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Substitution and cyclometallation reactions on Pt(II) phosphite complexes

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ABSTRACT

This paper describes the formation of newseries of platinum(II) complexes with phosphite and phosphine ligands. Treatment of *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$] with 2 equimolar of L, L = $P(O^iPr)_3$orP$(OPh)_3$, then adding 2 equimolar of L′, L′ = PPh_3 or 4-MePy, gave*cis*-[Me_2PtLL'] complexes,**1a**–**4a**, with some side products. Otherwise, reaction of *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$] with 4 equimolar of Me_2SO, then adding 2 equimolar of PPh_3, gave*cis*-[$Me_2Pt(Me_2SO$–$\kappa S)(PPh_3)$]. Addition of 1 equimolar of L, L = $P(OPh)_3$ and$P(O^iPr)_3$ and substitution of Me_2SO occurred to give*cis*-[Me_2PtLL']complexes, **2a** and **4a** with more selectivity. In order tocontrol steric and electronic effects of the ligands, 2 and 4 equimolar of $P(OPh)_3$ were added to *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$] during refluxing and complexes **1b**, [MePt(C^P))SMe_2)] and **2b**, [MePt(C^P){$P(OPh)_3$}],(C^P = {(κ^2-C,P)$P(OPh)_2(OC_6H_4)$})were formed respectively. With adding 1 equimolar of L, L = PPh_3, 4-MePy to complex **1b**, the products of substitution reactions were [MePt(C^P)L], **3b** and**4b**.

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1. Introduction

Chemists are interested in phosphines and phosphites due to the effects of their wide varieties of steric and electronic properties on manipulating the chemical behavior of complexes by changing the substitutions at the phosphorus atom [1–3]. Organometallicphosphite complexes are employed in a variety of metal catalyzed processes such as hydrogenation, hydroformylation, and hydrocyanation [4–6], but owing to the ability of phosphites to do Arbuzov-rearrangment [7] they are more reactive than phosphine analogues and also high solubility of their platinum complexes in organic solvents [8], made them to be less investigated in comparison with phosphine complexes.

Platinum complexes containing both phosphine and phosphite ligands have been rarely reported [9,10], besides, there are some examples of these complexes with other metals [11–13]. The first reason for this is difficulty of finding a suitable precursor which can decrease the electronic competition between phosphorus ligands during the reaction. So using a starting material with possibility of dissociating a coordinated ligand as a result of possessing the fragments and also inducing potential catalytic activity to the complexes [14], might be helpful. The second restrictive reason in synthesizing [$L_2Pt(PR_3)${$P(OR)_3$}] complexes refers to different size of phosphorous ligands which makesteric hindrance for entering the second ligand during the substitution.

In the present work Pt(II) complexes containing two different π-acceptor phosphorus ligands were synthesized such as [Me_2PtLL'] in which L = $P(OPh)_3$ or $P(O^iPr)_3$, L′ = $P(O^iPr)_3$, PPh_3 or 4-MePy from different precursors to examine their effect on substitution mechanism. Besides, in order to control electronic and steric effects of phosphorus ligands; some orthometallated complexes such as [MePt(C^P)L] in which C^P = {(κ^2-C,P)$P(OPh)_2(OC_6H_4)$} and L = $P(OPh)_3$, PPh_3, SMe_2 and 4-MePy were synthesized by C–H activation of triphenylphosphite ligand.

2. Experimental section

The ^{1}HNMR spectra were recorded on BrukerAvance DPX 250 MHz and BrukerAvance500 MHz Ultrashield spectrometers. ^{31}PNMR spectra were recorded on a BrukerAvance DRX 500 MHz and BrukerAvance400 MHz Ultrashield spectrometers. References were TMS (^{1}H) and H_3PO_4 (^{31}P). All the chemical shifts and coupling constants are in ppm and Hz, respectively. The phosphite complexes are usually oily and very soluble in organic solvents such as acetone, n-hexane and diethylether, therefore complete removal of solvent at the end of work up stage was not easy and this has

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usually been reflected in the microanalytical results. The dimeric precursor *cis*,*cis*-$[Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2]$ [15] and *cis*-$[Me_2P(Me_2SO{-}\kappa S)(PPh_3)]$ [16] were prepared by the literature methods. Triphenylphosphite $P(OPh)_3$, triisopropylphosphite $P(O^iPr)_3$, triphenylphosphine (PPh_3), 4-methylpyridine (4-MePy) and solvents were used as commercially available chemicals without any purification.

2.1. Cis-$[Me_2Pt\{P(OPh)_3\}(4\text{-}MePy)]$, **1a**

To a solution of *cis*,*cis*-$[Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2]$, (10 mg, 0.0174 mmol) in acetone (5 mL) 9.5 μL (0.035 mmol, 2 equimolar) of $P(OPh)_3$ was added. After stirring at room temperature for 1 h, the product was *cis*-$[Me_2Pt\{P(OPh)_3\}(SMe_2)]$. To the latter solution, 3.5 μL 4-MePy (0.035 mmol, 2 equimolar) was added. This was stirred at room temperature for 1 h. The solvent was removed under vacuum. The yellow oily product was obtained. Yield:60%.Anal. Calc. for $C_{26}H_{28}O_3NPPt$: C, 49.7; H, 4.5; N,2.2%. Found: C,49.0; H,4.5; N, 2.4%. NMR data in $CDCl_3$: δ (^{1}H) = 0.25 [d, ^2J(PtH) = 66.6 Hz, ^3J(PH) = 11.5 Hz, 3H, Me ligand *trans* to $P(OPh)_3$], 0.79 [d, ^2J(PtH) = 86.3 Hz, ^3J(PH) = 8.9 Hz, 3H, Me ligand *cis* to $P(OPh)_3$], 2.24 [s, 3H, methyl group of 4-methylpyridine], 7.81 [d,^3J(PtH) = 22.5 Hz, ^3J(HH) = 5.3 Hz, 2H, H^2 and H^6 of 4-methylpyridine], 8.30 [d, 2H, H^3 and H^5 of 4-methylpyridine], 6.50–7.50 [Ph groups on $P(OPh)_3$ ligand]; δ (^{31}P) = 117.4 [s, ^1J(PtP) = 3357.0 Hz, P on $P(OPh)_3$ ligand].

2.2. Cis-$[Me_2Pt\{P(OPh)_3\}(PPh_3)]$, **2a**

To a solution of *cis*-$[Me_2Pt(Me_2SO{-}\kappa S)(PPh_3)]$ (10 mg, 0.0177 mmol) in CH_2Cl_2 (5 mL) 4.8 μL (0.0177 mmol, 1 equimolar) of $P(OPh)_3$ was added. After stirring at room temperature for 2 h, the solvent was removed under vacuum to yield a white residue and then washed with 2 mL of diethylether. Yield:66.7%. Anal. Calc. for $C_{38}H_{36}O_3P_2Pt$: C, 57.2; H, 4.6%. Found: C,57.9; H,4.7%. NMR data in $CDCl_3$: δ (^{1}H) = 0.24 [dd, ^2J(PtH) = 68.5 Hz, ^3J(PH) = 10.1 Hz, ^3J(PH) = 9.1 Hz, 3H, Me ligand *trans* to $P(OPh)_3$], 0.72 [dd, ^2J(PtH) = 71.8 Hz, ^3J(PH) = 8.7 Hz, ^3J(PH) = 6.9Hz, 3H, Me ligand *cis* to $P(OPh)_3$], 6.60–7.70 [Ph groups on $P(OPh)_3$ and PPh_3 ligands]; δ (^{31}P) = 31.4 [d, ^1J(PtP) = 1775.5 Hz, ^2J(PP) = 14.9, P on PPh_3 ligand], 120.2 [d, ^1J(PtP) = 3269.4 Hz, ^2J(PP) = 14.9, P on $P(OPh)_3$ ligand].

2.3. Cis-$[Me_2Pt\{P(O^iPr)_3\}(4\text{-}MePy)]$,**3a**

Complex **3a** was made similarly using method for **1a**.Yield:65%.NMR data in $CDCl_3$: δ (^{1}H) = 0.28[d, ^2J(PtH) = 63.2 Hz,^3J(PH) = 10.5 Hz, 3H, Me ligand *trans* to $P(O^iPr)_3$],0.61 [d, ^2J(PtH) = 85.0 Hz,^3J(PH) = 7.9 Hz, 3H, Me ligand *cis* to $P(O^iPr)_3$],1.19 [d, ^3J(HH) = 6.2 Hz, 12H, 4Me of ^{i}Pr groups], 1.35 [d, ^3J(HH) = 6.2 Hz, 6H, 2Me of ^{i}Pr groups],2.33 [s, 3H, methyl group of 4-methylpyridine], 4.80[m, 3H, CH of ^{i}Pr groups], 7.77 [d,^3J(PtH) = 18.2 Hz, ^3J(HH) = 6.3 Hz, 2H, H^2 and H^6 of 4-methylpyridine], 8.36 [d, 2H, H^3 and H^5 of 4-methylpyridine].

2.4. Cis-$[Me_2Pt\{P(O^iPr)_3\}(PPh_3)]$, **4a**

Complex **4a** was made similarly using method for **2a**. Yield:%80. NMR data in $CDCl_3$: δ (^{1}H) = 0.04 [t, ^2J(PtH) = 64.4 Hz, ^3J(PH) = 9.3 Hz, 3H, Me ligand *trans* to PPh_3], 0.67 [t, ^2J(PtH) = 70.8 Hz, ^3J(PH) = 8.4 Hz, 3H, Me ligand *cis* to PPh_3], 0.93 [d, ^3J(HH) = 6.2 Hz, 12H, 4Me of ^{i}Pr groups], 1.26 [d, ^3J(HH) = 6.3 Hz, 6H, 2Me of ^{i}Pr groups], 4.60 [m, 3H, CH of ^{i}Pr groups], 7.00–7.70 [Ph groups on PPh_3 ligand]; δ (^{31}P) = 32.9 [d, ^1J(PtP) = 1757.0 Hz, ^2J(PP) = 22.5, P on PPh_3 ligand], 128.6 [d, ^1J(PtP) = 3153.0 Hz, ^2J(PP) = 22.5, P on $P(O^iPr)_3$ ligand].

2.5. [MePt(C^P)(SMe_2)], **1b**

A mixture of *cis*,*cis*-$[Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2]$, (10 mg, 0.0174 mmol) and $P(OPh)_3$ (0.035 mmol, 2equimolar) in 5 mL of toluene was refluxed at 70 °C for 1 h under Ar. Removal of all the volatiles under reduced pressure gave an oily yellow mixture, which was washed three times with diethylether (3*1 mL). The oily product was soluble in many organic solvents. Yield:75%. NMRdata in $CDCl_3$: δ (^{1}H) = 0.72 [d, ^2J(PtH) = 65.7 Hz, ^3J(PH) = 10.2 Hz, 3H, Me ligand], 2.33 [s, ^3J(PtH) = 28.8 Hz, 6H, 2Me of SMe_2 ligand], 6.80–7.40 [Ph groups on $P(OPh)_3$ ligand], 7.80 [dd, ^3J(PtH) = 70.6 Hz, ^4J(PH) = 7.6 Hz,^3J(HH) = 1.5Hz, H, CH group adjacent to C atom of C^P]; δ (^{31}P) = 151.5 [s, ^1J(PtP) = 3105.0 Hz, P on $P(OPh)_3$ ligand].

2.6. [MePt(C^P){$P(OPh)_3$}], **2b**

Cis,*cis*-$[Me_2Pt(\mu\text{-}SMe_2)_2PtMe_2]$, (10 mg, 0.0174 mmol) was added to the solution of $P(OPh)_3$ (0.070 mmol, 4 equimolar) in toluene (5 mL). The reaction mixture was refluxed for 30 h at 105 °C under Ar. Next, the solvent was evaporated *in vacuo* and then the mixture was washed three times with diethylether (3*1 mL) and gave an oily colorless product. Yield: 98.5%. Anal. Calc. for $C_{37}H_{32}O_6P_2Pt$: C, 53.6; H, 3.9%. Found: C,52.8; H,4.0%. NMR data in $CDCl_3$: δ (^{1}H) = 0.31 [dd, ^2J(PtH) = 67.7 Hz, $^3J(P_{trans}H)$ = 9.7 Hz, $^3J(P_{cis}H)$ = 7.6 Hz, 3H, Me ligand], 6.50–7.20 [Ph groups on $P(OPh)_3$ ligand], 7.70 [ddd, ^3J(PtH) = 56.7 Hz, $^4J(P_{cis}H)$ = 7.7 Hz, $^4J(P_{trans}H)$ = 9.4 Hz,^3J(HH) = 1.6Hz, H, CH group adjacent to C atom of C^P]; δ (^{31}P) = 120.8 [d, ^1J(PtP) = 3606.7 Hz, ^2J(PP) = 25.3, P on $P(OPh)_3$ ligand], 155.0 [d, ^1J(PtP) = 2852.4 Hz, ^2J(PP) = 25.3, P on C^P ligand].

2.7. [MePt(C^P)(PPh_3)], **3b**

To a solution of [MePt(C^P)(SMe_2)] (20 mg, 0.035 mmol) in toluene (5 mL) was added PPh_3 (9.15 mg, 0.035 mmol). The mixture was stirred at room temperature for 1 h. The solvent was removed under reduced pressure and the oily yellow product was obtained. Yield:75%. NMRdata in $CDCl_3$: δ (^{1}H) = 0.63 [dd, ^2J(PtH) = 66.5 Hz, $^3J(P_{trans}H)$ = 9.6 Hz, $^3J(P_{cis}H)$ = 7.6 Hz, 3H, Me ligand], 6.80–7.80 [Ph groups on $P(OPh)_3$ and PPh_3 ligands], 7.90 [t, ^3J(PtH) = 56.6 Hz, $^4J(P_{cis}H)$ = $^4J(P_{trans}H)$ = 6.0Hz, H, CH group adjacent to C atom of C^P]; δ (^{31}P) = 31.6 [d, ^1J(PtP) = 1867.0 Hz, ^2J(PP) = 17.8, P on PPh_3 ligand], 150.8 [d, ^1J(PtP) = 3058.0 Hz, ^2J(PP) = 17.8, P on $P(OPh)_3$ ligand].

2.8. [MePt(C^P)(4-MePy)], **4b**

This complex was prepared following a synthetic procedure similar to **3b**, described above. Yield:75%. NMR data in $CDCl_3$: δ (^{1}H) = 0.53 [d, ^2J(PtH) = 67.0 Hz, ^3J(PH) = 10.7 Hz, 3H, Me ligand], 2.21 [s, 3H, methyl group of 4-methylpyridine], 7.80–7.10 [Ph groups on $P(OPh)_3$ ligand],7.60 [d, ^3J(PtH) = 70.2 Hz, ^4J(PH) = 7.3Hz, H, CH group adjacent to C atom of C^P], 7.85 [d, ^3J(PtH) = 26.1 Hz, ^3J(HH) = 7.3 Hz, 2H, H^2 and H^6 of 4-methylpyridine], 8.35 [d, 2H, H^3 and H^5 of 4-methylpyridine; δ (^{31}P) = 148.5 [s, ^1J(PtP) = 3059.0 Hz, P on C^P ligand].

3. Results and discussion

3.1. Synthesis and substitution reactions of P-donor complexes

Since synthesized platinum(II) complexes containing both phosphine and phosphite ligands have been rarely reported, some efforts for producing such complexes is tabloid in current paper.

Starting from synthesis of monophosphite complexes, *cis*-[$Me_2PtL(SMe_2)$], L = $P(O^iPr)_3$, $P(OPh)_3$, as precursors [17] followed by *in situ* adding of 1 equimolar of L′ ligand (L′ = PPh_3, 4-MePy) to produce *cis*-[Me_2PtLL'] does not act 100% selective. As depicted in Scheme 1, after 1 h stirring reaction at room temperature, not only the predicted monosubstituted complex *cis*-[Me_2PtLL'], is formed, but also two disubstituted complexes *cis*-[Me_2PtL_2] and *cis*-[$Me_2PtL'_2$] are seen in the mixture of the reaction. Repeating the reaction in three solvents, tetrahydrofuran, acetone, and toluene makes the same results. For more investigation, it was decided to examine the formation of the precursors more carefully. It was found that the reaction of 1 equimolar of *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$] complex with 2 equimolar of the phosphite ligand L, L = $P(O^iPr)_3$ or $P(OPh)_3$, produces ~80%*cis*-[$Me_2PtL(SMe_2)$] and ~20% *cis*-[Me_2PtL_2] with small amount of the unreacted complex that sometimes can be seen in *cis*-[$Me_2Pt(SMe_2)_2$] form [18]. So in the next step adding 2equimolar of L′, caused formation of a mixture of products. Even by adding 1.5 equimolar of L, the same trend can be seen.

For getting more selectivity, another dimethylplatinum precursor,*cis*-[$Me_2Pt(Me_2SO{-}\kappa S)_2$]was chosen to react with 1 and 2 equimolar of PPh_3. The monosubstituted complex *cis*-[$Me_2Pt(Me_2$-$SO{-}\kappa S)(PPh_3)$], and disubstituted complex *cis*-[$Me_2Pt(PPh_3)_2$]were formed respectively, as Romeo et al. have pointed out [16]. Note that reaction of the starting complex *cis*-[$Me_2Pt(Me_2SO{-}\kappa S)_2$] with 1 equimolar. ofL (L = $P(O^iPr)_3$,$P(OPh)_3$)gives approximately 60% *cis*-[$Me_2Pt(Me_2SO{-}\kappa S)$L], 20% *cis*-[$Me_2PtL_2$] with 20% starting complex, as can be seen in Scheme 2.

All these observations could be explained in terms of the associative and dissociative substitution mechanisms which can be determined according to different nucleophilic discrimination of precursor and intermediate complexes and also diversity in leaving groups and nucleophilicity of entering groups which affect on electron density and steric hindrance of the complexes. In *cis*-[$Me_2Pt(Me_2SO{-}\kappa S)_2$], trans influence of strong σ-donors, i.e., methyl groups can induce bond weakening at the leaving group, Pt–S bond, leading to formation of a three coordinated intermediate. Moreover, the stabilization by the remaining set of three in plane ligands of 14-electron intermediate without changing the singlet ground state plays an important role in promoting reaction via a dissociative pathway [19,20]. Unlike [$Me_2Pt(Me_2S)$], three-coordinate [$Me_2Pt(Me_2SO{-}\kappa S)$] complex, has a sufficient long lifetime to distinguish different nucleophiles because of the tendency for the oxygen of the remaining sulfoxide to satiate the lack of electron by partial interaction at the vacant coordination site, as shown in Scheme 3 [21,22].

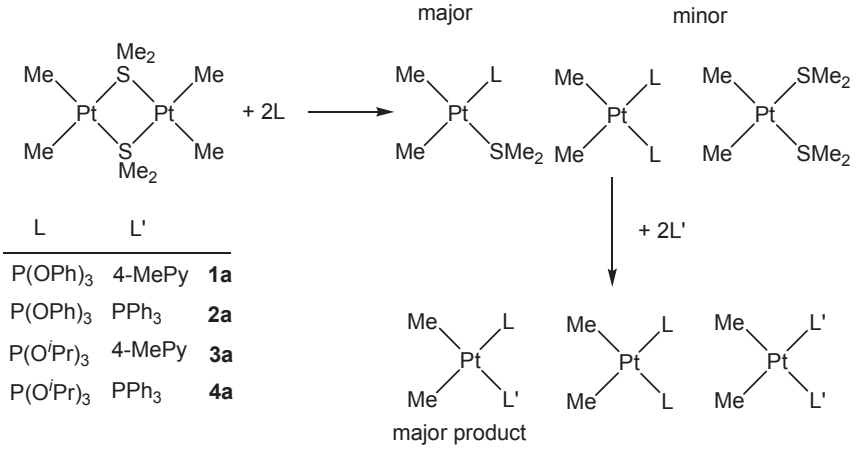
In addition, high electron density at the metal prevents the approach of the axially incoming nucleophile and forming penta-coordinated intermediate [16]. It seems that in *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$] precursor, two bridged SMe_2 can not produce enough electron density on two platinum center, thus associative substitution is preferred.

As Romeo et al. investigated the kinetic parameters of reaction of *cis*-[$Me_2Pt(Me_2SO{-}\kappa S)(PPh_3)$], with 1 equimolar of py ligand in $CHCl_3$ solution and found that this reaction proceed via a dissociative mechanism [16], it is likely that the reaction of 1 equimolar of nucleophiles (L = $P(O^iPr)_3$ or $P(OPh)_3$) with *cis*-[$Me_2Pt(Me_2$-$SO{-}\kappa S)(PPh_3)$], may also obey the dissociative mechanism due to low π-acceptor ability of PPh_3 as compared to L and high σ-donor ability of PPh_3 that induces high electron density at the metal center. As mentioned, synthesis of a complex holding one *cis* π-acceptor ligand (Me_2SO, $P(O^iPr)_3$, $P(OPh)_3$, 4-MePy)with one stronger σ-donor ligand (SMe_2, PPh_3) in a dimethylplatinum(II) complex, caused stability of complex, as well as, making the reaction proceed with high selectivity.

$^1H{-}^{31}P$ Heteronuclear Multiple Bond Correlation(HMBC)NMR spectrum of **2a** in $CDCl_3$ is depicted in Fig. 1. In the ^1H NMR spectrum of **2a**, two 1:1 triplets (each further coupled with the Pt center) at δ = 0.24, for Me ligand trans to $P(OPh)_3$, and at δ = 0.72, for Me ligand trans to PPh_3, are observed. The lower ^2J(PtH) value for the first signal, as compared to that of the second one, is due to the higher trans influence of $P(OPh)_3$ than PPh_3. In the ^{31}P NMR spectrum, two doublets at δ = 31.4 ppm with ^1J(PtP) = 1775.5 Hz for PPh_3 ligand and at δ = 120.2 with ^1J(PtP) = 3269.4 Hz and ^2J(PP) = 14.9 Hz for $P(OPh)_3$ ligand are observed. Two most important variables determining ^{31}P NMR chemical shifts and coupling constants are the electronegativity of substituents on phosphorus and the cone angle [23,24].

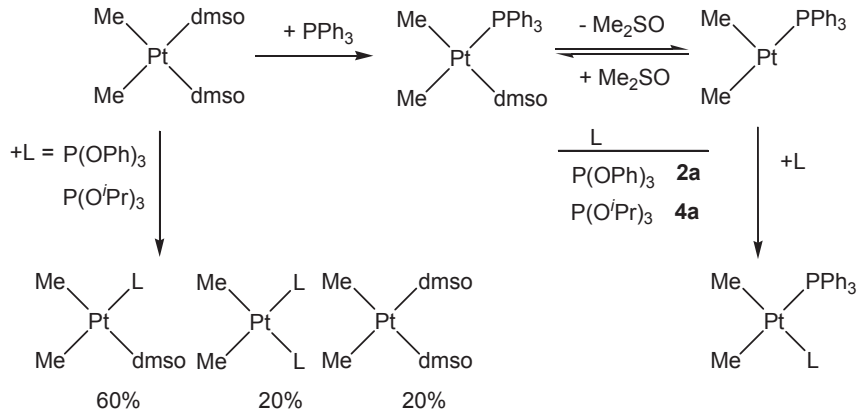
The complex **4a**, is similarly identified. In ^1H NMR spectrum in addition of two methyl groups coordinated to platinum, there can be seen two doublets in 2:1 ratio at δ = 0.93 [^3J(HH) = 6.2 Hz] resulting from the four methyl groups of two ^{i}Pr groups directed away from phosphorus lone pair, and at δ = 1.26 [^3J(HH) = 6.3 Hz] resulting from two methyl groups of the third ^{i}Pr group, taking up position toward the lone pair. Also the corresponding CH groups of ^{i}Pr, each appeared as two sets with relative intensity 2:1 at 4.60 ppm shows sufficient evidence of conformation of $P(O^iPr)_3$ in this complex [25,26].

For better comparison, selected ^1H NMR and$^{31}P\{^1H\}$ NMR data of new complexes and some analogues that have been reported

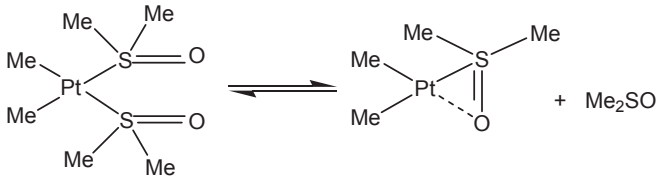


L	L'	
$P(OPh)_3$	4-MePy	**1a**
$P(OPh)_3$	PPh_3	**2a**
$P(O^iPr)_3$	4-MePy	**3a**
$P(O^iPr)_3$	PPh_3	**4a**

Scheme 1.



Scheme 2.



Scheme 3.

M-P(OR)$_3$ bond, so trans influence of P(O^{i}Pr)$_3$ is more than P(OPh)$_3$ and ^2J(PtH^a) of Me trans to it, is smaller. Also ^{31}P NMR chemical shift of P(O^{i}Pr)$_3$ is downfield compared to that of P(OPh)$_3$. In [Me$_2$Pt{P(OPh)$_3$}L] complexes (L = P(OPh)$_3$, PPh$_3$, SMe$_2$, 4-MePy) the ^1J(PtP^a) coupling increases slightly by changing the *cis* ligands in the sequence of P(OPh)$_3$ < PPh$_3$ < SMe$_2$ < 4-MePy, this is the same trend in ^2J(PtH^b) which shows that *cis* and *trans* influence are in the order of P(O^{i}Pr)$_3$ > P(OPh)$_3$ > PPh$_3$ > SMe$_2$ > 4-MePy. Also the small

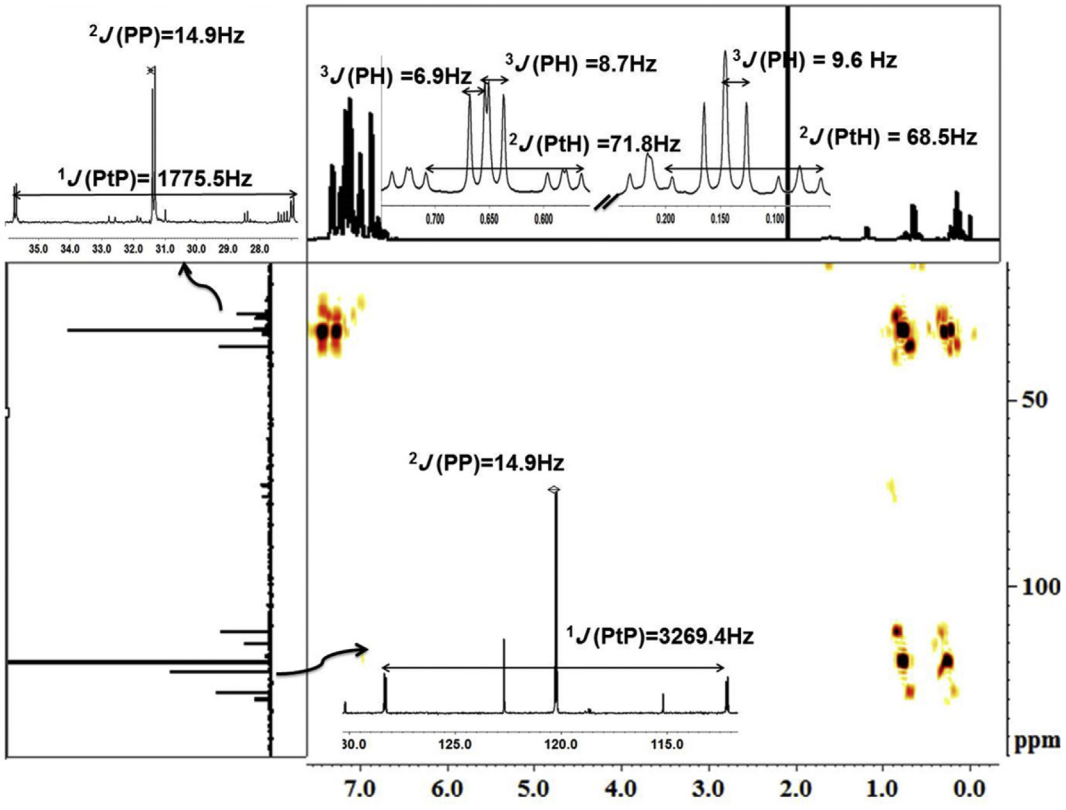
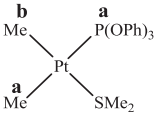
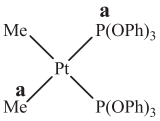
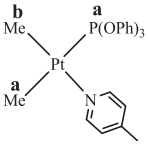
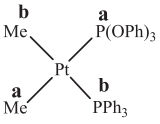
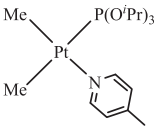
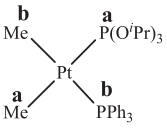


Fig. 1. ^{1}H–^{31}P HMBC NMR spectrum of *cis*-[Me$_2$Pt{P(OPh)$_3$}(PPh$_3$)] in CDCl$_3$.

previously [17] are collected in Table 1. According to ^2J(PtH^a) in [Me$_2$Pt{P(OPh)$_3$}(PPh$_3$)],**2a**, and [Me$_2$Pt{P(O^{i}Pr)$_3$}(PPh$_3$)], **4a**, σ-donor ability in P(OR)$_3$ ligands plays a dominating role in forming a magnitudes of the coupling constants, ^2J(PP) (Tables 1 and 2) are consistent with coupling between *cis*-phosphorus ligands [27,28].

Table 1
^{1}H and $^{31}P\{^{1}H\}$NMR data of non-cyclometallated *cis*-[Me_2PtLL'] complexes in $CDCl_3$. The chemical shifts and coupling constants are in ppm and Hz, respectively.

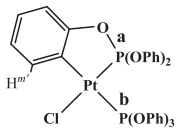
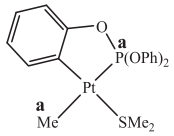
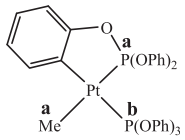
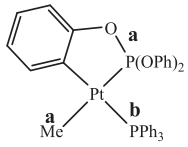
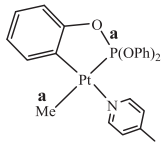
Structure	^{1}H NMR		$^{31}P\{^{1}H\}$ NMR		
	$\delta(CH_3)^a$ $^{2}J(PtH)$ $^{3}J(P^aH)$,$^{3}J(P^bH)$	$\delta(CH_3)^b$ $^{2}J(PtH)$ $^{3}J(P^aH)$, $^{3}J(P^bH)$	$\delta(P)^a$ $^{1}J(PtP)$	$\delta(P)^b$ $^{1}J(PtP)$	$^{2}J(P^aP^b)$
	0.36 65.4 Hz 10.8 Hz	0.80 85.8 8.9	116.1 3343.0		
Ref. [11]					
	0.14 70.6 7.8		119.8 3036.1		
Ref. [11]					
 1a	0.25 66.6 11.5	0.79 86.3 8.9	117.4 3357.0		
 2a	0.24 68.5 10.1, 9.1	0.72 71.8 6.9, 8.7	120.2 3269.4	31.4 1775.5	14.9
 3a	0.28 63.2 10.5	0.6 85.0 7.9			
 4a	0.04 64.4 9.3	0.67 70.8 8.4	128.6 3153.0	32.9 1757.0	22.5

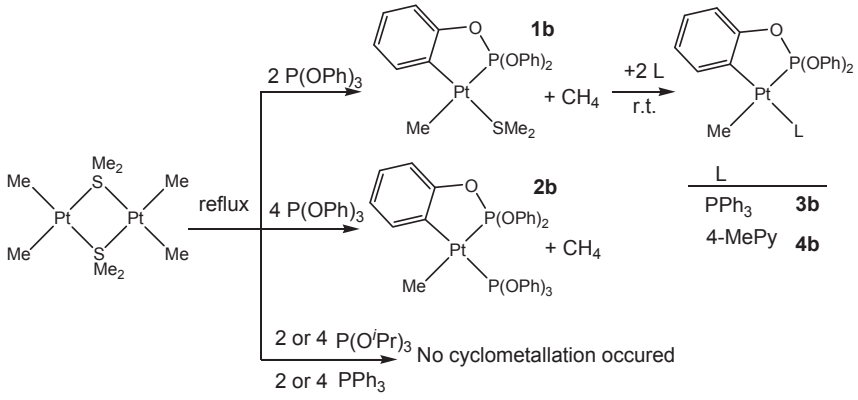
3.2. Synthesis and orthometallation reactions of the complexes

As part of continuing investigation of phosphorus complexes of the platinum metal, the results on the orthometallation reactions of triphenylphosphite in dimethylplatinum(II) complexes are reported in this section. Orthometallated complexes containing the unit M{(κ^2-C,P)P(OPh)$_2$(OC_6H_4)} are commonly made by heating complexes of triphenylphosphite in high boiling aromatic solvent since the process of intramolecular C–H activation is usually slow at room temperature [12,29,30] and strong tendency to afford sterically favoured, five-membered chelate rings is observed. The synthetic methods used to prepare the desired complexes are described in Scheme 4. Treatment of *cis*,*cis*-[$Me_2Pt(\mu$-$SMe_2)_2PtMe_2$], with 2 equimolar of $P(OPh)_3$ ligand in toluene at 70 °C for 1 h gives orthometallated complex **1b**, *cis*-[MePt(SMe_2){(κ^2-C,P)P(OPh)$_2$(OC_6H_4)}]. Start of cyclometallation reaction is predictable by observing a color change in solution from colorless to some yellow. This metal-carbon bond formation reaction involves activation of *ortho*-CH group of a phenyl moiety of triphenylphosphite and gives rise to a product with sterically favoured five-membered chelate rings in a good yield. SMe_2 as a leaving group vapors during the reaction with respect to high temperature of solution and passing argon gas during the reaction that causes an irreversible reaction. It was found that coordinated SMe_2 ligand, was easily substituted with entering ligands. So adding 1 equimolar of L (L = PPh_3, 4-MePy) to complex **1b** at room temperature, produced **3b** and **4b**.

In addition, orthoplatinated complex **2b**, is prepared by refluxing *cis*-[$Me_2Pt\{P(OPh)_3\}_2$], for 30 h in toluene in 105 °C. For further examination, we followed the progression of the reaction of *cis*-[$Me_2Pt\{P(OPh)_3\}_2$] in closed NMR tube in toluene-d_8 by ^{1}HNMR and $^{31}P\{H\}$ NMR which is shown in Fig. 2. During rising the temperature from 25°Cto 100 °C in 8 h, ^{1}HNMR shows one triplet signal at $\delta = 0.91$ ppm for methyl group in aliphatic region and three signal in aromatic region due to three kinds of hydrogens in phenyl ring, in 1:2:2 ratio, Fig. 2a. When the temperature of the sample is gradually raised from 100 °C–105 °C, conversion of *cis*-[$Me_2Pt\{P(OPh)_3\}_2$] to orthometallatedC^P complex **2b**,starts. During the course of the reaction, methane (CH_4) is formed and its signal is observed at $\delta = 0.21$ Hz, with no evidence for deuterated methane. Also a downfield signal with Pt satellites appears at 7.99 ppm for $H^{m\prime}$ (CH group adjacent to C atom of C^P) with coupling with

Table 2
^{1}H and $^{31}P\{^{1}H\}$NMR data of orthometallated *cis*-[XPt(C^P)L] complexes in $CDCl_3$.The chemical shifts and coupling constants are in ppm and Hz, respectively.

Structure	^{1}H NMR		$^{31}P\{^{1}H\}$ NMR		
	$\delta(CH_3)^a$ $^{2}J(PtH)$ $^{3}J(P^aH),^{3}J(P^bH)$	$\delta(H^{m'})$ $^{3}J(PtH)$ $^{4}J(P^aH),\ ^{3}J(P^bH)$	$\delta(P)^a$ $^{1}J(PtP)$	$\delta(P)^b$ $^{1}J(PtP)$	$^{2}J(P^aP^b)$
		12.0	100.5 6371.0	112.8 3229.0	29.0
Ref. [27]					
 1b	0.72 65.7 10.2	7.80 70.6 7.6	151.5 3105.0		
 2b	0.31 67.7 9.7, 7.6	7.70 56.3 7.7, 9.4	155.0 2852.4	120.8 3606.7	25.3
 3b	0.63 66.5 9.6, 7.6	7.90 56.6 6.0, 6.0	150.8 3058.0	31.6 1867.0	17.8
 4b	0.53 67.0 10.7	7.60 70.2 7.3	148.5 3059.5		



Scheme 4.

phosphorus through four bonds and having 1:3 ratio relative to methyl ligand. These are conspicuous evidences of forming new orthometallated complex **2b** (Fig. 2b).

Fig. 3 shows the $^{31}P\{^{1}H\}$NMR spectrum at 105 °C in the middle of reaction (after 16 h) with the expected singlet signal at $\delta = 123.2$ ppm showing the presence of *cis*-$[Me_2Pt\{P(OPh)_3\}_2]$, which cleanly disappears when the reaction is completed. 98.5% conversion to the orthometallated complex **2b** is achieved by refluxing the reaction mixture for 30 h. The nonequivalence of the two phosphorus donors is indicated by the observation of two resonances as two doublet signals a t$\delta = 120.8$ [$^{1}J(PtP) = 3606.7$ Hz] and 155.0 [$^{1}J(PtP) = 2852.4$ Hz]. The anomalous downfield signal

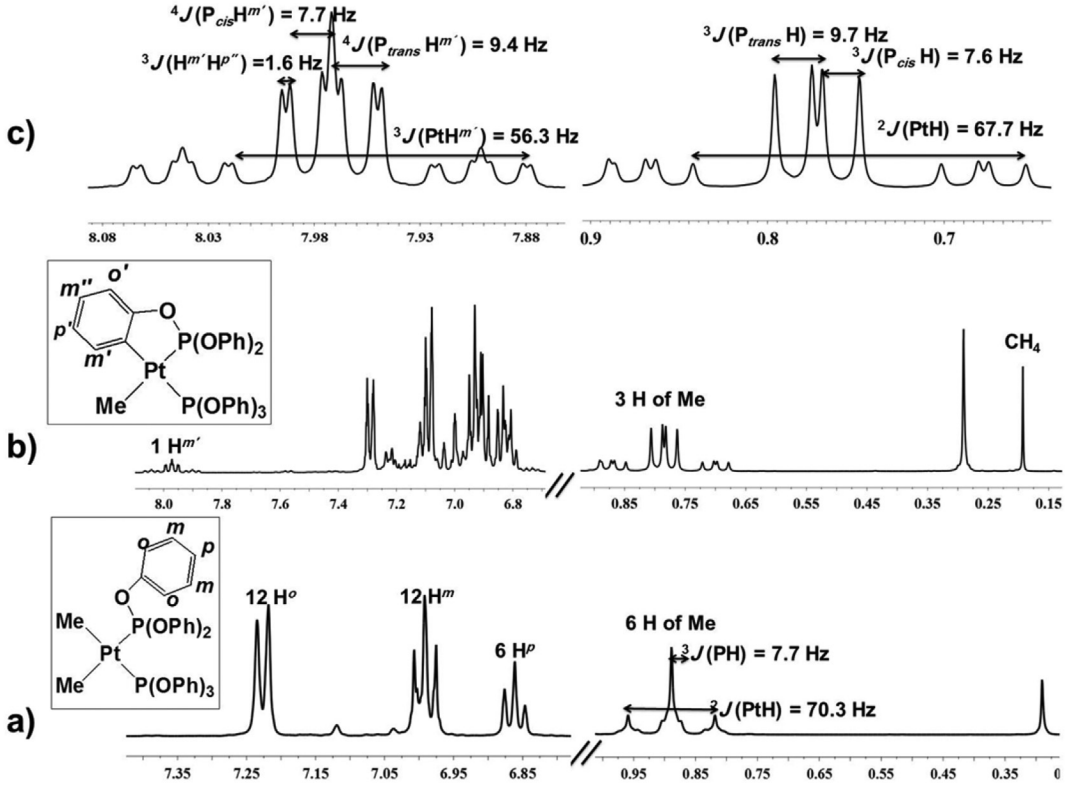


Fig. 2. ^{1}HNMR spectra of a) *cis*-[$Me_2Pt\{P(OPh)_3\}_2$] at 25–100 °C; b) *cis*-[$MePt\{(\kappa^2$-C,P)$P(OPh)_2(OC_6H_4)\}\{P(OPh)_3\}$], **2b**, after 30 h heating; c) expansion of b. in toluene-d_8. Assignments are given on the spectra.

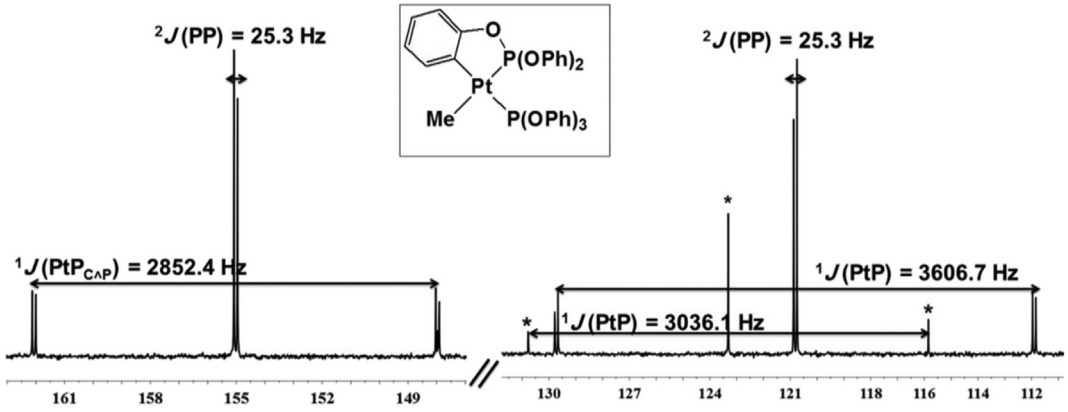


Fig. 3. ^{31}P NMR spectra of **2b** in the middle of the reaction, after 16 h reflux in toluene-$d_8$at 105 °C; unreacted *cis*-[$Me_2Pt\{P(OPh)_3\}_2$] is shown by *. Assignments are given on the spectrum.

observed at 155.0 ppm gives further support for the occurrence of orthometallation of triphenylphosphite because of appreciable differences between the electronic environment of phosphorus in cyclometallated and non-cyclometallated phosphite ligands [31]. As a result, $^1J(PtP^a)$ decreases because of decreasing π-acceptor ability of orthometallated phosphite and reduced electron density of platinum center as a result of elimination of one methyl ligandbut $^1J(PtP^b)$ increases because of changing its *trans* ligand and smaller *trans* influence of aryl compared to methyl group.

When the reaction is monitored by ^{1}H NMR spectroscopy, there is no evidence for the formation of a M − H bond in −20 to 2 ppm region in any of the spectra to assign any intermediate of oxidative addition. However, it should be mentioned that, for most cyclometallation processes, determination of the exact mechanism is far from being understood and experimental data does not provide convincing evidence.

It is reported that the ease of orthometallation of [$X_2Pt\{P(OPh)_3\}_2$] complexes depend on the tendency of X for acting as a leaving group and in comparison with dihalide platinum complexes (X = Cl, Br) [32] the rate of orthometallation of dimethyl complexes decreases due to higher methyl–platinum bond strength. Additionally, the smaller $^2J(PtP^a)$ observed in the *cis*-[$MePt(C\hat{}P)\{P(OPh)_3\}$] compound compared to that in *cis*-[$ClPt(C\hat{}P)\{P(OPh)_3\}$] indicates the larger *trans* effect of Me relative to chloride ligand. Also *cis*-[$ClPt(C\hat{}P)\{P(OPh)_3\}$] complex resonates at higher field. These observations show *trans* influence in the trend of

Me > Ph > Cl which should be noticed that it may be a result for these complexes that contain a phenyl derivative in a chelate form and the reverse behavior (Me < Ph) in other complexes has been reported previously [33,34]. Data of complexes **3b** and **4b** are summarized in Table 2 and can be interpreted in the same manner as above.

It is worthy of mention that attempts to form cyclometallated complexes with two other phosphorus ligands, PPh_3 and $P(O^iPr)_3$, under the same reaction conditions were unsuccessful.

4. Conclusion

Different precursors can perform reactions with different mechanisms due to different leaving group and spectator ligands. In order to synthesize dimethyl platinum(II) complexes containing both phosphite and phosphine ligands with high selectivity it is better to use some starting materials such as $[Me_2Pt(Me_2SO-\kappa S)_2]$ with possibility of dissociating a coordinated ligand. Also, the steric and electronic factors of phosphorus ligands which influence the reaction can be adjustable with orthometallation of $P(OPh)_3$ ligand. Orthometallation for formation of a five-membered chelate, leads to both a larger downfield shift in the ^{31}P chemical shift and also a smaller $^1J(Pt-P)$ in a cyclometallated ring relative to those in the non-cyclometallated species.

Acknowledgment

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