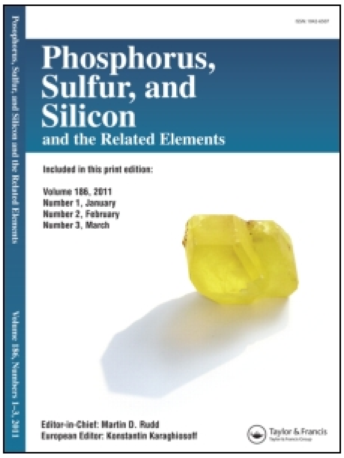

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Precious Metal-Phosphine Complexes for Homogeneous Catalysis: Synthesis and Characterization of a Complete Series of $Cp_2Fe(PPh_2)_2MX_2$ (M = Pt, Pd; X = Cl, Br, I, Ph)

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$Cp_2Fe(PPh_2)_2$ complexes of PdX_2(X = Cl, Br) and PtX_2(X = Cl, Br, I, Ph) have been synthesized in nearly quantitative yield with excellent purity by reacting the respective norbornadiene or 1,5-cyclooctadiene metal complexes with dppf. The palladium iodide complex, $dppfPdI_2$ has been isolated in 98 % yield by a 1:2 mole reaction of $dppfPdCl_2$ with NaI. Methods have been developed to isolate these complexes with and without the solvent (usually CH_2Cl_2) in the lattice. These compounds have been characterized by elemental, FTIR, multi-nuclear FTNMR and in some cases by single crystal X-Ray.

Keywords: ferrocenyl phosphine complexes of Pd and Pt; homogenous catalysts; NMR

INTRODUCTION

About a decade ago Hayashi reported the synthesis and superior catalytic activity of $dppfPdCl_2$ over the conventional bidentate phosphine complexes[1]. He attributed the higher catalytic activity and selectivity of this complex to its large bite angle, 99.07°. Since then several publications and patents appeared in the literature on the applications of $dppfPdCl_2$ in synthetic organic chemistry with respect to C-C couplings[2], chiral chemistry for enantiomeric catalysis[3] and also in supramolecular chemistry for the synthesis of macromolecular squares[4]. Our recent study on the synthesis and X-ray characterization of $dppfPtPh_2$ and $dppfPtI_2$ indicated that these complexes have larger bite angles[5] in comparison to the reported structure of $dppfPtCl_2$[6], explaining the role of substituents on the P-M-P bite angle. In order to make a systematic comparison of structural and catalytic studies, we decided to synthesize a complete series of dppfMX$_2$ (M = Pt, Pd and X = Cl, Br, I, Ph) compounds. The results of the study are summarized in this paper.

EXPERIMENTAL

The inert atmosphere techniques and instruments used in this study are the same as in the earlier report[5]. The precursors such as (NBD)MX$_2$, (COD)MX$_2$ and dppf were synthesized in the development lab using our methods[7]. The elemental assay were done at E & R Microanalytical Lab, NY and Robertson Microlit, NJ.

TABLE I. dppfMX$_2$ compounds isolated with yield and physical data.

Compounds	Method	Solvent	Yield	Color	M.p
dppfPdCl$_2$.S	(NBD)PdCl$_2$ + L	CH$_2$Cl$_2$	95%	orange red	290°C dec.
dppfPdCl$_2$	(NBD)PdCl$_2$ + L	acetone	96%	orange red	260°C dec.
dppfPdBr$_2$	(NBD)PdBr$_2$ + L	acetone	95%	purple red	295°C dec.
dppfPdBr$_2$.S	(COD)PdBr$_2$ + L	CH$_2$Cl$_2$	98%	purple red	305°C dec.
dppfPdI$_2$	dppfPdCl$_2$ + NaI	acetone	98%	violet	310°C dec.
dppfPtCl$_2$.S	(COD)PtCl$_2$ + L	CH$_2$Cl$_2$	95%	yellow	335°C dec.
dppfPtBr$_2$.S	(COD)PtBr$_2$ + L	CH$_2$Cl$_2$	97%	yellow	310°C dec.
dppfPtI$_2$.S	(COD)PtI$_2$ + L	CH$_2$Cl$_2$	96%	yellow	320°C dec.
dppfPtPh$_2$.S	(COD)PtPh$_2$ + L	CH$_2$Cl$_2$	97%	yellow	192°C dec.

General procedure for the synthesis of dppfMX$_2$: 10 mmols of dppf and (NBD)MX$_2$ or (COD)MX$_2$ were stirred at RT in the presence of acetone or CH$_2$Cl$_2$ (100ml) for an hour. The reaction mixture was then concentrated to ca. 20 ml under vacuum and ether (100 ml) was added. The crystalline solid was filtered, washed with ether and dried under vacuum to isolate 95-98% yield of dppfMX$_2$(M= Pt, X= Cl, Br, I, Ph; M = Pd, X= Cl, Br). Since dppfPdI$_2$ can not be synthesized by this route due to the unavailability of the NBD or COD precursor, it was synthesized by adding 21.3 mmol of NaI in a solution of 50 ml acetone to a stirred (15 min) mixture of dppf (10 mmol) and (COD)PdCl$_2$ (10 mmol) in 100 ml acetone. The mixture was stirred further for about 15 minutes, reduced the volume under vacuum to ca. 20 ml and ether (100 ml) was added to precipitate the product. The solid was filtered, washed thoroughly with 30% aqueous ethanol (125 ml), alcohol (50 ml) and ether (50 ml), and dried under vacuum. All the compounds gave satisfactory elemental assay.

RESULTS AND DISCUSSION

Table I shows the summary of the reactions carried out in the study. Reactions performed in CH_2Cl_2 give dppfMX_2.nCH_2Cl_2, where n = 0.33 -1, while acetone has been used to make the solvent free complexes. All the compounds have been isolated in very good yield with excellent purity. The synthesis of complexes using (NBD)MX_2 seems to be a new method. The PdI_2 complex, dppfPdI_2 has been synthesized by the halogen displacement method in ca. 98% yield, which is a far superior yield compared to the recently reported[8] modest to moderate yield synthesis of a similar complex, dpppPdI_2. Compounds, dppfMX_2 (M =Pd, X = Br, I; M = Pt, X= Br) have not been reported earlier, while dppfPtPh_2 and dppfPtI_2 have been reported recently by us[5].

TABLE II. ^{31}P, ^{1}H and ^{13}C NMR spectral data of dppfMX_2 in CD_2Cl_2

Atom	dppfPtCl_2	dppfPtBr_2	dppfPdCl_2	dppfPdBr_2	dppfPdI_2
P (δ) PPM	13.3	12.5	34.5	31.5	25
$^{2}J_{P-P'}$ (Hz)	11.2	7.3	19.7	22.6	5.3
$^{1}J_{Pt-P}$ (Hz)	3778.7	3729.3	--	--	--
C1 (δ) PPM	73.1	73.7	74.4	75.1	75.8
$^{1}J_{P-C1}$ (Hz)	70.7	66.7	56.5	54.3	48.5
$^{3}J_{P-C1}$ (Hz)	0.2	3.8	7.1	6.6	6.5
H2 (δ) PPM	4.21	4.2	4.22	4.2	4.16
C2 (δ) PPM	76.2	76.1	76.7	76.7	76.6
$^{2}J_{P-C2} + {}^{4}J_{P-C2}$ (Hz)	10.7	10.4	10.7	10.7	10.5
H3 (δ) PPM	4.39	4.37	4.42	4.4	4.37
C3 (δ) PPM	74.4	74.3	74.5	74.4	74.1
$^{3}J_{P-C3} + {}^{5}J_{P-C3}$ (Hz)	8.0	8.0	7.8	7.5	7.4
C4 (δ) PPM	131.3	132.2	132.3	133.2	134.5
$^{1}J_{P-C4}$ (Hz)	67.1	66.6	57.7	56.8	54.5
$^{3}J_{P-C4}$ (Hz)	~0	1.0	~0	~0	0.5
$^{2}J_{Pt-C4}$ (Hz)	26.9	30.6			
H5 (δ) PPM	7.86	7.89	7.89	7.9	7.89
C5 (δ) PPM	135.3	135.3	135.3	135.4	135.5
$^{2}J_{P-C5} + {}^{4}J_{P-C5}$ (Hz)	11.1	10.9	11.8	11.5	11.3
H6 (δ) PPM	7.42	7.43	7.44	7.44	7.43
C6 (δ) PPM	128.3	128.2	128.5	128.4	128.2
$^{3}J_{P-C6} + {}^{5}J_{P-C6}$ (Hz)	11.6	11.6	11.6	11.4	11.3
H7 (δ) PPM	7.52	7.52	7.54	7.53	7.51
C7 (δ) PPM	131.6	131.6	131.7	131.6	131.4
$^{4}J_{P-C7}$ (Hz)	2.6	2.8	2.7	< 3	2.8

^1H, ^{13}C and ^{31}P NMR chemical shifts and scalar couplings were obtained in CD_2Cl_2 using the previously described methods[5]. All multiplet patterns are high order and the J values were generally not directly derived from line separations, but from computer simulation[5]. The J values in Table II are given as absolute values. However, $^1J_{P\text{-}C}$ and $^3J_{P'\text{-}C}$ for C1 and C4 are of similar sign for all complexes to get proper computer simulations. Pt satellites were observed at C2 and C5 for $dppfPtCl_2$ and $dppfPtBr_2$, but values could not be obtained since the satellites were broader than the parent peaks and they overlapped lines 1 and 5 of pentuplet pattern for these carbons. Generally ^1H shifts, ^{13}C shifts and P-C couplings exhibited only small changes on changing the metal or halogen. Pd complexes gave higher frequency ^{31}P shifts than the Pt complexes, as expected from their positions in the periodic table[9]. There was little pattern that could be discerned from the $^2J_{P\text{-}P'}$ coupling constants. We earlier observed that the $^2J_{P\text{-}P'}$ is 7.0 and 15.8 Hz ($CDCl_3$) for $dppfPtI_2$ and $dppfPtPh_2$ respectively[5]. For a given halogen the Pd complex had a larger $^2J_{P\text{-}P'}$ than the Pt complexes due to their respective positions in the periodic table[9]. However, for a given metal it is presently difficult to precisely comment on the effects of X substituent and the bite angle on $^2J_{P\text{-}P'}$ due to the unavailability of the X-ray structures of $dppfPdX_2$ (X = Br and I) and $dppfPtBr_2$. These effects as well as the catalytic activities of these complexes will be described in a future publication.

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