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Simple cycloplatination of triphenylphosphine

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Abstract

The reaction of $[PtCl(PPh_3)_3]Cl$ with AgO_3SCF_3 in $CHCl_3/MeOH$ at ambient temperature gives $[Pt(PPh_2C_6H_4)(PPh_3)_2]O_3SCF_3$ (**3**) in quantitative yield within a few minutes. The cyclometallated complex **3** has been characterized by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopies. Complete ^1H and ^{13}C assignments have been made by use of various one- and two-dimensional NMR techniques.

1. Introduction

There are three thoroughly characterized examples of cycloplatination of triphenylphosphine [1–3]. There are also complexes in which the presence of cyclometallated triphenylphosphine has been postulated from IR, Raman, partial ^1H NMR data and molecular weight determinations [4–8]. The methods used to make the first set comprised transmetallation and intramolecular C–H activation. The C–H activation required rather vigorous reaction conditions, *i.e.* a temperature of 130°C for 24 h [1] or one of 185°C for 1 h [3]. We report here a simple C–H activation of triphenylphosphine proceeding at ambient temperature within a few minutes and in quantitative yield.

2. Experimental section

NMR spectra were recorded on Bruker AC 200, AM 300 and AMX 500 spectrometers. The 1D TOCSY experiment was recorded at 11.7440 T under the following conditions: 270° Gaussian pulse, shape defined by 1000 points, 1% truncation level, MLEV 17 mixing, 10 kHz spin-lock field, 48 ms mixing time, WALTZ 16 ^{31}P decoupling. The one-bond ^1H, ^{13}C shift correlation experiment was acquired as a ^1H detected phase sensitive spectrum via heteronuclear multiple quantum coherence (HMQC) [9] at 7.0463 T. The long range ^1H, ^{13}C correlation was measured by the technique of heteronuclear multiple bond connectivity by multiple quantum NMR (HMBC) [10] at 7.0463 T.

2.1. *Preparation of the cyclometallated complex 3*

A solution of $[Pt(PPh_3)_3Cl]Cl$ (105.3 mg, 0.1 mmol) in $CHCl_3/MeOH$ (0.35 ml + 0.1 ml) was added to one of AgO_3SCF_3 (54 mg, 0.21 mmol) in MeOH (0.05 ml). The resulting suspension was stirred for 10 min, after which ^{31}P NMR spectroscopy showed that the product had been formed quantitatively. The mixture was centrifuged, the solvent removed *in vacuo*, and the residue washed with MeOH (0.5 ml). The precipitate was separated by centrifugation and dissolved in CH_2Cl_2 (0.4 ml), and the solution shaken with H_2O (2×0.2 ml). The CH_2Cl_2 solution was evaporated *in vacuo* and the residue recrystallized from CH_2Cl_2/Et_2O to yield colourless crystals, mp 275–276°C (dec.) (C 55.7, H 3.5; calcd. for $C_{55}H_{44}F_3O_3P_3PtS \cdot CH_2Cl_2$: C 55.40, H 3.82%.)

3. Results and discussion

The complex $[Pt(PPh_3)_3Cl]Cl$ (**1**) was found to react with AgO_3SCF_3 in $CHCl_3/MeOH$ as shown in the scheme below.

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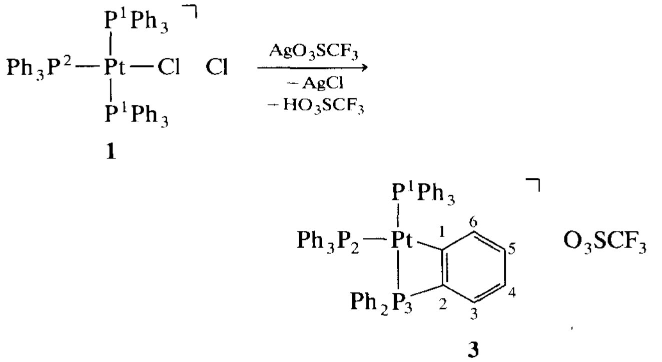

TABLE 1. ^{31}P NMR data for **1**, **2** and **3** [a]

	1	**2**	**3**
δ P1	23.8	25.7	21.6
δ P2	13.1	3.2	17.5
δ P3			−68.3
J(P1P2)	19	19	17.1
J(P1P3)			366
J(P2P3)			17.1
J(PtP1)	2482	2493	2842
J(PtP2)	3638	3927	2006
J(PtP3)			2134

[a] chemical shifts relative to 85% H_3PO_4

The formation of **3** at ambient temperature was complete within 10 min. Monitoring of the reaction by ^{31}P NMR spectroscopy revealed the presence of an intermediate, **2**, in the first few minutes. According to ^{31}P NMR spectroscopy (see NMR characterization below) the coordination sphere of platinum in **2** consists of three PPh_3 ligands and one ligand with a weaker *trans* influence [11] than Cl^-. Potential candidates for the fourth coordination position are $CF_3SO_3^-$ or MeOH. It is also possible that various ligands are in rapid exchange on the NMR time scale. The cyclometallated complex **3** is thought to be formed via **2** as intermediate. The mechanism of the intramolecular C–H activation has been discussed in detail and is well established [12–14]. The ease of formation of **3** is thought to be due to the ease of dissociation of the "non-phosphorus" ligand in **2**, or to the electrophilic character of the platinum centre in **2**. The intermolecular C–H activation of benzene using $[Pt(PMe_3)_2(CH_2C(CH_3)_3)(O_3SCF_3)]$ has recently been reported [15]. The formation of the Pt–C bond involves stoichiometric formation of the very strong acid HO_3SCF_3; the stability towards acids of cyclometallated compounds has been noted previously [16].

3.1. *NMR spectroscopies*

3.1.1. *^{31}P NMR*

The ^{31}P NMR parameters of **1**–**3** are shown in Table 1. The data for **1** are almost identical with those for $[Pt(PPh_3)_3Cl]BF_4$ [17] . Compound **2** exhibits a large coupling constant ^1J(PtP2), indicating that a ligand with a weak *trans* influence is positioned *trans* to P2.

The ^{31}P NMR spectrum of **3** consists of three groups of signals, centred at 21.6, 17.5 and −68.3 ppm. The most characteristic feature is the shift of −68.3 ppm, indicating the phosphorus atom is part of a four membered ring [18]. Shifts in this region were observed for related cycloplatinated ring systems, and rationalized in terms of the ring contribution ΔR [18]. This signal is thus attributed to P3. The coupling constant ^2J(P1P3) is 366 Hz, and this shows P1 to be *trans* to P3. The value of ^1J(PtP2) is compatible with a carbon atom *trans* to P2. The coupling constant ^1J(PtP1) is relatively large, whilst ^1J(PtP3) is relatively small. The same effect was observed for $[Pt(dppm)PR_3Cl]^+$ [19], and seems to be a general phenomenon for complexes containing strained phosphorus chelate rings and monodentate phosphine ligands [20].

3.1.2. *^{13}C and ^1H NMR*

The spectrum from the quaternary carbon atoms, recorded by use of the QUADT [21*] sequence, shows five signal groups. The carbon atom C1 of the cyclometallated ring is readily recognized from its *trans* ^2J(PC) (104.3 Hz) and the one bond Pt–C coupling constant (644 Hz); similar data were observed for $[PtPh_2(PBu_3)_2]$ [22]. The signal with the outstandingly high shift of 150.2 ppm is assigned to C2 on the basis of the ^1J(PC) coupling, which is also observed in the ^{31}P NMR spectrum. The remaining three quaternary carbon signals belong to the three sets of phenyl groups attached to the phosphorus atoms 1, 2 and 3. These assignments are confirmed by a long range ^1H, ^{13}C correlation spectrum (*vide infra*). This experiment also reveals that C2 is correlated to the ^1H signal at 6.47 ppm. The selective excitation of this proton in a $\{^{31}P\}$-selective, 1D TOCSY experiment (Fig. 1) leads to a spectrum consisting of signals from the four hydrogen atoms of the cyclometallated ring. The signal H6 was located because of its Pt–H coupling of 44 Hz (a similar coupling constant has been observed for $[PtPh_2(PBu_3)_2]$ [22]) and is compatible with the multiplicity in the TOCSY experiment. The other hydrogen atoms of the cyclometallated ring were assigned on the basis of selectively ^1H decoupled ^1H NMR spectra. A one bond $\{^{31}P\}$ ^1H, ^{13}C correlation revealed the ^{13}C shifts of the corresponding carbon atoms.

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* Reference number with an asterisk indicates a note in the list of references.

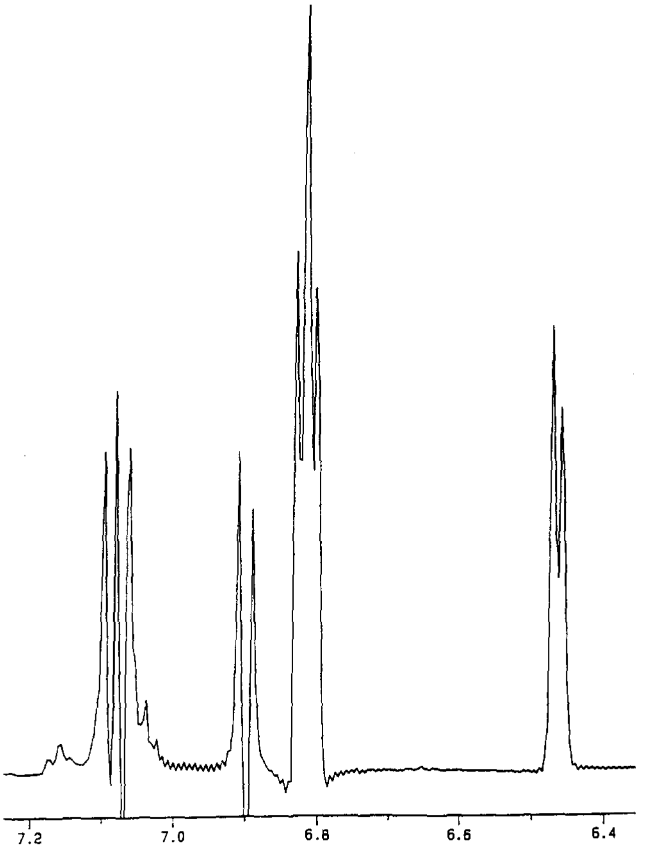


Fig. 1. Selective {^{31}P} 1D TOCSY of **3** excited at the position of H6 showing the ^{1}H signals of the metallated ring only.

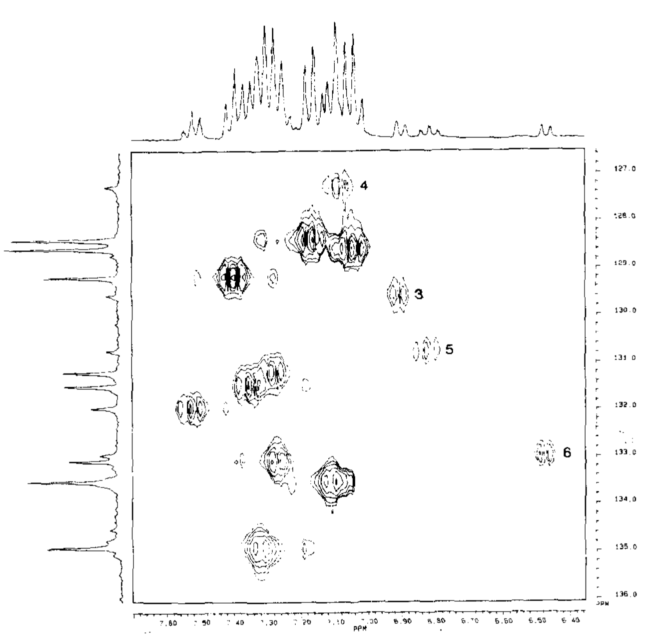


Fig. 2. Two dimensional one bond {^{31}P} ^{13}C, ^{1}H chemical shift correlation for **3**. The labelled cross peaks are due to the metallated ring.

The characterization of the phenyl groups starts with a distinction between *ortho* and *meta* or *para* positions in a one bond {^{31}P} ^{1}H, ^{13}C correlation experiment (Fig. 2) according to the multiplicities of the signals. The further distinction between *meta* and *para* position is possible because the P–C couplings of *para* carbons are markedly smaller (< 3 Hz) than those involving the *meta* carbons (> 10 Hz). The assignment of the *ortho* and *meta* or *para* C–H groups and the *ipso* carbon atoms to individual phenyl groups was made by detection of long range ^{1}H, ^{13}C connectivity.

TABLE 2. ^{13}C and ^{1}H NMR data for **1** and **3** [a]

Compound	*n*	*i*	*o*	*m*	*p*		
1	1 [b]	127.6	134.1	128.0	131.1		
		(61.1)	(11.6)	(10.7)			
1	2 [b]	127.6	133.7	128.1	131.6		
		(63.1)	(10.9)	(11.4)	(2.7)		
3	1 [b]	129.6 (25.0)	134.9 (22.5)	128.4	131.4		
		(53.9) [e]	(11.5) [e]	(10.8)	(2.6)		
			7.32	7.17	7.36		
3	2 [b]	130.7 (16.0)	133.4 (14.3)	128.5	131.1		
		(50.8) [e]	(12.1)	(10.6)	(2.4)		
			7.11	7.02	7.29		
3	3 [b]	124.8 (12.0)	133.0 (13.3)	129.2	132.0		
		(52.6) [e]	(11.8) [e]	(11.6)	(3.0)		
			7.27	7.40	7.53		
		1	2	3	4	5	6
3	3 [c]	140.3 (644)	150.2 (31.4)	129.5	127.2	130.7	132.9
		[d,e]	(61.1) [c]	[e]	[e]	[e]	[e]
				6.91	7.09	6.83	6.47

[a] δC *J*(PtC), *J*(P*n*C), δ H. [b] phenyl group attached to phosphorus labelled *n*. [c] metallated arene ring. [d] *J*(P2C) = 104.4. [e] Additional P–C couplings involving unidentified phosphorus atoms are observed.

TABLE 3. Effects of metallation on ^{13}C shifts

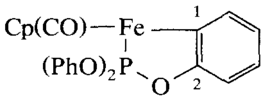
	$\delta C1$	$\delta C2$
$[PtPh_2(PBu_3)_2]$ [a]	163.8	136.5
PhH	128.5	128.5
Δ	35.3	8.0
1 [b] + Δ	169.4	135.6
3	140.3	150.2

[a] ref. 20. [b] $C_i = C_2$, $C_o = C_1$

The final assignment of the phenyl groups to specific phosphorus atoms is based on selectively ^{31}P decoupled DEPT and QUADT experiments and on the observation of the ^{1}J(PC (*ipso*)) couplings in both, ^{13}C and ^{31}P NMR spectra. The samples were at natural abundance for ^{13}C.

The ^{1}H and ^{13}C NMR data of **3** are listed in Table 2. The most interesting features of the ^{13}C data are the shifts of the quaternary carbons, because two of them (C1 and C2) are part of a four membered ring. We were interested to see whether ring contributions analogous to those established in ^{31}P NMR [18] also show up in ^{13}C NMR spectra. Table 3 describes the effect of the metallation of benzene on the ^{13}C chemical shifts of the *ipso* and *ortho* carbon atoms. A rough estimate of the effect of a ^{13}C ring contribution was carried out by adding the effects of the metallation of benzene to the data of **1** (Table 3). This shows that C1 is found at frequencies > 20 ppm lower than expected, whilst the resonance of C2 is unexpectedly high.

In $[PtMe_2(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$) [23] the signal from the methylene carbon, which is part of a four membered ring, has been reported to be shifted towards lower frequencies. A ^{13}C NMR investigation [24] of the five membered cyclometallated ring (see diagram of **4** below) showed that C1 is shifted towards low frequencies, whilst C2 moves up compared with that for the non-metallated complex $[Fe(Cp)(Ph)(CO)(P(OPh)_3]$.



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3.1.3. ^{195}Pt NMR

The ^{195}Pt resonance of **3** appears at −4443 ppm. This is at a significantly higher frequency than expected for a platinum complex with a P_3C coordination sphere, *e.g.* −4919 ppm for $[Pt(pp_2)Me]^+$ ($pp_2 = PhP(CH_2CH_2PPh_2)_2$) [25]. It is known that the presence of four-membered dppm-chelate rings causes an increase of the ^{195}Pt shift: the shift of $[PtMe_2(dppm)]$ is *ca.* 700 ppm higher than that for $[PtMe_2(dppe)]$ (dppe = $Ph_2PCH_2CH_2PPh_2$) and $[PtMe_2(dppp)]$ (dppp = $Ph_2P(CH_2)_3PPh_2$) [23]. The effect is additive, as can be seen from the ^{195}Pt shifts of $[Pt(dppe)_2]^{2+}$, $[Pt(dppe)(dppm)]^{2+}$ and $[Pt(dppm)_2]^{2+}$ at −5294, −4822 and −4272 ppm respectively [26]. The four-membered PtCCP ring thus seems to exert a similar effect on the Pt shift as a PtPCP chelate ring.

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