Journal of Organometallic Chemistry
Elsevier Sequoia S.A., Lausanne
Printed in The Netherlands

OXIDATIVE ADDITIONS TO NICKEL(0): PREPARATION AND PROPERTIES OF A NEW SERIES OF ARYLNICKEL(II) COMPLEXES

M. HIDAI, T. KASHIWAGI, T. IKEUCHI AND Y. UCHIDA
Department of Industrial Chemistry, The University of Tokyo, Hongo, Tokyo (Japan)

(Received February 8th, 1971)

SUMMARY

A new series of stable arylnickel(II) complexes of the type $(PPh_3)_2Ni(aryl)X$ ($X = Cl, Br$) were prepared by oxidative additions of aryl halides to $Ni(PPh_3)_4$, where aryl is not only an *ortho*-substituted, but also phenyl or a *meta*- or *para*-substituted aromatic ligand. The order of decrease in their thermal stability was *o*-tolyl > *p*-chlorophenyl > *m*- or *p*-tolyl.

INTRODUCTION

The chemistry of oxidative-addition reactions of covalent molecules to low-valent transition metal complexes is currently receiving considerable attention, particularly in relationship to transition metal catalysis.

Series of stable σ-bonded arylnickel(II) complexes of the types $(PR_3)_2Ni(aryl)X$ and $(PR_3)_2Ni(aryl)_2$, where aryl is only an *ortho*-substituted aryl group, have been prepared by the reaction of compounds of the type $(PR_3)_2NiX_2$ with aryl Grignard reagents or alkali-metal compounds[1-6], and recently by the reaction of aryl halides with nickel(0) complex[7]. However, the preparation of the unsubstituted or *meta*- or *para*-substituted aryl analog remains equivocal. Ikeda *et al.*[8] have reported in a recent preliminary communication that the phenyl nickel compound $NiCl(C_6H_5)(Bipy)\cdot\frac{1}{2}C_6H_5Cl$ is obtained by the treatment of $Ni(Bipy)Et_2$ with chlorobenzene.

We wish now to report the preparation of a new series of stable arylnickel(II) complexes of the type $(PPh_3)_2Ni(aryl)X$ by the oxidative additions of aryl halides to $Ni(PPh_3)_4$, where aryl is not only an *ortho*-substituted, but also an unsubstituted or a *meta*- or *para*-substituted aromatic ligand. Furthermore, their thermal stability will be discussed.

RESULTS AND DISCUSSION

A new series of arylnickel(II) complexes of the type $(PPh_3)_2Ni(aryl)X$ were isolated as brownish-yellow crystals in a high yield by the reaction of aryl halides with $Ni(PPh_3)_4$ at room temperature. Similar arylnickel(II) complexes could not be isolated in a pure state by using *p*-nitro- or *p*-aminochlorobenzene. The reaction of

$$Ni(PPh_3)_4 + Ar\text{–}X \longrightarrow (PPh_3)_2Ni(Ar)X$$
$$Ar = \text{aryl}, X = Cl \text{ or } Br$$

nickel(0) complexes such as $Ni(PPh_2CH_3)_4$ and $Ni(Ph_2PCH_2CH_2PPh_2)_2$ with chlorobenzene at room temperature did not give any oxidative addition product.

The arylnickel(II) complexes obtained are fairly air-stable and soluble in toluene, chlorobenzene, but insoluble in petroleum ether.

The infrared spectrum of the *p*-tolylnickel(II) compound $(PPh_3)_2Ni(p\text{-}C_6H_4CH_3)Cl$ showed a sharp band at 782 cm^{-1} which can be attributed to the aromatic C–H out-of-plane deformation frequency characteristic of a two-adjacent-hydrogen system and is about 24 cm^{-1} lower than that of free *p*-chlorotoluene. An analogous low-shift of the aromatic C–H out-of-plane deformation frequency was observed in the case of other *para*-substituted arylnickel(II) compounds. The *m*-tolylnickel(II) compound $(PPh_3)_2Ni(m\text{-}C_6H_4CH_3)Cl$ exhibited a sharp absorption at 822 cm^{-1} which is assignable to the aromatic C–H out-of-plane deformation frequency characteristic of a one-adjacent-hydrogen system and is about 35 cm^{-1} lower than that of free *m*-chlorotoluene. However, assignment of the aromatic C–H out-of-plane deformation frequency characteristic of an *ortho*-substituted aryl group is difficult since absorptions of triphenylphosphine occur in the same region.

The far-infrared spectrum of the phenylnickel(II) compound $(PPh_3)_2Ni(C_6H_5)Cl$ showed a band at 348 cm^{-1} which disappeared in the corresponding bromide and can therefore be assigned to the nickel–chlorine stretching frequency. Other arylnickel(II) complexes also exhibited a band assignable to the nickel–chlorine stretching frequency in a range of 338–348 cm^{-1} (Table 1).

The arylnickel(II) complexes obtained here exhibited the same brownish-yellow color as the *trans*-square planar *ortho*-arylnickel(II) complexes prepared by Chatt *et al.*[1]. The nickel–chlorine stretching frequencies of *trans*-square planar com-

TABLE 1

ANALYTICAL AND PHYSICAL DATA FOR A SERIES OF ARYLNICKEL(II) COMPLEXES

Compound	M.p. (decompn.) (°C)	ν(Ni–X) (cm^{-1})	Analysis found (calcd.) (%)		
			C	H	Cl
$(PPh_3)_2Ni(C_6H_5)Cl$	122–123	348	73.1 (72.5)	5.0 (5.1)	5.2 (5.1)
$(PPh_3)_2Ni(C_6H_5)Br$	124–125	322?	68.4 (68.1)	4.8 (4.8)	
$(PPh_3)_2Ni(o\text{-}C_6H_4CH_3)Cl$	174–175	340	72.5 (72.8)	5.1 (5.3)	5.1 (5.0)
$(PPh_3)_2Ni(m\text{-}C_6H_4CH_3)Cl$	107–108	345	72.1 (72.8)	5.1 (5.3)	5.5 (5.0)
$(PPh_3)_2Ni(p\text{-}C_6H_4CH_3)Cl$	115–116.5	345	73.7 (72.8)	5.1 (5.3)	5.0 (5.0)
$(PPh_3)_2Ni(p\text{-}C_6H_4Cl)Cl$	139–141	338	69.1 (69.0)	4.9 (4.7)	8.8 (9.7)
$(PPh_3)_2Ni(p\text{-}C_6H_4NCO)Cl$		340	70.0 (70.2)	4.7 (4.7)	4.7 (4.7)
$(PPh_3)_2Ni(p\text{-}C_6H_4OCH_3)Cl$	111–115	345	71.8 (71.1)	5.5 (5.1)	5.2 (4.9)

plexes of the type $(PR_3)_2NiCl_2$ are observed at about 400 cm^{-1}, while that of the *cis*-square planar complex $(Ph_2PCH_2CH_2PPh_2)NiCl_2$ is observed at 330 and 320 cm^{-1}, lower than that of the *trans*-compounds owing to the higher *trans*-effect of the phosphine[9]. The nickel–chlorine stretching frequencies of the arylnickel(II) complexes obtained are a little higher than that found in *cis*-square planar and tetrahedral complexes (340–300 cm^{-1})[9]. From these results, it seems reasonable to consider that the arylnickel(II) compounds obtained have a *trans*-square planar configuration about nickel and their nickel–chlorine stretching frequencies occur in a region of 338–348 cm^{-1} since the order of decreasing *trans*-effect is expected to be $PR_3 >$ aryl group $>$ Cl.

As described before, Chatt *et al.*[1] have prepared series of stable *ortho*-substituted arylnickel(II) complexes of the types $(PR_3)_2Ni(aryl)X$ and $(PR_3)_2Ni(aryl)_2$, but could not obtain *meta*- or *para*-substituted arylnickel(II) complexes in a pure state since they decomposed in solution. They gave an explanation for the enhanced stability of *ortho*-substituted arylnickel(II) complexes: for steric reasons the *ortho*-substituent was considered to hold the plane of the aryl group vertical to the plane of the complex and so increase the stability by lowering the energy of the highest filled orbital (the d_{xy}) by double bonding (using the π^*-orbitals of the aryl group). The *ortho*-substituent will also increase the inertness of the complex by steric blocking of an axial coordination site. We have now succeeded in the preparation of phenyl or *meta*- or *para*-substituted arylnickel(II) complexes of the type $(PPh_3)_2Ni(aryl)Cl$ in a pure state as well as the *o*-tolylnickel(II) complex. The former complexes showed the same air-stability in a pure state as the latter complex. Their thermal decomposition points under nitrogen are shown in Table 1. The order of decrease in their thermal stability was *o*-tolyl $>$ *p*-chlorophenyl $>$ phenyl $>$ *p*-tolyl $\approx$ p-methoxyphenyl $>$ *m*-tolyl. The *o*-tolylnickel(II) complex is markedly stable compared with *m*- or *p*-tolylnickel(II) complexes as supposed by Chatt *et al.* The thermal stability of *p*-chlorophenylnickel(II) complex lies between that of the *o*-tolyl complex and that of the phenyl complex. The chlorophenyl group with the greater electronegativity would tend to remove much more charge from nickel, consequently the ionic resonance energy of the chlorophenyl–nickel bond would be greater than that of phenyl–nickel bond.

EXPERIMENTAL

Thermal decomposition points were determined under a nitrogen atmosphere.

All reactions were run under a nitrogen atmosphere in a small Schlenk-type flask containing a magnetic stirring bar. All operations for preparing arylnickel(II) complexes are very similar, so several typical examples are described below.

Preparation of tetrakis(triphenylphosphine)nickel(0)

The complex was prepared by the published procedure[10].

To a stirred mixture of nickel(II) acetylacetonate (5 g, 19.5 mmoles), triphenylphosphine (20.5 g, 78.3 mmoles) and 200 ml of ether was added 8 ml of diethylaluminum monoethoxide at 0°. The mixture was stirred for 30 min, and the homogeneous reddish-brown solution obtained was allowed to stand undisturbed at room temperature for about one day. The reddish-brown crystals which precipitated were separated by filtration, washed with ether, and dried under vacuum. An additional quantity of the complex was obtained by cooling the filtrate (16 g, 80% yield), m.p. 123–128° (dec.).

trans-Bis(triphenylphosphine)phenylchloronickel(II)

To a stirred mixture of tetrakis(triphenylphosphine)nickel(0) (0.94 g, 0.85 mmole) and 15 ml of toluene was added 0.5 ml (4.9 mmole) of chlorobenzene at room temperature. After stirring the solution for 10–20 min, the homogeneous solution obtained was allowed to stand undisturbed for about one day. The original deep red color disappeared and a yellowish-brown solution resulted. Then brownish-yellow crystals precipitated, which was separated by filtration, washed with petroleum ether and dried under vacuum. An additional quantity of the complex was obtained by addition of petroleum ether to the filtrate (0.42 g, 71% yield).

trans-Bis(triphenylphosphine)phenylbromonickel(II)

Prepared from tetrakis(triphenylphosphine)nickel(0) (0.563 g, 0.51 mmole), bromobenzene (0.3 ml, 2.9 mmole) and toluene (8 ml), it formed yellowish-brown crystals (0.26 g, 70% yield).

trans-Bis(triphenylphosphine)para-tolylchloronickel(II)

To a stirred solution of tetrakis(triphenylphosphine)nickel(0) (0.55 g, 0.50 mmole) and 15 ml of toluene was added 0.25 ml (2.1 mmole) of *p*-chlorotoluene at room temperature. The mixture was stirred for 1 h and then concentrated to ca. 7 ml by evaporating the solvent. Addition of petroleum ether to the concentrated solution precipitated brownish-yellow crystals, which was washed with petroleum ether and dried under vacuum (0.125 g, 35% yield).

REFERENCES

1 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, (1960) 1719.
2 J. R. Phillips, D. T. Rosevear and F. G. A. Stone, *J. Organometal. Chem.*, 2 (1964) 455.
3 J. R. Moss and B. L. Shaw, *J. Chem. Soc. A*, (1966) 1793.
4 R. G. Miller, D. R. Fahey and D. P. Kuhlman, *J. Amer. Chem. Soc.*, 90 (1968) 6248.
5 R. G. Miller, R. D. Stauffer, R. D. Fahey and D. R. Parnell, *J. Amer. Chem. Soc.*, 92 (1970) 1511.
6 M. D. Rausch and F. E. Tibbetts, *Inorg. Chem.*, 9 (1970) 512.
7 D. R. Fahey, *J. Amer. Chem. Soc.*, 92 (1970) 404.
8 M. Uchino, A. Yamamoto and S. Ikeda, *J. Organometal. Chem.*, 24 (1970) C63.
9 P. M. Boorman and A. J. Carty, *Inorg. Nucl. Chem. Lett.*, 4 (1968) 101.
10 G. Wilke, E. W. Müller, M. Kröner, P. Heimbach and H. Breil, *Ger. Pat.*, 1,191,375 (1965).