Journal of Organometallic Chemistry, 174 (1979) 115—120
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ORGANOMETALLIC COMPOUNDS OF TRANSITION METALS CONTAINING PHOSPHINE AND PERCHLORARYL LIGANDS

VI *. MONO- AND BIS(PENTACHLOROPHENYL) COMPLEXES OF NICKEL AND PALLADIUM

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(Received February 5th, 1979)

Summary

New organometallic compounds of nickel(II) and palladium(II) containing C_6Cl_5 and bipy ligands are described, viz.: $[NiX(C_6Cl_5)bipy]$ (X = NCS, NO_2), $[PdX(C_6Cl_5)bipy]$ (X = Cl, Br), and $[M(C_6Cl_5)L\ bipy]\ ClO_4$ (M = Ni, Pd; L = PPh_3, py).

The replacement of the nitrogen-containing ligand by the phosphines PEt_3, PPh_3, and dpe in the new compounds and in the previously reported $[NiCl(C_6Cl_5)bipy]$ and $[Pd(C_6Cl_5)_2bipy]$ has been studied. Substitution occurs with PEt_3 or dpe in the neutral compounds (but not in the cationic compounds) and in this way the new compounds $[PdX(C_6Cl_5)dpe]$ (X = Cl, Br), *cis*-$[Pd(C_6Cl_5)_2(PEt_3)_2]$ and $[Pd(C_6Cl_5)_2dpe]$ have been obtained.

The action of gaseous HCl on *cis*-$[Pd(C_6Cl_5)_2(PEt_3)_2]$ leads to the new compound *cis*-$[PdCl(C_6Cl_5)(PEt_3)_2]$, and also cleaves the Pd—C_6Cl_5 bonds of $[Pd(C_6Cl_5)_2dpe]$, the first phosphine-containing pentachlorophenyl complex of Ni, Pd, or Pt which decomposes under these conditions.

Introduction

A number of organometallic compounds of transition metals containing the pentachlorophenyl group and tertiary phosphines as stabilizing ligands have been reported [1]. In contrast, the only known compounds containing amine ligands are the neutral species $[NiCl(C_6Cl_5)bipy]$ [2], $[Pd(C_6Cl_5)_2bipy]$ [3] and $[Pd(C_6Cl_5)_2L_2]$ (L = py, phen, bam) [4] and the ionic complex $[Ni(C_6Cl_5)(3,5\text{-lut})_3]ClO_4$ [5].

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* For part V see ref. 1.

We have prepared new pentachlorophenyl derivatives of Ni and Pd containing bipy in order to compare its behaviour with that of the analogous phosphine-containing compounds. Furthermore, we thought that the possibility of replacement of the nitrogen-containing ligand by phosphines might provide a route to organometallic compounds which cannot be made via C_6Cl_5Li or C_6Cl_5MgX, and $[MX_2(PR_3)_2]$.

Several reasons have been put forward to account for the stability of the transition metal organometallic compounds with σ(M—C) bonds containing ligands of the type phosphine, CO, C_5H_5 etc. The most important are the π-acceptor abilities of the ligands [6], their volume [7], and the fact that coordination to the central atom may block the coordination sites required for decomposition reactions to occur [8].

The stability of the next compounds, which is not much less than that of those containing mono- or bi-dentate tertiary phosphines, indicates the last factor to be the more important.

Results and discussion

Preparation

The compounds containing pentachlorophenyl and bipy ligands were prepared by action of C_6Cl_5MgCl or C_6Cl_5Li on $[MX_2bipy]$. On treating $[PdCl_2bipy]$ with C_6Cl_5MgX, $[PdCl(C_6Cl_5)bipy]$ or $[PdBr(C_6Cl_5)bipy]$ is obtained depending on whether the Grignard reagent is prepared with benzyl chloride or 1,2-dibromoethane as initiator. This agrees with previous results which indicate the tendency of Pd to form compounds with Br as ligand when ethyl bromide or 1,2-dibromoethane is used as initiator for the preparation of the Grignard reagent.

$[NiCl(C_6Cl_5)bipy]$ and $[Pd(C_6Cl_5)_2bipy]$ were made by published methods [2,3]. As found for the complexes containing phosphines [2,9], treatment of the acetone solution of the compounds $[MX(C_6Cl_5)bipy]$ with $AgClO_4$, filtering off the AgX formed, and addition of neutral base gives the cationic complexes $[M(C_6Cl_5)L\ bipy]\ ClO_4$ (L = PPh_3, py), Likewise, replacement of Cl by other anionic ligand (NCS^-, NO_2^-) occurs on treating the compounds in acetone with an excess of the appropiate alkali metal salts; in contrast to the behaviour of the complexes containing phosphine, the reaction must be carried out at room temperature [9].

The action of an excess of PEt_3, PPh_3, or dpe on the benzene or chloroform solutions of $[MX(C_6Cl_5)bipy]$ leads to *trans*-$[MX(C_6Cl_5)(PR_3)_2]$ and *cis*-$[MX(C_6Cl_5)dpe]$, which were previously reported [9—11] except for $[PdX(C_6Cl_5)dpe]$ (X = Cl, Br). Analogously, treatment of $[Pd(C_6Cl_5)_2bipy]$ with PEt_3 or dpe gives the new compounds *cis*-$[Pd(C_6Cl_5)_2(PEt_3)_2]$ and *cis*-$[Pd(C_6Cl_5)_2\ dpe]$, while the starting material is recovered unchanged on using PPh_3. *cis—trans* Isomerization occurs in these reactions except for *cis*-$[Pd(C_6Cl_5)_2(bipy)]$; this difference may be attributed to the two coordinated C_6Cl_5 groups which would inhibit the formation of the pentacoordinated intermediate which is formed in the presence of free phosphines in this type of isomerization.

Recently Uson et al. reported [4] that replacement of pyridine by phosphine does not take place with *trans*-[Pd(C_6Cl_5)$_2$py$_2$]. The different behaviour may be attributed to the different configuration, and therefore to the differing ease of formation of the pentacoordinated intermediate involved in the associative substitution mechanism; formation of the intermediate will be more favoured for [Pd(C_6Cl_5)$_2$bipy] than for *trans*-[Pd(C_6Cl_5)$_2$py$_2$] where the bulky C_6Cl_5 groups would occupy axial positions. This agrees with the fact that the bulkier PPh_3 does not replace bipy; since the reaction has an associative mechanism, it must be sensitive to the volume of the entering ligand.

On trying to introduce PPh_3 in place of bipy in [NiNO$_2$(C_6Cl_5)bipy] in order to prepare [NiNO$_2$(C_6Cl_5)(PPh_3)$_2$] (not obtainable by metathesis from [NiCl(C_6Cl_5)(PPh_3)$_2$] [10]), decomposition of the starting product occurs.

The action of PPh_3 or dpe on the ionic compounds [M(C_6Cl_5) py bipy]ClO_4 does not in any case lead to replacement of bipy; in the case of the palladium complex, [Pd(C_6Cl_5)PPh$_3$bipy]ClO_4 is formed. The results are in keeping with the harder acid character of nickel as compared to palladium in [M(C_6Cl_5) py bipy]$^+$, and with the fact that both cations are harder acids than the neutral complexes mentioned above.

The action of PEt_3 on the $CHCl_3$ solutions of [M(C_6Cl_5)L bipy]ClO_4 (L = py, PPh_3) gives the neutral compounds [MCl(C_6Cl_5)(PEt_3)$_2$]. Since the reaction does not occur in solvents such as acetone, the chloride ligand which becomes attached to the metal must come from the $CHCl_3$.

Action of hydrogen chloride

The feature of the results in Table 1 is the ready decomposition of the nickel complexes, which contrasts with the behaviour of complexes containing phosphine ligands, in which the σ(Ni—C_6Cl_5) bond is not broken under these conditions [7]. The compounds containing Pd and bipy show a greater resistance towards HCl than those with Ni, but decomposition occurs on prolonged action in contrast with the behaviour of the compounds containing phosphines [9].

The action of HCl on *cis*-[Pd(C_6Cl_5)$_2$(PEt_3)$_2$] gives *cis*-[PdCl(C_6Cl_5)(PEt_3)$_2$] as the only organometallic product. The *trans* isomer is also known [9]. This is one of the few examples of organometallic compounds of phosphines and pal-

TABLE 1

ACTION OF HCl ON THE CHLOROFORM SOLUTION OF THE PENTACHLOROPHENYL COMPLEXES AT 18° C

Initial complex	Time (h)	Products
[NiX(C_6Cl_5)(bipy)]	1/2	Ni^{2+}, C_6Cl_5H
[Ni(C_6Cl_5)L(bipy)] ClO_4	1/2	Ni^{2+}, C_6Cl_5H
[Pd(C_6Cl_5)$_2$(bipy)]	6	[Pd(C_6Cl_5)$_2$(bipy)] [PdCl(C_6Cl_5)bipy], HC_6Cl_5, Pd^{2+}
[PdX(C_6Cl_5)(bipy)] [Pd(C_6Cl_5)L(bipy)] ClO_4	6	[PdX(C_6Cl_5)(bipy)], HC_6Cl_5 Pd^{2+}
cis-[Pd(C_6Cl_5)$_2$(PEt_3)$_2$]	6	*cis*-[PdCl(C_6Cl_5)(PEt_3)$_2$] HC_6Cl_5
[Pd(C_6Cl_5)$_2$(dpe)]	6	[$PdCl_2$(dpe)], HC_6Cl_5
[PdX(C_6Cl_5)(dpe)]	2.5	[$PdCl_2$(dpe)], HC_6Cl_5

ladium in which both isomers have been isolated. The configuration of *cis*-$[PdCl(C_6Cl_5)(PEt_3)_2]$ is assigned on the basis of the PMR spectrum, which shows the signals of the methyl protons as two superimposed triplets (sufficiently different, from the pseudoquintuplet observed in the *trans* isomer) partially overlapped with the signals of the methylene protons. Furthermore, the isomers give different X-ray powder diffraction patterns, melting points, and infrared spectra (bands due to ν(Pd—Cl) appear at 292 and 280 cm^{-1} for the *trans* and *cis* isomers, respectively. The solutions of *cis*-$[PdCl(C_6Cl_5)(PEt_3)_2]$ readily give the *trans* isomer on addition of a small amount of PEt_3.

The characterization of the *cis* isomer enables us to propose a *cis* configuration for its parent compound $[Pd(C_6Cl_5)_2(PEt_3)_2]$. Furthermore the latter shows a different melting point (255—256° C), from *trans*-$[Pd(C_6Cl_5)_2(PEt_3)_2]$ which melts without decomposition at 268° C and is obtained from *trans*-$[Pd(C_6Cl_5)_2(tht)_2]$ [4].

It is noteworthy that $[Pd(C_6Cl_5)_2dpe]$ is the first phosphine-containing organometallic complex of the nickel group in which the $\sigma(M—C_6Cl_5)$ bond is cleaved under the conditions used. This cannot be attributed to the *trans* effect of the phosphine on the σ(M—C) bond because such cleavage does not occur in *cis*-$[PdCl(C_6Cl_5)(PEt_3)_2]$.

TABLE 2

ANALYTICAL DATA

Compound	Found (calcd.)(%)				Decomposition temperature (°C)
	C	H	N	Total halogen	
$[Ni(NCS)(C_6Cl_5)(bipy)]$	39.1 (39.06)	1.5 (1.53)	7.9 (8.04)	33.5 (33.99)	211—215
$[Ni(NO_2)(C_6Cl_5)(bipy)]$	37.6 (37.63)	1.6 (1.71)	7.7 (8.23)	34.6 (34.79)	205—210
$[Ni(C_6Cl_5)(py)(bipy)]ClO_4$	39.2 (39.20)	2.0 (2.02)	6.5 (6.50)	32.9 (33.13)	218—220
$[Ni(C_6Cl_5)(PPh_3)(bipy)]ClO_4$	49.7 (49.41)	3.2 (2.78)	3.3 (3.39)	25.9 (25.80)	142—143
$[PdCl(C_6Cl_5)bipy]$	34.9 (35.11)	1.5 (1.47)	4.9 (5.11)	38.7 (38.89)	247—250
$[PdBr(C_6Cl_5)bipy]$	32.3 (32.47)	1.3 (1.36)	4.7 (4.73)	43.2 (43.45)	305—310
$[PdCl(C_6Cl_5)dpe]$	48.6 (48.67)	3.2 (3.06)	—	27.0 (26.93)	254—256
$[PdBr(C_6Cl_5)dpe]$	46.0 (46.08)	2.9 (2.90)	—	30.8 (30.83)	252—257
$[Pd(C_6Cl_5)_2dpe]$	45.7 (45.48)	2.4 (2.41)	—	35.3 (35.33)	275—276
cis-$[Pd(C_6Cl_5)_2(PEt_3)_2]$	34.2 (34.26)	3.6 (3.59)	—	42.2 (42.14)	255—256
cis$[PdCl(C_6Cl_5)(PEt_3)_2]$	34.4 (34.45)	4.1 (4.82)	—	34.0 (33.90)	129—131
$[Pd(C_6Cl_5)(py)(bipy)]ClO_4$	36.8 (36.53)	1.9 (1.89)	6.0 (6.08)	30.0 (30.80)	218—220
$[Pd(C_6Cl_5)(PPh_3)(bipy)]ClO_4$	45.5 (46.74)	2.7 (2.65)	3.0 (3.20)	25.0 (24.34)	190—195

Action of chlorine

Passage of chlorine through the CCl_4 solutions of the complexes leads to decomposition; in no case was formation of palladium(IV) compounds detected.

Characterization

Analytical data and decomposition temperatures for the new compounds are given in Table 2. Magnetic measurements reveal diamagnetic character, indicating square-planar geometry. Values of the molar conductivity (10^{-4} M) in anhydrous acetone at 18°C correspond to non-electrolytes for the neutral compounds (1—3 cm^2 S mol^{-1}) and to 1 : 1 electrolytes for the cationic complexes (130—140 cm^2 S mol^{-1}). They are soluble in benzene, chloroform, dichloromethane, and acetone and hardly soluble in ethanol and ether. The compounds with two pentachlorophenyl groups have low solubilities. The ionic species are sparingly soluble in non-polar solvents. Chloroform solutions of *cis*-$[PdCl(C_6Cl_5)(PEt_3)_2]$ isomerize slowly to the *trans* form. The infrared spectra show the bands due to coordinated C_6Cl_5 [9] and to the other ligands.

Experimental

Preparation of the Grignard reagents and reactions involving PEt_3 were carried out under dry oxygen-free nitrogen. $[NiCl(C_6Cl_5)bipy]$ and $[Pd(C_6Cl_5)_2bipy]$ were made by published methods [2,3].

Preparation of $[PdX(C_6Cl_5)bipy]$ (X = Cl, Br)

A solution of pentachlorophenylmagnesium halide prepared from 0.24 g of magnesium (10 mmol) and 2.8 g of hexachlorobenzene (10 mmol) in 25 ml of THF and initiated with benzyl chloride (for X = Cl) or 1,2-dibromoethane (for X = Br), was added to 2 g of $[PdCl_2bipy]$ (6 mmol). The solution was refluxed for 4 h and then concentrated. On adding methanol, $[PdX(C_6Cl_5)bipy]$ (X = Cl, Br) was precipitated. The products were recrystallized from chloroform/methanol. Yield 60—70%.

Metathetical reactions

An excess of KNO_2 or KNCS was added to 1 g of $[NiCl(C_6Cl_5)bipy]$ in 100 ml of acetone. The solution was stirred at room temperature for 2 h and then evaporated to dryness. The residue was washed with water and recrystallized from chloroform/methanol. Yields 80—90%.

Ionic compounds

$AgClO_4$ (1.1 mmol) was added to a solution of $[MCl(C_6Cl_5)bipy]$ (1 mmol) in 50—100 ml of acetone. After 30 min the AgCl formed was filtered off and an excess of L (pyridine or PPh_3) was added. The solution was stirred at room temperature for 3 h and then concentrated. On adding methanol, $[M(C_6Cl_5)L\ bipy]ClO_4$ was precipitated. The compounds were recrystallized from dichloromethane/ethanol. Yields 70%.

Replacement of bipy by phosphines

An excess of the appropriate phosphine (PEt_3, PPh_3, dpe) was added to either a suspension of $[Pd(C_6Cl_5)_2bipy]$ (1 mmol) in benzene (50 ml) or a solution of $[MX(C_6Cl_5)bipy]$ (1 mmol) in chloroform (50 ml). The mixtures were refluxed for 8 h for M = Pd and 2 h for M = Ni, except that the substitution involving dpe and M = Pd were carried out at room temperature. After concentration, methanol was added to precipitate phosphine complexes. These were recrystallized from acetone/methanol. Yields 70—80%.

Preparation of cis-$[PdCl(C_6Cl_5)(PEt_3)_2]$

A stream of HCl was passed through a suspension of *cis*-$[Pd(C_6Cl_5)_2(PEt_3)_2]$ (0.5 g) in chloroform (20 ml) for 6 h. After removal the excess of HCl and concentration, methanol was added to precipitate $[PdCl(C_6Cl_5)(PEt_3)_2]$, which was recrystallized from dichloromethane/ethanol. Yield 80%.

Analyses

C, H and N determinations were carried out at the Institute of Applied Organic Chemistry of Catalunya. Halogens were determined by Schöniger's method.

Spectra

Infrared spectra were recorded on a Beckman IR 20A spectrophotometer an and samples were prepared as KBr disks or Nujol mulls. PMR were recorded on a Perkin—Elmer R-12A using CCl_4 or $CDCl_3$ as solvents and TMS as reference.

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