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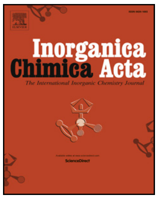

Research paper

Oxidative addition of methylene chloride to Me-DuPhos complexes of palladium and rhodium

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ABSTRACT

Oxidative addition of methylene chloride to Pd((*R*,*R*)-Me-DuPhos)(L) (**1**–**3**; L = P(*t*-Bu)$_3$, PCy$_3$, or *trans*-stilbene) gave Pd((*R*,*R*)-Me-DuPhos)(CH$_2$Cl)(Cl) (**4**). Treatment of [Rh(COD)(Cl)]$_2$ with (*R*,*R*)-Me-DuPhos at low temperature in THF or CH$_2$Cl$_2$ afforded [Rh((*R*,*R*)-Me-DuPhos)(Cl)]$_2$ (**5**). At room temperature, these reactions also gave the byproduct [Rh((*R*,*R*)-Me-DuPhos)$_2$][Cl], which was prepared independently as the BF$_4$ salt **6**. When **5** was generated in CH$_2$Cl$_2$, oxidative addition of both C—Cl bonds yielded the bridging carbene complex (Rh((*R*,*R*)-Me-DuPhos)(Cl))$_2$(μ-Cl)$_2$(μ-CH$_2$) (**8**). Both **6** and **8** were crystallographically characterized.

1. Introduction

Oxidative addition, a fundamental process in organometallic chemistry and catalysis, has been studied in detail for such classic substrates as H$_2$, MeI, or aryl halides [1]. Oxidative addition involving less reactive molecules is more challenging, but also potentially useful. For example, methylene chloride is commonly used as an unreactive solvent, but it can also be a substrate in stoichiometric and catalytic C—Cl oxidative addition processes. This metal-mediated cleavage is an important step in such processes as Pd-catalyzed carbonylation [2] and alkoxycarbonylation [3], and in metal-catalyzed cross-coupling with Grignard reagents [4]. Metal-catalyzed hydrodechlorination of CH$_2$Cl$_2$ is of interest for environmental remediation of this chlorinated pollutant [5], and dichloromethane has also been used as a source of the CH$_2$ fragment for studies of Fischer-Tropsch type C—C bond formation [6].

To understand the individual steps in such catalytic processes, stoichiometric examples of methylene chloride oxidative addition have been studied in detail, with comparison to other C—Cl activations [7], to develop structure-reactivity relationships and to identify ligands which promote this reaction. In this manuscript, we focus on palladium and rhodium complexes, for which several well-defined examples of single and double C—Cl oxidative addition of methylene chloride are known. For example, Pd(PCy$_3$)$_2$(dba) (dba = dibenzylideneacetone) reacted with methylene chloride solvent at room temperature to yield *trans*-Pd(PCy$_3$)$_2$(CH$_2$Cl)(Cl) (**A** in Chart 1), but less basic phosphines such as P(CH$_2$Ph)$_3$ or PPh$_3$ did not induce this reaction [2]. Similar oxidative additions of CH$_2$Cl$_2$ to Pd(0) phosphine complexes with monodentate ligands gave *trans* complexes **B**-**C** [8], while bidentate ligands yielded *cis* products **D**-**E** [9–11]. Rhodium(I) phosphine complexes, in contrast, often yielded dinuclear products featuring a bridging carbene group via oxidative addition of both C—Cl bonds (**F**-**G**, Chart 1) [12].

Although these examples include a variety of phosphine ligands, with different P-substituents, steric demand, and, for the chelates, bite angles, no chiral phosphines have been used. To investigate the possibility of *asymmetric* catalytic processes using CH$_2$Cl$_2$ as a reagent [2–4,13], we report here use of the commercially available electron-rich chiral bis(phosphine) (*R*,*R*)-Me-DuPhos (1,2-Bis[(2*R*,5*R*)-2,5-*dimethylphospholano*]benzene) [14] to support oxidative addition of methylene chloride to Pd(0) and Rh(I) complexes.

2. Results and discussion

2.1. Oxidative addition of CH$_2$Cl$_2$ to Pd(0) Me-DuPhos complexes

Reduction of Pd((*R*,*R*)-Me-DuPhos)Cl$_2$ with NaBH(OMe)$_3$ in the presence of a bulky tertiary phosphine gave the three-coordinate complexes Pd((*R*,*R*)-Me-DuPhos)(PR$_3$) (R = *t*-Bu (**1**), Cy (**2**), Scheme 1) [15], which were identified by their characteristic A$_2$X ^{31}P{^{1}H} NMR spectra (J = 91 and 96 Hz, respectively). We previously reported

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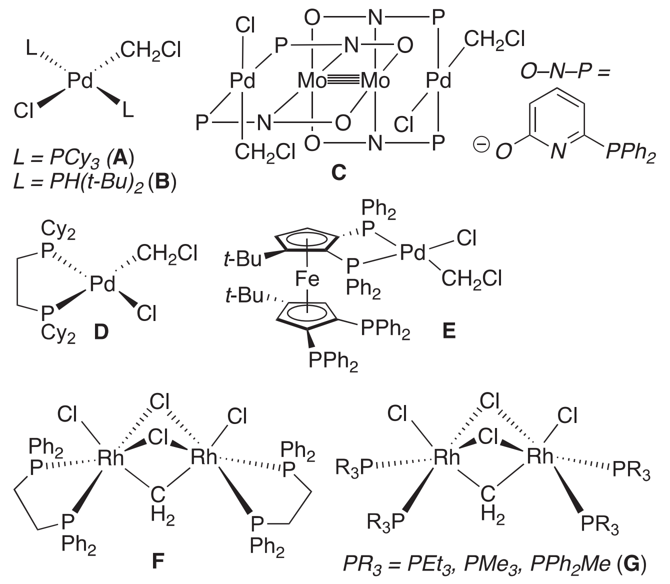


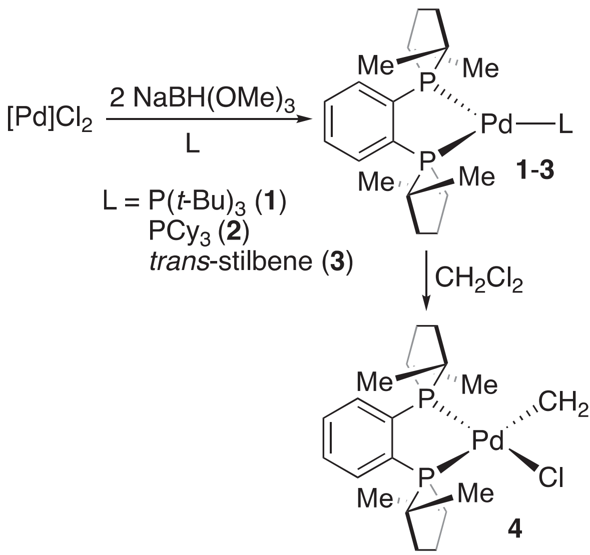
Chart 1. Palladium and Rhodium Phosphine Complexes Formed by Oxidative Addition of Methylene Chloride.

synthesis of Pd((*R,R*)-Me-DuPhos)(*trans*-stilbene) (**3**) by a similar route [16]. Attempts to isolate phosphine complexes **1–2** resulted in decomposition to yield $Pd(Me\text{-}DuPhos)_2$ [17], which was formed immediately in similar reactions with PPh_3, P(*o*-Tol)$_3$ and PEt_3, in which three-coordinate species were not observed.

When CH_2Cl_2 was added to **1–3**, a rapid reaction gave the air-stable yellow oxidative addition product, Pd((*R,R*)-Me-DuPhos)(CH_2Cl)(Cl) (**4**, Scheme 1), which was identified by elemental analyses and multinuclear NMR spectroscopy. As in **D** and **E** (Chart 1 [9]), the ^{31}P NMR nuclei *trans* to the CH_2Cl and Cl groups were inequivalent, giving rise to signals at δ 78.9 and 72.1 (C_6D_6), with $J_{PP(cis)}$ = 27.5 Hz. The chloromethyl group in **4** was identified by a $^{13}C\{^1H\}$ NMR signal at δ 37.9 (d, J_{PC} = 141 Hz) in $CDCl_3$. With the chiral DuPhos ligand, the CH_2Cl ^1H nuclei were inequivalent, giving rise to two signals at δ 4.71 and 4.00 (C_6D_6). These protons coupled to each other (J_{HH} = 6 Hz) and to both DuPhos ^{31}P nuclei (J_{PH} = 3 and 1 Hz, for δ 4.71, and J_{PH} = 11 and 1 Hz, for δ 4.00), giving rise to doublet of doublet of doublet patterns.

2.2. Synthesis of Rh(I) Me-DuPhos complexes

As recently reported [18], treatment of $[Rh(COD)(Cl)]_2$ with (*R,R*)-Me-DuPhos at low temperature in THF gave [Rh((*R,R*)-Me-DuPhos)(Cl)]$_2$ (**5**, Scheme 2; COD = 1,5-cyclooctadiene). At room temperature, the undesired cation [Rh((*R,R*)-Me-DuPhos)$_2$][Cl] (**6**), as well as the unsymmetrical dimer [Rh(COD)(μ-Cl)$_2$Rh((*R,R*)-Me-DuPhos)] (**7**), were also formed and identified by $^{31}P\{^1H\}$ NMR spectroscopy. Reactions using other Rh(I) precursors bearing cyclooctadiene, cyclooctene, or norbornadiene ligands also produced some of cation **6** [18]. We made similar observations, and independently prepared **6** as the BF_4 salt from $[Rh(COD)_2][BF_4]$ and two equiv of Me-DuPhos (Scheme 2). The crystal structure of **6** (Fig. 1, CCDC 1553938; see also the Supporting Information for details of the crystal and molecular structures) showed the expected square planar coordination with small distortions, presumably caused by the DuPhos bite angle of 83.94(3)°. The structure was similar to that of the related *o*-phenylenebis(phosphine) complex $[Rh(dppbz)_2]^+$ (dppbz = *o*-$C_6H_4(PPh_2)_2$, Table 1) [19], with slightly larger angular distortions, perhaps due to steric differences between the PPh_2 and 2,5-dimethylphospholanyl donor groups.



Scheme 1. Oxidative Addition of Methylene Chloride to Pd(0) Me-DuPhos Complexes ([Pd] = Pd((*R,R*)-Me-DuPhos)).

2.3. Oxidative addition of CH_2Cl_2 to a Rh(I) Me-DuPhos complex

Switching the solvent for the reaction of $[Rh(COD)(Cl)]_2$ with 2 equiv of Me-DuPhos from THF to CH_2Cl_2 gave similar results, with an added twist, as shown by monitoring the mixtures with $^{31}P\{^1H\}$ NMR spectroscopy (Scheme 2). As in THF, at room temperature, a mixture of bis-chelate cation **6**, Cl-bridged dimer **5**, and unsymmetrical dimer **7** was initially formed [18]. Slow addition of Me-DuPhos at −78 °C in THF [18] or CH_2Cl_2 selectively gave **5**; in CH_2Cl_2, only a little (6%) of **6** was formed. Cation **6** was inert under these conditions, but complex **5**, whether generated at −78 or 25 °C, reacted further with the CH_2Cl_2 solvent at room temperature via oxidative addition to yield the yellow dinuclear Rh(III) complex (Rh(*R,R*)-Me-DuPhos)(Cl))$_2$(μ-Cl)$_2$(μ-CH_2) (**8**, Scheme 2). Complex **8** was easily separated from the byproducts by selective crystallization, and then characterized by elemental analysis, mass spectrometry, and NMR spectroscopy. The inequivalent ^{31}P nuclei in **8** (δ 91.9 and 88.3, CD_2Cl_2) showed a *cis* J_{PP} of 14 Hz and Rh-P couplings of 153 and 154 Hz, respectively. The μ-CH_2 group gave rise to a broad ^1H NMR signal at δ 4.31 and a $^{13}C\{^1H\}$ NMR triplet ($J_{Rh\text{-}C}$ = 21 Hz) at δ 48.6 in CD_2Cl_2. The structure of **8** (Fig. 2, CCDC 1553931; see the Supporting Information for more details) was similar to those of analogous bridging carbene dirhodium complexes derived from methylene chloride (see structures **F**-**G** in Chart 1, and Table 2) [12].

3. Conclusions

Me-DuPhos supports oxidative addition of methylene chloride under mild conditions to Pd(0) or Rh(I) complexes. The resulting chiral metal-chloromethyl and μ-carbene complexes are now available for further investigation of stoichiometric and catalytic transformations of these groups. In particular, we hope to extend the Pd(Me-DuPhos)-catalyzed asymmetric cross-coupling of secondary phosphines PH(R)(R') with aryl iodides, which gave enantiomerically enriched P-stereogenic tertiary phosphines PAr(R)(R') [20], to methylene chloride. This reaction might enable catalytic asymmetric synthesis of P-stereogenic chloromethylphosphines, P(CH_2Cl)(R)(R') [21], in which nucleophilic attack at the CH_2Cl group could give bidentate bis(phosphines) [22]. In addition, we plan to investigate conversion of the chlorides in rhodium μ-CH_2 complex **8** to hydride or alkyl ligands, as models for C−H and C−C bond formation in Fischer-Tropsch type processes [23].