Isophthalaldimine compounds of palladium, platinum and rhodium.

Hoogervorst, W.J.

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Summary

The chelate effect exhibited by a a covalently bound $\kappa C,\kappa D$ ($D = \text{coordinating group}$) didentate ligand is often used to stabilize a metal-carbon bond. By adding another chelating group to the system, in such a way that it results in a $\kappa D,\kappa C,\kappa D'$ tridentate ligand, the metal is bound stronger to the ligand system, which may result in a more stable organometallic compound. Since the first publication of such a [D-C-D] ligand system ($D = \text{phosphine}$), much research concerning this type of ligands having several donor groups 'D' has been performed. Only a limited amount of this research concerns organometallic derivatives of [D-C-D] ligands in which, next to the organic ligand, an additional organic fragment is bound to the metal. Such diorganometallic compounds are relevant to (catalytic) reactions in which C-C bonds are formed or broken.

In this thesis new research concerning the synthesis and selected reactions of palladium, platinum and rhodium compounds containing the isophthalaldimin e ligand (A, see Figure 1), which can act as a covalently bound $\kappa N,\kappa C,\kappa N'$ tridentate ligand, is described. In contrast to related [D-C-D] ligands, the isophthalaldimin e ligand had hardly been investigated. After the preparation of metal halide derivatives (B) of the isophthalaldimin e ligand, it was attempted to convert these compounds into organometallic derivatives, which may have two coordinating hydrocarbon fragments in a trans configuration (C). Such compounds are relevant in view of reductive elimination processes and C-C bond activation reactions.

Figure 1.

The first research concerning late-transition metal chemistry of isophthalaldimin e ligands performed in our laboratory is described in chapter 2. Unfortunately, attempts to selectively ortho,ortho metallate the ligand (1, $X = \text{H}$, see Scheme 1) were unsuccessful. Fortunately, a selective cyclopalladation has resulted in two isophthalaldimin e palladium(II) chloride compounds (2, see Scheme 1). The best applicable route for the preparation of palladium halide derivatives of the isophthalaldimin e ligand bearing a broad range of imine substituents
appeared to be the oxidative addition of a carbon-bromine bond to a palladium(0) precursor which resulted in isophthalaldimine palladium(II) bromide compounds (3, see Scheme 1).

Several compounds 3 have been subjected to a transmetallation with methyl lithium, dimethylzinc, tetramethyltin and lithium trimethylsilylacetylide. However, none of these reactions has resulted in the observation of a diorganopalladium compound. In the reactions with the methyl lithium in some cases a transmetallation occurred, but in each case side reactions, such as addition to an imine moiety, occurred. In the reactions in which a transmetallation took place (R = isopropyl, 4-methoxyphenyl), next to side products, also a reductively C-C coupled product (4) was observed (Scheme 2). In other reactions (e.g. R = 2,6-diisopropylphenyl) only undesired reactions took place. The reaction with lithium trimethylsilylacetylide was more selective and a clean transmetallation occurred, after which a reductively C-C coupled product (5) was obtained (Scheme 2).

Unfortunately, no detailed insight in the reductive C-C coupling processes has been gained. If the diorganopalladium compounds are formed, they are thermally unstable. When comparing the isophthalaldimine ligand system to other [D-C-D] type ligands, which have been investigated by other research groups, it becomes clear that comparable diorganopalladium compounds containing the bis(dimethylaminomethyl)phenyl [N-C-N] ligand system are also unstable. If, instead of imines or amines, the stronger coordinating phosphines are used as donor groups in a [D-C-D] ligand, its organopalladium derivatives are stable at room temperature.
In chapter 3 a number of isophthalaldimine platinum(II) bromide compounds (6, Scheme 3, \( R = \text{methyl to 2,6-diisopropylphenyl} \)) is described, which have been prepared via oxidative addition of a 2-bromo-isophthalaldimine 1 to a platinum(0) precursor. Attempts to transmetallate compounds 6 with methyl lithium were not successful due to a derailment of the reaction caused by the high reactivity of methyl lithium towards the isophthalaldimine ligand system. In contrast to this, if the milder dimethylzinc is applied, a clean transmetallation and a stable isophthalaldimine platinum(II) methyl compound (7, Scheme 3) is formed for sterically demanding imine substituents \((R = 2,6\text{-dimethylphenyl, 2,6-diisopropylphenyl})\). For compound 7 \((R = 2,6\text{-diisopropylphenyl})\), a single crystal X-ray structure analysis has been determined, which is the first structure of a trans aryl platinum methyl compound.

If compound 7 \((R = 2,6\text{-diisopropylphenyl})\) is subjected to additional ligands such as carbon monoxide or pyridine this results in the displacement of one imine moiety and the formation of 8, see Scheme 4. The complex formed isomerizes to 9, see Scheme 4. In the case of \(L = \) carbon monoxide the isomerization only takes place photochemically.
In chapter 4 the investigations of the transmetallation of isophthalaldimine platinum(II) bromide compounds (6) and lithium acetylides (R' = SiMe₃, p-tolyl) is described, see Scheme 5. The structure of the diorganoplatinum(II) compounds formed appears to be very much influenced by the substituent on the imine moiety. For the sterically demanding substituents tert-butyl, cyclohexyl and 2,6-diisopropylphenyl, analogously to the transmetallation described in chapter 3, a trans-diorganoplatinum compound (10) has been isolated. For the smaller aryl substituents phenyl, 4-methylphenyl, 4-methoxyphenyl and 3,5-dimethylphenyl cis-diorganoplatinum compounds (11) are formed, which are dimers via mutual π-bonding of the platinum-acetylide moieties. For aryl substituents with an intermediate size, also cis-diorganoplatinum compounds (12) are formed, however, these are not dimers and contain a non-coordinating acetylide moiety. In compounds 12 a THF molecule is probably coordinated to the platinum.

The postulated interconversions between compounds 6, 10, 11 en 12 have been depicted in Scheme 5. In the metathesis step a compound of type 10 is formed. During the reaction this compound can react with an additional lithium acetylide, which results in the formation of 12. Although their structures are much related, it has been established that 12 is not involved in the formation of 11. If the imine substituents are relatively small, 10 may dimerize and isomerize to furnish 11.

If compound 10 (R = 2,6-diisopropylphenyl) is subjected to additional ligands (carbon monoxide or pyridine), after a (reversible) displacement of an imine moiety, analogous to chapter 3 (Scheme 4), compounds 13 are formed, see Scheme 6. Isomerization of compounds 13 results in the formation of compounds 14, of which structural analogues are formed when compounds 11 (R = 4-methylphenyl or R = 4-methoxyphenyl) are subjected to the same additional ligands (carbon monoxide or pyridine).
Chapter 5 concerns the synthesis and reactivity of isophthalaldimine rhodium(III) compounds. Oxidative addition of a 2-bromo- or 2-iodo-isophthalaldimine to a rhodium(I) chloride dimer results in a mixture of three isophthalaldimine rhodium(III) dihalide compounds (15, Scheme 7) in a 1:2:1 ratio, which is the result of exchange and statistical redistribution of the chloride and bromide or iodo anions. The isolated mixtures can be converted to pure isophthalaldimine rhodium(III) dibromide or diiodide compounds by an anion exchange with sodium bromide or sodium iodide. From these compounds, in which rhodium is five-coordinated, the six-coordinated adducts with an additional THF, water, pyridine or triphenylphosphine ligand were formed.

The transmetallation of the isophthalaldimine rhodium(III) dihalide compounds with dimethylzinc results in the formation of stable five-coordinated isophthalaldimine rhodium(III) methyl halide compounds (16, Scheme 7).
Final remarks

This thesis concerns organometallic chemistry of several late transition metals with the isophthalaldimine ligand. A number of new palladium, platinum and rhodium derivatives, which have a metal-carbon bond, have been prepared. These compounds are thermally stable organometallic compounds due to the strong coordination of the imine moieties to the covalently bound metal. For platinum and rhodium also organometallic derivatives, which have a second organic fragment bound to the metal, have been isolated. In the isophthalaldimine ligand system the imine substituents can be easily varied, which results in a tunable metal surrounding. In most of the metal complexes the isophthalaldimine ligand acts as a tridentate ligand, but also a didentate coordination mode appeared to be possible.

Although the metal complexes of the isophthalaldimine ligand show much similarities to the related complexes of bis(amine) and bis(phosphine) ligand systems, the isophthalaldimine ligand is much more rigid. In the isophthalaldimine ligand, which, due to conjugation and minimization of steric hindrance, will have the structure D (Figure 2), the angles α and β are fixed and only a rotation around the aryl-C=N bond is possible. During the formation of a metal derivative of the isophthalaldimine ligand by activation of, for example, a Caryl-X bond, this rigidity will hamper the precoordination of the imine moieties to the metal (E, Figure 2), compared to an amine or phosphine analog. This may explain the relative reluctance of these systems, as compared to the related amine and phosphine analogues, to undergo C-H activation of the ipso C-H bond.

![Figure 2.](image)

The isophthalaldimine ligand seems to be a rather versatile ligand for late transition metals and the first explorations in this hardly investigated area described in this thesis, are inviting to perform further research aimed at other metals, C-element bond activation and polymerization reactions.