to the mixture with stirring, to give a pale yellow suspension. On raising the temperature of the system, it turned to a yellowish brown suspension at -20°C and then to a wine red solution. After stirring for 1 hr, the solution was filtered and the filtrate was condensed to one-third of the initial volume. After being kept for 1 day at -78°C, the red crystals which had formed were filtered, washed with diethyl ether at -78°C and dried in vacuum. The yellowish orange powder of PhNi(acac)(PEt$_3$)$_2$ weighed 4.85 g (52 % of the theoretical amount based on Ni(acac)$_2$ used). Recrystallization from a 1 : 1 mixture of dichloromethane and diethyl ether in the presence of triethylphosphine gave red prisms. Analytical data and physical properties are listed in Table 1.

5) Preparation of PhNi(acac)PEt$_3$

Recrystallization of PhNi(acac)(PEt$_3$)$_2$ from diethyl ether in the absence of extra triethylphosphine gave red crystals. The red crystals turned to lemon yellow powder on prolonged evacuation at room temperature. Analytical data listed in Table 1 indicates that the powder can be formulated as PhNi(acac)-(PEt_3).

6) Pyrolyses of PhNi(acac)(PR_3)$_n$

a) Pyrolysis in the solid state

PhNi(acac)PPh_3 (0.08 g, 0.179 mmol) was heated at 170°C *in vacuo* for 20 minutes to afford a black oil. The organic pyrolysis products were identified as benzene (0.006 mmol) and biphenyl (0.108 mmol) by GLC analysis of the diethyl ether solution of the black oil using toluene as an internal standard. Pyrolysis of PhNi(acac)-(PEt_3)$_2$ in the solid state was carried out similarly using 0.137 g (0.291 mmol) of the complex.

b) Pyrolysis in toluene

A toluene solution of PhNi(acac)PPh_3 (0.095 g, 0.192 mmol) was heated at 95°C *in vacuo* for 2 hrs. The color of the solution changed from yellow through red, then to black. The pyrolysis products were identified as benzene (0.0144 mmol) and biphenyl (0.186 mmol).

Pyrolysis of PhNi(acac)(PEt_3)$_2$ (0.153 g, 0.324 mmol) in toluene was carried out similarly *in vacuo*, heating at 95°C for 51 hrs. A considerable amount of the starting phenylnickel complex remained undecomposed. In order to obtain accurately the amount of biphenyl produced by pyrolysis, the system was treated with gaseous HCl prior to the GLC analysis. This procedure affords benzene quantitatively from the unreacted phenylnickel complex which is known to give biphenyl on thermal treatment, *e.g.*, pyrolysis in the GLC injection room. The net amount of biphenyl produced through pyrolysis was found to be 0.045 mmol (28 %).

7) Reactions of PhNi(acac)(PR_3)$_n$ with organic halogen compounds

To a flask containing PhNi(acac)PPh_3 (0.354 g, 0.678 mmol), ethyl iodide (2 ml) was added by a vacuum distillation. The initially red solution gradually turned to a red suspension in one day on stirring at room temperature. Ethylbenzene (0.170 mmol) was formed, as judged by GLC analysis. Formation of ethylene, ethane and biphenyl also was detected qualitatively by GLC analysis. The other reactions of PhNi(acac)$(PR_3)_n$ with various organic halogen compounds were carried out in similar fashion.

8) Reactions of PhNi(acac)$(PR_3)_n$ with various olefins

Since the method is general, a typical reaction will be described below and the organic reaction products are listed in Table 5-7.

a) Reactions with ethylene and propylene

A 200 ml flask containing PhNi(acac)PPh_3 (0.37 g, 0.745 mmol) and diethyl ether (2 ml) was degassed by the freeze-thaw method. The flask was filled with 1 atm. of ethylene at room temperature and the mixture was stirred for 2 days. The initially lemon yellow suspension turned to yellow orange. The reaction products were analyzed by GLC. The other reactions of phenylnickel complexes with ethylene and propylene were carried out similarly. In the case of PhNi(acac)$(PEt_3)_2$, a considerable amount of the starting phenyl complex remained unreacted on the reaction with ethylene or propylene. The amount of biphenyl produced in the reaction was measured accurately by the method described in (6-b).

b) Reactions with other olefinic compounds.

To a flask containing PhNi(acac)PPh_3 (0.435 g, 0.874 mmol), vinyl acetate (1.5 ml) was added by a vacuum distillation and the mixture was stirred at room temperature for 7 days. The initially lemon yellow suspension remained unchanged all through the reaction. The reaction products were analyzed by GLC. Similarly carried out were the other reactions of PhNi(acac)$(PR_3)_n$ with vinyl acetate, methyl acrylate, allyl acetate, allyl formate, allyl bromide, allyl phenyl ether and diallyl ether. The reactions with styrene and allyl alcohol were carried out similarly in the presence of diethyl ether as solvent. Methyl hydrocinnamate, the reaction product between PhNi(acac)PPh_3 and methyl acrylate, was identified by ^{1}H-NMR spectrum of the product collected by means of preparative GLC.

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