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Cyclometallation of trimesitylphosphine

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Abstract

Synthetic and spectral (^{1}H, ^{13}C and ^{31}P NMR) details are presented for the formation of cyclometallated palladium(II) and platinum(II) dimers by reaction of trimesitylphosphine with MCl_2 and MCl_2Y_2 ($M = Pd$, Pt; $Y = CH_3CN$, PhCN, $\frac{1}{2}$COD) and for the corresponding halide metathesis products. These dimers are very stable with a strong M–C bond. There were no non-cyclometallated products isolated and cyclopalladation is definitely more facile than cycloplatination. The latter two observations are unusual with respect to the known reactivity of phosphines with palladium(II) and platinum(II) centres. Geometric isomerism is observed for the Pt species.

Introduction

The relevance of internal metallation of various organic ligands to homogeneous catalysis has prompted many studies, including several involving tertiary phosphine ligands [1,2]. Shaw and co-workers [3] have clearly shown that bulky substituents on phosphorus increase the tendency for cyclometallation although rigorous reaction conditions are usually required. Possible mechanisms and the various factors influencing cyclometallation of tertiary phosphines have been discussed [3,4] but are incompletely understood. Nevertheless, it has been generally accepted that cyclometallation is favoured for platinum(II) over palladium(II).

Our structural studies of steric effects in tertiary phosphine complexes led us to investigate the chemistry of trimesitylphosphine in several environments [5]. The question of whether or not this very bulky ligand [2,6] would undergo internal metallation with palladium(II) and platinum(II) centres increased in interest when we found no evidence for the internal metallation of tri-*o*-tolylphosphine in Pt(P-*o*-tolyl$_3$)$_2$X$_2$ ($X = Cl$, I) [7]. A preliminary communication of the present study has appeared elsewhere [8].

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Experimental

General

Palladium and platinum dichloride were used as received (Johnson-Matthey and Mallory Ltd.) or converted into the more soluble acetonitrile, benzonitrile or cycloocta-1,5-diene adducts by literature methods [9]. Trimesitylphosphine was commercially available (Organometallics Inc.) and used as received.

Reactions were carried out in non-aqueous media under dinitrogen using standard Schlenk-line procedures. Solvents were dried by standard methods. Purification of crude products was effected by column chromatography on silica gel (Baker 60–200 mesh) followed by recrystallization. All products were dried several days in vacuo prior to physical measurements.

Physical measurements

Elemental analyses were performed by MHW Laboratories, Phoenix, Arizona and decomposition points were measured in unsealed capillary tubes on a Gallenkamp Melting Point Apparatus calibrated against a series of melting point standards. Infrared spectra (525–180 cm^{-1}) were recorded on a PE-180 spectrophotometer as Nujol mulls between polyethylene plates. The ^{1}H, ^{13}C and ^{31}P NMR spectra were acquired on a Bruker WH-400 spectrometer operating in the pulsed FT mode at 400.13, 100.61 and 161.98 MHz respectively at 297 K. Sample solutions were prepared in $CDCl_3$ and chemical shifts to high frequency of the reference positions for TMS (^{1}H and ^{13}C) or external 80% H_3PO_4 (^{31}P) each defined as exactly zero, are positive.

Preparation of complexes

$[Pd(Pmes_2C_6H_2(CH_3)_2CH_2)(Cl)]_2$. A mixture of $PdCl_2(PhCN)_2$ (0.190 g, 0.500 mmol) and $Pmes_3$ (0.389 g, 1.000 mmol) in CH_2Cl_2 (20.0 cm^3) was stirred at ambient temperatures (0.5 h) and reduced to dryness to give a pale yellow residue which was washed several times with n-hexane and then chromatographed (50% CH_2Cl_2/n-hexane). The yellow fraction collected was reduced to dryness, washed with low boiling point petroleum ether and recrystallized from CH_2Cl_2/n-hexane to afford yellow needles, yield 0.160 g (98.1%).

The above was the highest yield procedure. For similar reactions in C_6H_6 (93.2%), $CHCl_3$ (89.2–96.3%) and absolute EtOH (87.2%) or with equimolar amounts of $PdCl_2(PhCN)_2$ and $Pmes_3$ (94.3%), the yields were lower as is indicated. Similarly, reaction of $Pmes_3$ with $PdCl_2(CH_3CN)_2$ led to a range of yields (84–98%) depending upon conditions. Reactions with $PdCl_2$ (70–80%) are much slower (8–10 h at ambient temperatures) and led to significant amounts of palladium(0). There was no reaction observed between $Pmes_3$ and $PdCl_2$(COD) even under long reflux (36–48 h) in toluene and xylene.

$[Pt(Pmes_2C_6H_2(CH_3)_2CH_2)(Cl)]_2$. A mixture of $PtCl_2(CH_3CN)_2$ (0.628 g, 1.804 mmol), $Pmes_3$ (1.402 g, 3.608 mmol) and triethylamine (0.183 g, 1.808 mmol) in toluene (125.0 cm^3) was heated under reflux (6 h), filtered while still hot (to remove platinum(0)) concentrated to dryness to give a very pale yellow residue and washed with n-hexane. The resulting white residue was chromatographed (50% $CHCl_3$/n-hexane) with the colourless fraction collected reduced to dryness, washed with n-hexane and recrystallized from $CHCl_3$/n-hexane to afford a white solid, yield 0.550 g (49.2%).

Table 1

Best yield and analytical data for the $[M(P–C)X]_2$ [a] complexes prepared

M	X	Yield (%)	Dec. (°C) [b]	Analysis (Found (calcd.) (%))			ν(M–Cl) (cm^{-1})
				C	H	X	
Pd	Cl	98.1	285	61.38	6.02	6.23	279(s), 249(m)
				(61.26)	(6.09)	(6.70)	
Pd	Br	44.0	283	56.66	5.72	14.06	
				(56.52)	(5.62)	(13.93)	
Pd	I	83.3	284	52.41	5.04	20.16	
				(52.24)	(5.20)	(20.44)	
Pt	Cl	49.2	276	53.23	5.14	5.97	282(s), 248(m)
				(52.47)	(5.22)	(5.74)	
Pt	Br	86.2	285	48.89	5.00	12.06	
				(48.95)	(4.87)	(12.06)	
Pt	I	82.2	280	46.05	4.81	18.12	
				(45.71)	(4.55)	(17.89)	

[a] P–C = $Pmes_2C_6H_2(CH_3)_2CH_2$. [b] Decomposition occurs over a temperature range starting at the values shown.

Any change in solvent, reflux time, starting material and/or the amount of triethylamine added led to lower yields (< 40%). There was no reaction for $PtCl_2(COD)$.

$[M(Pmes_2C_6H_2(CH_3)_2CH_2)(X)]_2$. For M = Pd, Pt and X = Br, I, the appropriate chloro-bridged complex was treated with either KX or NaX in acetone in 1/2 molar ratios at ambient temperatures. The end of reaction was signalled by precipitation of product. Reaction times were longer for X = I than for X = Br and for M = Pt than for M = Pd.

Best yield and analytical data for these complexes and their chloro analogues appear in Table 1.

Results and discussion

In contradiction to the usual trend observed [3,4], our results indicate that for the bulky trimesitylphosphine ligand ($Pmes_3$), cyclopalladation is favoured over cycloplatination. The former proceeds smoothly at ambient temperatures with marked colour changes in relatively short periods of time (0.5 h), whereas the latter process requires both reflux conditions and the presence of a stoichiometric amount of base. We view this reversal as a fairly clear indication that the intimate mechanisms for cyclometallation (i.e., M–C bond formation) are different for palladium(II) and platinum(II) and separate studies are pursuing this further.

Although either cyclopalladation or cycloplatination does occur faster or slower and with varying yields in a given solvent, there is no real solvent dependence on the final product distribution. In every case where reaction occurs, only one metal-phosphine product can be isolated. This is unlike the situation for the bulky trialkyl ligand, tri-t-butylphosphine [4]. This and the observed lack of reaction with $MCl_2(COD)$ (M = Pd, Pt) corroborating some earlier work by Clark et al. [10] serve to demonstrate the steric effects of the large mesityl substituents. Clearly, $Pmes_3$ is too large to displace the coordinated diolefin ligand.

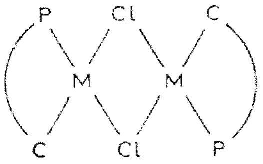
Table 2

^{1}H and ^{31}P NMR data for $[M(P-C)X]_2$ [a,b]

M	X	$\delta(^{31}P)$ (ppm) ($^1J(^{195}Pt-^{31}P)$ Hz)	$\delta(^1H)$ (ppm) ($^4J(^{31}P-^1H)$ Hz)
Pd	Cl	28.39	[c] 6.78(2.85)6.72 6.48 3.27 2.35 2.26 2.23 1.64
Pd	Br	29.94	[c] 6.79(2.60) 6.71 6.74 3.35 2.36 2.26 2.23 1.64
Pd	I	30.69	[c] 6.73(br) 6.61 6.38 3 36 2.31 2.19 2.14 1.58
Pt	Cl	8.35(5118) [e]	[d,e] 6.84 6.77(3.02) 6 46 3.17 2.32 2.26 2.24 1.67
		9.20(5191)	[d] 6.84 6.77(br) 6.45 3.15 2.30 2.28 2.20 1.63
Pt	Br	11.17(5059) [e]	[c,e] 6.77(2.97) 6.70 6.44 3.18 2.32 2.25 2.23 1.65
		11.97(5135)	[d] 6.81 6.76(br) 6.43 3.14 2.34 2.23 2.17 1.62
Pt	I	15.34(4748) [e]	[c,e] 6.80(2.16) 6.77 6.42 3.13 2.36 2.26 2.21 1.67
		15.64(4839)	[c] 6.83(3.00) 6.77 6.41 3.16 235 2.25 2.19 1.63

[a] Pmes$_3$ ($CDCl_3$) $\delta(^{31}P)$ −35.77 ppm; $\delta(^1H)$ 6.78 (2.82 Hz), 2.25, 2.04 ppm (relative integration 6/9/18). [b] br = broad singlet. [c] Relative integration 4/1/1/2/12/6/3/3. [d] Relative integration 1/4/1/2/12/6/3/3. [e] Major isomer.

Thus, from the standpoint of the minimization of steric crowding, it is reasonable that upon reaction with palladium(II) or platinum(II), Pmes$_3$ should favour both dimerization and internal metallation. Our analytical and more detailed spectral data support our earlier structural assignment [8] abbreviated below. This structure as drawn represents the *trans* or *anti* configuration which places the two P-donors in positions *trans* to each other relative to the M–M vector. This arrangement should aid in further minimizing the steric interactions between substituents on P but our high field NMR data for the M = Pt case indicate that a stable *cis*-isomer may also be formed. We had not observed this previously [8] owing to the insensitivity of infrared measurements for the identification of geometric isomers and our earlier use of a weaker magnetic field for the NMR measurements.



(P-C = $Pmes_2C_6H_2(CH_3)_2CH_2$;
M = Pd , Pt)

The ^{1}H NMR spectra for the $[Pd(P-C)X]_2$ (X = Cl, Br, I) complexes (Table 2) are relatively uncomplicated, showing in each case the presence of only one species to which we assign a *trans*-configuration on the basis of the arguments given above. For the X = Cl case, the resonance at δ 6.78 ppm corresponds to the equivalent *meta*-protons of the non-metallated mesityl rings. Their position and coupling to phosphorus are very similar to those observed for the corresponding protons of free Pmes$_3$. The *meta*-proton signals of the metallated ring at δ 6.72 and 6.48 ppm are magnetically inequivalent as expected, show no coupling to phosphorus, and are shielded. The peak at δ 3.27 ppm is assigned to the two protons on the metallating carbon atom and is diagnostic of cyclometallation. These protons are deshielded

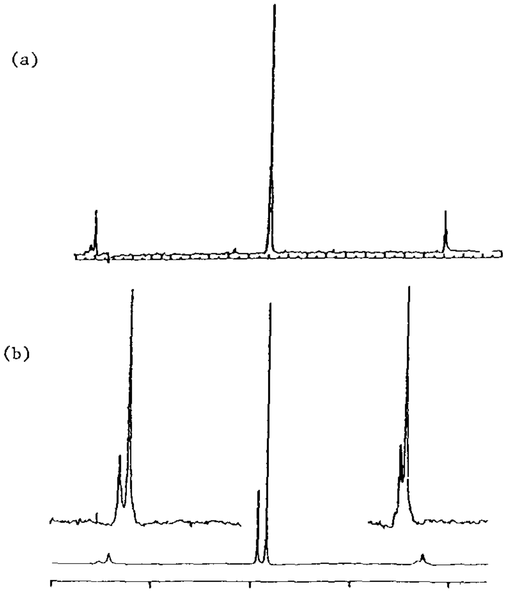


Fig. 1. ^{31}P NMR spectra for [Pt(P–C)Cl]$_2$ at (a) low and (b) high magnetic fields.

with respect to the other methyl protons especially those on the same ring. In the aliphatic region, the two downfield peaks at δ 2.35 and 2.28 ppm are assigned to the *ortho*- and *para*-methyl protons, respectively, of the non-metallated rings and are only slightly deshielded from free ligand positions. The final two resonances at δ 2.23 and 1.64 ppm are assigned to the *para*- and *ortho*-methyl protons respectively of the metallated ring and are significantly shielded. Assignments for the analogous bromo and iodo complexes are made in a similar way.

The ^{1}H NMR spectra for [Pt(P–C)X]$_2$ (X = Cl, Br, I) are assigned as above but based on a mixture of coexisting geometric isomers. The major isomer is assigned the *trans*-configuration on the basis of steric arguments and solution studies. The ratio of major/minor isomer was observed to decrease with increasing dielectric constant of solvent. Thus, the major isomer can be assigned a *trans*-geometry since this geometry, with an expected negligible dipole moment, would be less favoured than the *cis*-geometry by polar solvents [13]. A similar study using ^{31}P NMR corroborated this conclusion. The major/minor isomeric ratio also decreases as Cl > Br > I (i.e. 3.7 > 3.2 > 2.6). This may be a steric effect but electronic effects cannot be completely ruled out.

The low field (24.288 MHz) ^{31}P NMR spectrum for the platinum(II) species, shown in Fig. 1, is a single line with a set of symmetric ^{195}Pt satellites (δ 5.13 ppm, $^1J(^{195}\text{Pt}-^{31}\text{P})$ 5120 Hz). At higher field, two central lines in the ratio 3/1 and two sets of ^{195}Pt satellites are observed. These high field spectra change in position and/or coupling constant values only, with change in temperature. This suggests that the two sets of signals observed for the platinum(II) case really do correspond to the two geometric isomers and are not due to a mixture of rotational isomers arising from restricted rotations within the P–C moiety.

The coupling constants observed for the [Pt(P–C)X]$_2$ (X = Cl, Br, I) complexes are large, but this seems to be the case in general for halo-bridged dimers (3900–5500 Hz) [11]. Comparable values for monomeric species are much lower [12]. Unfortunately, there were no $^3J(^{195}Pt-^{31}P)$ coupling constants observed for our complexes although they have been reported for some chloro-bridged species [13].

Upon descending the halogen family, $\delta(^{31}P)$ increases as does $\delta(^1H)$ (metallation region) while $^1J(^{195}Pt-^{31}P)$ decreases. These trends suggest that the M–P bond may be weakening with decreasing bridging atom electronegativity. This is reasonable since the halide polarizabilities increase as $Cl < Br < I$ which means that the M–X bond should increase in covalency as $Cl < Br < I$ with a concomitant increase in *trans*-effect. Also, the $\delta(^{31}P)$ values seem to be inversely correlated with coupling to platinum-195 implying that a strong M–P bond (i.e., high ^1J value) corresponds to increased shielding of the phosphorus centre and increased electron density between the metal and phosphorus. Thus, the relative $\delta(^{31}P)$ shift values for the halide complexes can be rationalized.

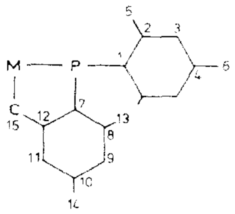
The ^{13}C NMR spectra are more difficult to assign and there is very little literature precedence. Generally, the chemical shifts for carbon atoms directly bound to a metal fall in a unique region of the ^{13}C chemical shift range [14] downfield of normal positions. This seems to be the case for the very few metallated systems studied [12,15]. Stewart et al. [16] found that for *ortho*-metallated triphenyl-

Table 3

^{13}C NMR assignments for $Pmes_3$ and *trans*-$[M(P-C)Cl]_2$ (M = Pd, Pt); δ(ppm) ($^nJ(^{31}P-^{13}C)$ Hz) [a]

Carbon atom	$Pmes_3$	Pd	Pt
1	131.54(17.42)	132.68(~ 36)	133.05(28.91)
2	142.62(16.13)	142.00(9.98)	142.11(9.65)
3	129.67	131.18(8.27)	131.29(8.77)
4	137.47	139.94	139.98
5	22.74(15.36)	24.49(9.40)	24.39(7.12)
6	20.93	21.05	21.06
7		126.08(40.16)	126.20(54.04)
8		124.29(24.23)	124.80(16.87)
9		129.75	129.43
10		141.48	140.89
11		141.64	141.47
12		158.43(30.48)	160.12(b)
13		22.85(16.54)	22.65(b)
14		21.19	[b]
15		29.81	[b]

[a] Assignments are based on the scheme:



[b] Not assigned.

phosphite, the positions for the carbons of the non-metallated rings do not change appreciably relative to the free phosphite positions whereas positions for carbons of the metallated ring can shift in either direction by up to 50 ppm.

Our assignments appear in Table 3. The positions for carbon atoms of the non-metallated rings are either unshifted or slightly deshielded relative to free $Pmes_3$ in either the aromatic or aliphatic regions. Coupling to phosphorus except for the *ipso* carbon is decreased. The effects for carbons of the metallated ring are much more pronounced. Here, all the carbon atoms are magnetically inequivalent and different from their counterparts on the non-metallated rings. C(15) is severely deshielded as expected [14] but disappointingly shows no measurable coupling to phosphorus. In the case of the platinum(II) complex, which is complicated by the presence of the *cis*-isomer, a ${}^1J({}^{195}Pt-{}^{13}C)$ value could not be measured even though these values are reportedly high (400–2000 Hz) [12]. The C(12) and C(11) positions are deshielded relative to either C(8) and C(9) or C(2) and C(3). The *para* positions, C(10) and C(14), are also deshielded relative to C(4) and C(6) but to a much lesser extent. C(8), C(9) and C(13) are each more shielded relative to C(2), C(3) and C(5) positions.

These ${}^{13}C$ NMR spectral assignments are wholly consistent with the ${}^1H$ and ${}^{31}P$ NMR assignments. The observed shift of electron density from one side of the metallated ring to the other could be envisaged as occurring through the C(15)–M–P σ bonds without the need to invoke M–P π-bonding.

All the species discussed here proved to be stable either as solids or in solution over very long periods of time. There were no reactions observed with HX (X = F, Cl) or X_2 (X = H, Cl, Br) suggesting that the M–C bond remains intact even though one might expect the metallating carbon to be susceptible to electrophilic attack. The M–C bond is broken however under reduction conditions. These reduction reactions and a wide range of bridge-cleavage reactions are still under investigation.

Conclusions

Cyclometallated dimers are formed as the only products in the reaction of the extremely bulky phosphine, trimesitylphosphine, with divalent Pd and Pt centres. The observation that cyclopalladation occurs much more readily than cycloplatination is unusual and suggests a different mechanism.

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