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[PtOTf(triphos)]OTf and [$PtMe_2$(triphos-P,P′)] as versatile synthons of platinum(II)-triphos species

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Abstract

The new complex [PtOTf(triphos)]OTf (triphos = bis(2-diphenylphosphinoethyl)phenyl-phosphine, OTf = CF_3SO_3) (**1**) can be most efficiently prepared by adding triflic acid to the known complex [$PtMe_2$(triphos-P,P′)] (**5**) where triphos acts as a bidentate ligand. The fluxional behaviours of **1** and **5** in solution and their reactivity have been investigated by NMR: [PtOTf(triphos)]OTf is a very electrophilic complex and its reactivity is dominated by the tendency of the labile ligand OTf to be replaced by a variety of nucleophiles, while the chemistry of [$PtMe_2$(triphos-P,P′)] is controlled by the proclivity of the third phosphorus to coordinate to platinum, as soon as a vacancy is created via Pt–Me protonolysis.

Keywords: Platinum complexes; Triphosphine complexes; Triflate complexes

1. Introduction

The coordination chemistry of linear and tripodal triphosphines is still a topic of general interest because of their ability to give complexes with a variety of metals, to support metal–metal bonds and to stabilise unusual coordination numbers. Moreover their practical value is recognised because of their applications in homogeneous catalysis [1].

Another lively field of coordination chemistry is the study of metal complexes containing poorly coordinated ligands. In particular, transition metal complexes containing a coordinated triflate have assumed an increasingly important role in mechanistic and synthetic endeavours [2].

Therefore, we reasoned that transition metal complexes where a tridentate phosphine is associated with the presence of a coordinate triflate on the same metallic centre should be powerful tools for mechanistic investigations and versatile inorganic synthons. For several reasons the mono-cationic Pt(II) complex [PtOTf(triphos)]OTf is a very convenient example of this class of compounds: platinum has a consolidated catalytic value, much is known about the relative ligand affinity to this metal, mainly in terms of hard-soft reactivity, Pt(II) complexes are stable and finally the coexistence of two NMR active nuclei (^{31}P and ^{195}Pt) makes this technique extremely diagnostic for mechanistic studies and for the identification of reaction products.

Because of the inductive effects of CF_3 and SO_3, CF_3SO_3 is one of the strongest electron withdrawing groups and therefore is an excellent leaving group. Moreover, in [PtOTf(triphos)]OTf, the high tendency of the OTf group to dissociate is enhanced by the strong labilising effect of the *trans* phosphine. Consequently the metal centre becomes very electrophilic and the complex behaves as a Lewis acid, showing a remarkable susceptibility to nucleophilic attack at platinum.

For all the above reasons, [PtOTf(triphos)]OTf can be regarded as a stabilised form of the coordinatively unsaturated species $[Pt(triphos)]^{2+}$; in fact on the one hand it can be readily isolated as a solid and does not show any tendency to decompose in an inert solvent, on the other hand the labile OTf can be replaced by a wide number of electron donors. These observations suggest

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a potential catalytic role for this complex in processes where electron-donating substrates need to be activated by the coordination to a metal-based Lewis acid [3].

Another source of several Pt-triphos complexes is $[PtMe_2(triphos\text{-}P,P')]$, where triphos acts as a bidentate ligand. In this paper it will be also shown how the tendency of the dangling phosphorus to coordinate to platinum makes this complex very susceptible to Pt–C protonolysis.

2. Experimental

2.1. General procedures

[PtCl(triphos)]Cl [4], $[PtMe_2(COD)]$ [5] and $[PtMe_2(dppe)]$ [6] were prepared by literature methods.

All the other chemicals were purchased (reagent grade) and solvents were distilled before using. Elemental analyses were performed using a Carlo Erba instrument model EA1110. FT-IR spectra were recorded on a Nicolet 510P FT-IR instrument in KBr. NMR spectra were recorded on a Bruker AM spectrometer 200 MHz for ^1H NMR (TMS internal reference), 188.15 MHz for $^{19}F\{^1H\}$ NMR (neat $CFCl_3$ external reference) and 81.15 MHz for $^{31}P\{^1H\}$ NMR (H_3PO_4 85% external reference). MS-FAB (fast atomic bombardment) spectra were acquired by a Hewlett–Packard MS engine HP5989 A mass spectrometer using a *p*-nitrobenzylalcohol matrix.

2.2. Synthesis of [PtOTf(triphos)]OTf (1) (Scheme 1)

2.2.1. Method a

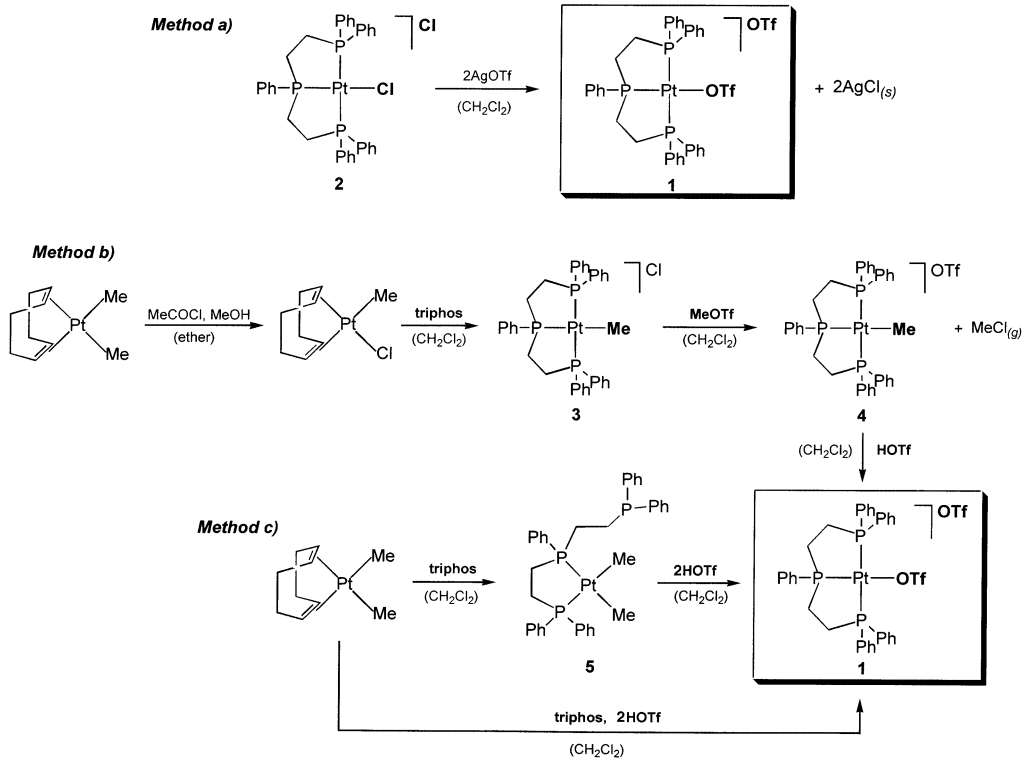
[PtCl(triphos)]Cl (**2**) (200 mg, 0.25 mmol) was dissolved in 5 ml of CH_2Cl_2 and treated with 2 equiv. of AgOTf: the reaction mixture was stirred at room temperature (r.t.) for 15 min and the AgCl filtered off over celite. The clear solution was taken to dryness under reduced pressure and the product, obtained as a white powder, dried over P_2O_5 (200 mg, 77%).

2.2.2. Method b

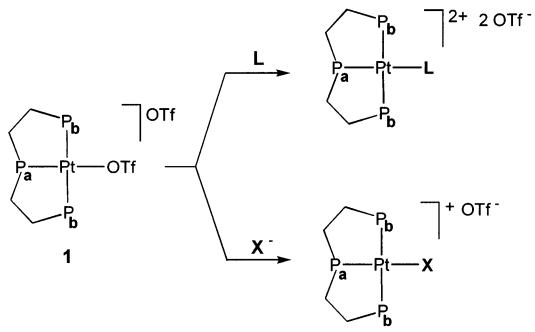
We have previously reported this route [7].

2.2.3. Method c

$[PtMe_2(COD)]$ (200 mg, 0.6 mmol) was dissolved in 5 ml of anhydrous CH_2Cl_2 and the solution was kept under nitrogen atmosphere; 1 equiv. of triphos dissolved in the same solvent was added dropwise and the reaction mixture was stirred at r.t. for 15 min. After this time, 2.1 equiv. of HOTf were added and the solution stirred for a further 10 min. The solution was then rapidly washed with H_2O and the volume reduced by half. The product was precipitated with diethyl ether as a white powder, filtered, washed with diethyl ether and dried over P_2O_5, (525 mg, 85%). *Anal.* Calc. for $C_{36}H_{33}F_6O_6P_3PtS_2$: C, 42.07; H, 3.24; S, 6.24. Found: C, 42.25; H, 3.29; S, 6.18%. IR (cm^{-1}, KBr): $\nu_{coord\text{-}OTf}$ 1339, ν_{OTf} 1269. MS-FAB$^+$: m/z 878, $[PtOTf(triphos)]^+$;



Scheme 1.



L = Acetone, Acetonitrile, PPh_3, SMe_2, Pyridine, N-Acetyl-Methionine, CO

X^- = Cl^-, Br^-, I^-, SMe^-, N_3^-, OH^-, CN^-, $PhCC^-$

Scheme 2.

Table 1
^{31}P NMR data of $[PtL(triphos)]^{2+}$

L	δP_a	$^1J_{PtP_a}$ (Hz)	δP_b	$^1J_{PtP_b}$ (Hz)
Acetone	80.5	3482	49.9	2482
Acetonitrile	84.7	3294	47.8	2370
PPh_3 [a]	94.0	2147	44.5	2375
SMe_2	91.9	2738	47.9	2412
Pyridine	78.3	2886	50.1	2436
N-Acetyl-methionine	91.6	2788	47.7	2418
CO	97.3	2674	48.3	2192

[a] P_c (coordinated PPh_3): δP_c 12.7, $^1J_{PtP_c} = 2570$ Hz, $^2J_{P_cP_a} = 298$ Hz, $^2J_{P_cP_b} = 22$ Hz.

729, $[Pt(triphos)]^{+\bullet}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 77.6 (s, $^1J_{PtP_a} = 3314$ Hz, P_a); δ 46.5 (s, $^1J_{PtP_b} = 2517$ Hz, P_b). $^{19}F\{^1H\}$ NMR ($CDCl_3$): δ −78.3 [s, (CF_3SO_3)].

2.3. Synthesis of *[PtMe$_2$(triphos-P,P′)]* (**5**)

To a solution of $[PtMe_2(COD)]$ (200 mg, 0.6 mmol) in 5 ml of anhydrous CH_2Cl_2 a second solution containing 1 equiv. of triphos dissolved in 5 ml of CH_2Cl_2 was added dropwise. The reaction mixture was stirred at r.t. for 15 min and then taken to dryness under reduced pressure. The product, obtained as a white powder, was washed with *n*-hexane and dried over P_2O_5 (364 mg, 80%). *Anal.* Calc. for $C_{36}H_{39}P_3Pt$: C, 56.99; H, 5.18. Found: C, 56.73; H, 4.98%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ 47.5 (t, $^1J_{PtP} = 1795$ Hz, $^2J_{PP} = 20$ Hz). ^1H NMR ($CDCl_3$): $Pt(CH_3)_2$ δ 0.65 [dt (5 lines 1:2:2:2:1) with satellites, $^2J_{PtH} = 70$ Hz, $^3J_{P_aH} = 7.5$ Hz, $^3J_{P_bH} = 4$ Hz, 3H] and δ 0.75 [dt (5 lines 1:2:2:2:1) with satellites, $^2J_{PtH} = 70$ Hz, $^3J_{P_aH} = 7.5$ Hz, $^3J_{P_bH} = 4$ Hz, 3H], CH_2P δ 1.8–2.5 [unresolved multiplet, 8H], *Ph*P δ 7.2–7.8 [unresolved multiplet, 25H].

2.4. Generation and NMR observation of solvento complexes in solution (Scheme 2)

In a typical experiment, **1** (15 mg, 0.0145 mmol) was dissolved in acetone or acetonitrile (0.5 ml) and the $^{31}P\{^1H\}$ NMR spectrum was observed after 10 min (see Scheme 2 and Table 1 for data).

The identity of the solvento complexes was also confirmed by the NMR observation of the same species either when complex **2** was treated with an excess of $AgBF_4$ in acetone or acetonitrile or when an excess of HBF_4 was added to a solution of **5** in the same solvents.

2.5. Preparation of bicationic complexes (Scheme 2)

2.5.1. Synthesis of *[Pt(PPh$_3$)(triphos)](OTf)$_2$*

A total of 25.5 mg (0.097 mmol) of PPh_3 was dissolved in 2 ml of dichloromethane and the solution was added dropwise to a second solution containing 100 mg (0.097 mmol) of **1** in 2 ml of the same solvent. After checking the completeness of the reaction by $^{31}P\{^1H\}$ NMR, the volume was reduced in vacuo to about 0.5 ml and Et_2O was added to precipitate the product as a white solid which was filtered and washed several times with diethyl ether (90.4 mg, 72%).

Anal. Calc. for $C_{54}H_{48}F_6O_6P_4PtS_2$: C, 50.27; H, 3.72; S, 4.96. Found: C, 49.98; H, 3.76; S, 4.69%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): see Table 1.

2.5.2. Synthesis of *[Pt(SMe$_2$)(triphos)](OTf)$_2$*

A total of 36 μl (0.5 mmol) of SMe_2 was added to a solution containing 100 mg (0.097 mmol) of **1** in 2 ml of dichloromethane. After checking the completeness of the reaction by $^{31}P\{^1H\}$ NMR, the work up of the reaction was the same as the previous (85 mg, 80%).

Anal. Calc. for $C_{38}H_{39}F_6O_6P_3PtS_3$: C, 41.87; H, 3.58; S, 8.81. Found: C, 42.40; H, 3.59; S, 8.35%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): see Table 1. ^1H NMR ($CDCl_3$), relevant data: $PtS(CH_3)_2$: δ 1.92 (d with satellites $^3J_{HPt} = 35$ Hz, $^4J_{HP} = 3.5$ Hz).

2.5.3. Synthesis of *[Pt(py)(triphos)](OTf)$_2$*

The procedure was the same as in the previous reaction, using 39 μl (0.5 mmol) of distilled pyridine. The product was obtained as a white solid (78 mg, 72%).

Anal. Calc. for $C_{41}H_{38}F_6NO_6P_3PtS_2$: C, 44.40; H, 3.52; N, 1.26; S, 5.80. Found: C, 44.91; H, 3.46; N, 1.10; S, 5.52%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): see Table 1.

2.5.4. Synthesis of *[Pt(N-acetylmethionine)(triphos)](OTf)$_2$*

A solution of 23 mg (0.12 mmol) of *N*-acetyl-methionine in 2 ml of dichloromethane was added dropwise to a second solution containing 100 mg (0.097

mmol) of **1** in 2 ml of the same solvent. After checking the completeness of the reaction by $^{31}P\{^1H\}$ NMR, the volume was reduced in vacuo to about 0.5 ml and Et_2O was added to precipitate the product as a white solid which was filtered off and washed several time with ether (96 mg, 81%).

Anal. Calc. for $C_{43}H_{46}F_6NO_9P_3PtS_3$: C, 42.36; H, 3.80; N, 1.15; S, 7.89. Found: C, 42.51; H, 3.85; N, 1.10; S, 7.99%. $^{31}P\{^1H\}$ NMR ($CDCl_3$): see Table 1.

2.5.5. Synthesis of [Pt(CO)(triphos)](OTf)$_2$

Carbon monoxide was bubbled for 30 min into a solution containing 51 mg of [PtOTf(triphos)]OTf (0.05 mmol) in 5 ml of CH_2Cl_2; the volume was then reduced to a half under CO atmosphere and the product precipitated as a white powder with diethyl ether. The solid was filtered and washed several times with ether (40 mg, 76%). *Anal.* Calc. for $C_{37}H_{33}F_6O_7P_3PtS_2$: C, 42.09; H, 3.15; S, 6.07. Found: C, 42.83; H, 3.35; S, 5.85%. IR (cm^{-1}, KBr): ν_{OTf} 1269, ν_{CO} 2110. $^{31}P\{^1H\}$ NMR ($CDCl_3$): see Table 1.

2.6. Estimate of the relative rates of substitution at platinum in [PtOTf(triphos)]OTf (**1**) and [PtCl(triphos)]Cl (**2**) with X^- ($X^- = N_3^-$, SMe^- and I^-)

Two equimolar (3×10^{-2} M) solutions of [PtOTf(triphos)]OTf and [PtCl(triphos)]Cl in $CDCl_3$ were prepared and three couples of 0.5-ml aliquots were placed in NMR tubes.

A total of 8.6 mg of NBu_4N_3 (2 equiv.) were added to each tubes of the first pair, 5.2 mg (5 equiv.) of NaSMe to the second, and 11 mg of NBu_4I (2 equiv.) to the third pair and the completeness of the reactions was monitored by $^{31}P\{^1H\}$ NMR: in each case **1** was completely reacted at the first observation (after 2 min) while in the solutions containing **2**, beside the reaction products, the reagent complex was still the main species after 24 h (% of [PtCl(triphos)]Cl in the reaction mixture after 24 h: 78% with N_3^-, 67% with SMe^- and 62% with I^-). The $^{31}P\{^1H\}$ NMR data of the products are reported in Table 2.

Table 2
^{31}P NMR data of $[PtX(triphos)]^+$

X	δP_a	$^1J_{PtP_a}$ (Hz)	δP_b	$^1J_{PtP_b}$ (Hz)
OTf	77.6	3314	46.5	2517
Cl	88.2	3065	43.1	2456
Br	89.8	3016	42.6	2449
I	92.3	2902	42.7	2417
SMe	89.7	2190	45.4	2639
N_3	81.8	2780	42.5	2553
OH	76.2	2622	40.6	2619
CN	91.7	2216	41.4	2373
PhCC	91.8	1998	38.8	2483
OTs	77.5	3458	47.2	2521
CF_3COO	74.8	3362	46.1	2494

2.7. Synthesis of mono-cationic complexes (Scheme 2)

2.7.1. Synthesis of [PtN$_3$(triphos)]OTf

A total of 17 mg (0.06 mmol) of tetra-*n*-butylammonium azide were added to a solution of [PtOTf(triphos)]OTf (0.05 mmol, 51 mg) in 5 ml of CH_2Cl_2. The reaction mixture was stirred at r.t. for 15 min and then the volume reduced to a half. The product was precipitated as a white powder by adding diethyl ether and the solid filtered and washed several times with ether (40 mg, 86%). *Anal.* Calc. for $C_{35}H_{33}F_3N_3O_3P_3PtS$: C, 45.66; H, 3.61; N, 4.56; S, 3.48. Found: C, 45.67; H, 3.58; N, 4.62; S, 3.55%. IR (cm^{-1}, KBr): ν_{OTf} 1271, ν_{N3} 2043. MS-FAB$^+$: *m*/*z* 771, $[PtN_3(triphos)]^+$; 744, $[PtN(triphos)]^{+\bullet}$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): see Table 2.

2.7.2. Synthesis of [PtCCPh(triphos)]OTf

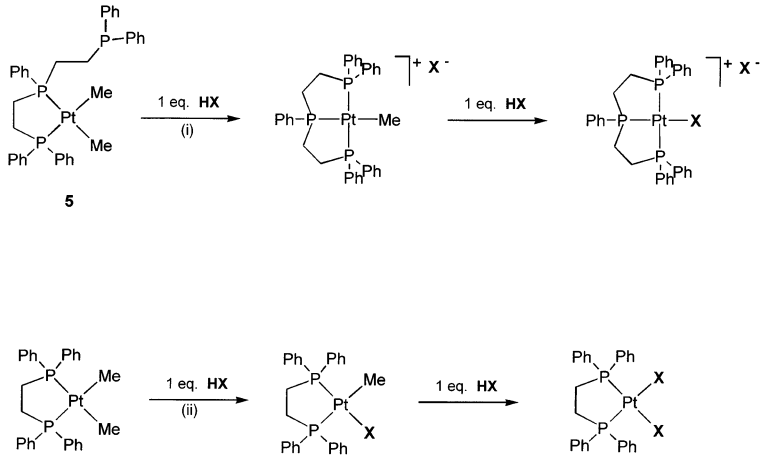
A total of 0.3 mmol of phenylacetylene were added to a solution of [PtOTf(triphos)]OTf (0.05 mmol, 51 mg) in 5 ml of CH_2Cl_2 and the mixture was stirred at r.t. for 2 h. After this time the volume was reduced to a half under reduced pressure and the product was precipitated with diethyl ether. The white powder was filtered, washed with diethyl ether and dried over P_2O_5, (40 mg, 80%). *Anal.* Calc. for $C_{43}H_{38}F_3O_3P_3PtS$: C, 52.71; H, 3.91; S, 3.27. Found: C, 52.73; H, 4.03; S, 3.10%. IR (cm^{-1}, KBr): ν_{OTf} 1263, $\nu_{C\equiv C}$ 2114. MS-FAB$^+$: *m*/*z* 830, $[Pt(C\equiv CPh)(triphos)]^+$; 729, $[Pt(triphos)]^+$. $^{31}P\{^1H\}$ NMR ($CDCl_3$): see Table 2.

2.8. Protonolysis of [PtMe$_2$(triphos-*P*,*P*′)], (5)-NMR experiments and comparison with [PtMe$_2$(dppe)] (Scheme 3)

Three 0.5-ml aliquots of a 3×10^{-2} M solution of complex **5** in CH_2Cl_2 were placed in NMR tubes and a large excess of HOTf (10 μl), CF_3COOH (10 μl) and $HOTs{\cdot}H_2O$ (*p*-toluensulfonic acid) (10 mg) were added, respectively. After 5 min, the $^{31}P\{^1H\}$ NMR spectra showed the formation of the final products [Pt(triphos)X]X (X = OTf, $OOCCF_3$, OTs).

In a group of analogue experiments a stoichiometric amount (2.1 equiv.) of the above acids was used: it was observed that step (i) was complete in 5 min in each case. Step (ii) is slower and occurred at different times depending on the acid: using HOTf step (ii) is complete in 10 min, in the case of HOTs the reaction mixture contained 50% of the final product after 18 h and only 10% in the case of CF_3COOH, after the same time.

The same experiment performed with an excess of weaker acids, PhOH, HF (48% aq.) and $CH_3COCH_2COCH_3$, gave the complete conversion of



Scheme 3.

$[PtMe_2(triphos)]$ to $[Pt(triphos)Me]^+$ after about 10 min. No sign of the second step product was observed after 24 h. In a set of comparison reactions it was found that using the same weak acids in the same conditions, $[PtMe_2(dppe)]$ did not react at an appreciable extent after 24 h.

3. Results and discussion

3.1. Synthesis of [PtOTf(triphos)]OTf (1)

The preparation of complex **1**, [PtOTf(triphos)]OTf, has not been described until our recent preliminary report of this work [7].

The metal bonding of a poorly coordinating ligand such as OTf can be induced by creating a vacancy in the coordination sphere of a suitable parent complex in the presence of the weak donor ligand in a non coordinating solvent. This can be obtained by two conventional approaches: (i) abstraction of a metal coordinated halide from a parent complex using silver or thallium reagents; (ii) C-protonation of a coordinated R alkyl group (CH_3 in most cases) with release of the corresponding hydrocarbon RH.

We found both the above routes successful for the preparation of [PtOTf(triphos)]OTf: in fact it can be prepared either treating the corresponding chloride complex [PtCl(triphos)]Cl (**2**), with silver triflate, in the same way reported before for the palladium analogue [8] (Scheme 1, method a) or treating [PtMe(triphos)]OTf (**4**), with triflic acid (Scheme 1, method b). Nevertheless both reactions show some disadvantages: the first route requires the use of light-sensitive hygroscopic silver salts while the second needs several steps as we reported before [7].

We propose here a third very convenient synthetic route to complex **1** (Scheme 1, method c): the precursor $[PtMe_2(COD)]$ is treated in sequence with 1 equiv. of triphos to give the known complex $[PtMe_2(triphos\text{-}P,P')]$ (**5**), where the triphosphine acts as a bidentate ligand [9]. The solution containing **5** is then treated with 2 equiv. of triflic acid to give **1** by double Pt–C protonolysis. The synthesis is performed through two simple and fast steps in sequence (there is no need to isolate the intermediate **5**) and product **1** is recovered very cleanly in good yield (85%).

3.2. Solution behaviour of 1 by NMR

We characterised **1** in the solid state through its X-rays crystal structure [7], while its characterisation in solution is based on NMR observations. The $^{31}P\{^1H\}$ NMR shows two singlets with satellites at 77.6 ppm ($^1J_{PtP_a} = 3314$ Hz) and 46.5 ppm ($^1J_{PtP_b} = 2517$ Hz) due to the P *trans* to OTf (P_a) and to two mutually *trans* equivalent P_b, respectively. The large value of $^1J_{PtP_a}$ reflects the low *trans* effect of OTf, when compared with other triphos Pt complexes, e.g. in [Pt(triphos)Cl]Cl $^1J_{PtP_a} = 3065$ Hz (Table 2). These values also show that all P–Pt coupling constants in (triphos)Pt systems are smaller than the corresponding constants in single five-membered ring analogues [10].

We have already underlined that the line width of the P_b signal is strongly dependent on a few physical conditions as medium polarity, concentration and temperature and we tentatively ascribed this to the fluxional behaviour described in Scheme 4: the nucleophilic attack of the external OTf on platinum induces the detachment of P_b, which then rapidly exchanges with P'_b, via the five coordinate trigonal bipyramidal intermediate (**a**).

This hypothesis is supported by the analysis of the conditions inducing the broadening of the signal of P_b: in a polar solvent like CD_3NO_2, P_b is sharp, because the solvation of the two ions $[Pt(triphos)OTf]^+$ and OTf^-

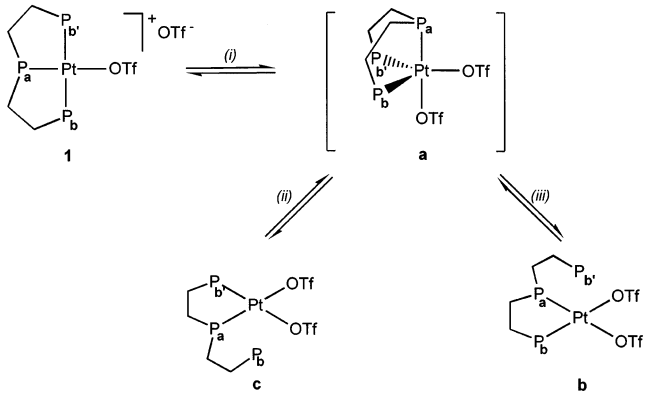
favours the ion pair indicated as **1** (left side) in equilibrium (i). The line broadening appears in low-polarity solvents like $CDCl_3$, where the favoured species is **a**, whose fluxionality requires rapid exchange between **a–b–c**. In the same solvent the line broadening disappears at high concentration because the overall process becomes very rapid. A further support to the hypothesis that a fluxional behaviour is operating is offered by a low temperature NMR experiment. At -55°C in $CDCl_3$, the situation described by equilibrium (i) is frozen and two $^{31}P\{^1H\}$ NMR patterns are observed [78.2 ppm (3579 Hz) and 47.6 ppm (2460 Hz) for the first; 77.7 ppm (3121 Hz, broad) and 44.3 ppm (2501 Hz, broad) for the other] which we tentatively attribute to the two species **1** and **a**, observed in a 1:1 ratio. Increasing the temperature, the above patterns coalesce at 0°C. This experiment supports the hypothesis that the fluxionality is initiated by the nucleophilic attack of the external OTf on platinum. The addition of external OTf^- (LiOTf or $AsPh_4OTf$) to a $CDCl_3$ solution does not have any appreciable effect on the line width: this observation indicates that the concentration of OTf does not affect the rate of the exchange.

3.3. Substitution reactions of coordinated OTf in [PtOTf(triphos)]OTf (1)

The labile OTf ligand in [PtOTf(triphos)]OTf is readily substituted by other anions or electron-donating molecules offering a convenient route to a large number of Pt(triphos) complexes (Scheme 2) [2]. The $^{31}P\{^1H\}$ NMR data of the substitution products are listed in Tables 1 and 2.

3.3.1. Solvents

Pt solvento complexes are of great interest because of their common use in mechanistic studies and because they are involved as intermediates in many transition metal catalysed processes [11].



Scheme 4.

We dissolved **1** in some potentially coordinating solvents (S = acetonitrile, acetone, water, methanol) with the aim to check if they are able to replace OTf on platinum, as depicted in Eq. (1):

$$[Pt{-}OTf]^+ + S \rightarrow [Pt{-}S]^{2+} + OTf^- \quad (1)$$

The $^{31}P\{^1H\}$ NMR data observed for **1** in acetonitrile and acetone are reported in Table 1 [12]: the recorded data show small differences with the data of **1** in a non coordinating solvent as $CDCl_3$. In order to exclude that these changes are due to solvent effects, we generated the genuine solvento complexes by two different routes: (i) by treating the chloride complex **2** with an excess of $AgBF_4$ in acetone or acetonitrile and (ii) by treating the dimethyl complex **5** with an excess of HBF_4 in the solvent to be coordinated. In every case the obtained solvento complex had $^{31}P\{^1H\}$ NMR data exactly coincident with those of the species derived from the OTf complex. Attempts to isolate these solvento complexes were unsuccessful.

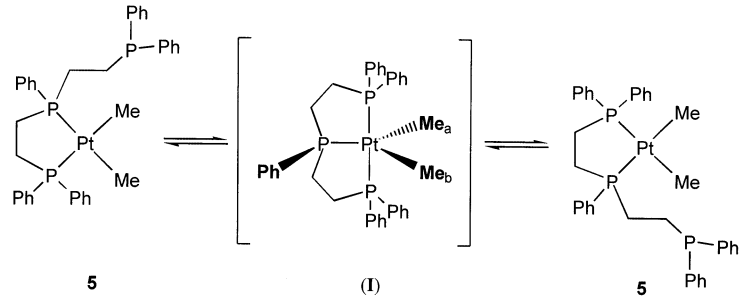
The addition of water or methanol to a solution of **1** in $CDCl_3$ or CH_3NO_2 does not induce any significant change in the $^{31}P\{^1H\}$ NMR spectrum, indicating that OTf is not replaced by these solvents in these conditions.

3.3.2. Neutral ligands

Besides the above-mentioned coordinating solvents, some other neutral σ donors 'L' can also replace OTf giving di-cationic complexes $[PtL(triphos)](OTf)_2$. We found that the exchange occurs with P (PPh_3), N (py,) and S (SMe_2) donors (see Section 2 and Table 1 for complete characterisation).

The OTf ligand can also be replaced by more hindered molecules as *N*-acetyl-L-methionine, giving a product whose $^{31}P\{^1H\}$ NMR data are consistent with those of the reported complex bearing the amino acid as *S* coordinated monodentate ligand [13]. It has been suggested that this adduct could have some biological significance; it has been prepared before by adding the ligand to [PtCl(triphos)]Cl in the presence of $AgNO_3$. Our preparation from [PtOTf(triphos)]OTf has the advantage to avoid the reported contamination with the side-product $[PtONO_2(triphos)]NO_3$.

After prolonged (30 min) bubbling of CO into a solution of [PtOTf(triphos)]OTf in $CDCl_3$, the carbonyl Pt complex $[Pt(CO)(triphos)](OTf)_2$ can be identified in solution by $^{31}P\{^1H\}$ NMR (Pt–P coupling constant for P_a 2674 Hz typical of phosphorus *trans* to CO [14]). The starting complex **1** is recovered as the only Pt containing species when the solution is taken to dryness in vacuo as shown by the $^{31}P\{^1H\}$ NMR spectrum of the residue redissolved in $CDCl_3$. This indicates that the equilibrium in Eq. (2) is present in solution, lying on its right side when the CO pressure is high.



Scheme 5.

$$[(\text{triphos})\text{Pt}-\text{OTf}]^+ + \text{CO} \leftrightarrows [(\text{triphos})\text{Pt}-\text{CO}]^{2+} + \text{OTf}^- \quad (2)$$

$[Pt(CO)(triphos)](OTf)_2$ can be isolated as a solid by precipitation with Et_2O under CO pressure. The IR spectrum shows the typical ν(CO) at 2110 cm^{-1}. When the isolated compound is redissolved in $CDCl_3$, the pattern of $[Pt(CO)(triphos)](OTf)_2$ is initially observed with **1** as a secondary species (approximately 20% after 3 min) whose concentration reaches about 50% in 2 h; finally, after 48 h complex **1** becomes the only detectable species. The observed lability of the coordinated CO might be ascribed to the scarce metal to CO backdonation, the platinum being highly electrophilic. The relevance of this ability of Pt(triphos) to bond and to release CO in hydroformylation catalysis is at present under investigation.

3.3.3. Anionic ligands

OTf on platinum is rapidly substituted by a large number of anionic nucleophiles X^-, giving a series of monocationic Pt complexes [PtX(triphos)]OTf, Scheme 2, where the value of $^1J_{PtP_a}$ can be used as an indicator of the *trans* influence of the ligand occupying the forth position (Table 2) [15].

Besides the expected reactions of **1** with Br^-, I^-, SMe^- and N_3^-, which occur much faster than on [PtCl(triphos)]Cl (see Section 2), the reaction with LiOH and water in chloroform gives a species which we tentatively attribute to complex $[PtOH(triphos)]^+$. The same species appears also as a secondary product in the $^{31}P\{^1H\}$ NMR spectra of solutions of **1** in the presence of non-anhydrous basic nucleophiles as pyridine or NEt_3.

3.3.4. Organometallics

Coordinated OTf can be replaced also by anionic C donor ligands such as CN, CCPh [8], as proved by the small value of the $^1J_{PtP}$ of P_a in $^{31}P\{^1H\}$ NMR of the products (Table 1). For CCPh the coordination occurs via a spontaneous deprotonation without the assistance of an external base (Eq. (3)).

$$[\text{PtOTf(triphos)}]^+ + \text{HC}\equiv\text{CPh} \underset{\mathbf{1}}{\leftrightarrows} [\text{PtC}\equiv\text{CPh(triphos)}]^+ + \text{HOTf} \quad (3)$$

Complex [PtCCPh(triphos)]OTf has been isolated and its identity was confirmed by elemental analysis, IR, MS-FAB (see Section 2). The triflate complex **1** is re-obtained when an excess of triflic acid is added to a $CDCl_3$ solution of [PtCCPh(triphos)]OTf.

When [PtCCPh(triphos)]OTf is generated in $CDCl_3$ inside a NMR tube from **1** and HC≡CPh, an ageing effect is observed whereby the equilibrium in Eq. (3) is completely shifted to the left after 3 days.

3.4. NMR characterisation of *5*

We have previously mentioned complex [$PtMe_2$-(triphos-P,P′)] (**5**), as an intermediate in the synthesis of **1** (Scheme 1, method c). It originates from the substitution of the easy replaceable chelating diolefin COD with triphos acting as a bidentate ligand, the third phosphorus dangling out of the coordination sphere. The preparation of **5** was reported before as well as a $^{31}P\{^1H\}$ NMR study of its fluxional, temperature-dependent behaviour in solution [9]. The structure of **5** was described in terms of the equilibrium in Scheme 5, fast on the NMR scale at r.t. In these conditions the $^{31}P\{^1H\}$ NMR spectrum appears as a triplet with satellites due to the central phosphorus P_a coupled with the two external ones (P_b and $P_{b'}$). They are equivalent because of the fast exchange and for the same reason their signal is so broad to disappear in the spectrum baseline.

It is worth noticing that Meek and co-authors tentatively proposed an exchange mechanism through a five-coordinated intermediate. In order to verify this hypothesis we analysed the ^1H NMR of **5**. In $CDCl_3$ at r.t. (rapid exchange conditions, as shown by $^{31}P\{^1H\}$ NMR) two distinct and identical patterns for the Pt–Me groups are observed [0.65 and 0.75 ppm (doublets of triplets with satellites, see Section 2)], indicating that the two methyl groups do not become equivalent as a result of the fluxionality. These observations fit the structure of the trigonal bipyramidal intermediate **I**. In

fact in that arrangement the two Pt–Me groups are chemically inequivalent (note that the phenyl group on the central phosphorus is always *cis* to one Me and *trans* to the other with respect to the P3Pt plane), but they have the same geometrical relations with all the P atoms: therefore two signals are observed with identical coupling patterns.

3.5. Reactivity of [$PtMe_2$(triphos-P,P′)] (**5**)

The addition of 2 equiv. of strong acids as HOTf, HOTs and CF_3COOH, to a solution of **5** in dichloromethane gives [Pt(triphos)Me]X as a primary product which then evolves to [Pt(triphos)X]X (X = OTf, OTs, CF_3COO) as shown by $^{31}P\{^1H\}$ NMR. The first step is fast, while the second is slower [16] (see Section 2).

The protonolysis of **5** by a non coordinating acid (HBF_4) in the presence of acetone or acetonitrile gives the above mentioned solvento complexes very cleanly.

The treatment of **5** with HBF_4 in a non coordinating solvent (CH_2Cl_2 or benzene) gives an unidentified species with all three P atoms bonded to platinum (δP_a 48.7, $^1J_{PtP_a}$ 2464 Hz and δP_b 77.3, $^1J_{PtP_b}$ 3675 Hz), except in $CHCl_3$ where the chloride complex **2** was observed as the only Pt containing species after 24 h.

In a series of NMR experiments we compared the susceptibility of **5** and [$PtMe_2$(dppe)] to Pt-methyl protonolysis (Scheme 3). We observed that **5** undergoes the first step very quickly (less then 10 min) even with extremely weak acids like PhOH, HF or $CH_3COCH_2COCH_3$, which do not show any tendency to induce protonolysis in [$PtMe_2$(dppe)] after 24 h (see Section 2).

The driving force of the Pt–Me protonolysis in both complexes is the formation of CH_4 but in our opinion the remarkable susceptibility of **5** to this reaction can be ascribed to the presence of an additional driving force in this system, namely the great tendency of the third phosphorus to coordinate, evolving to species where triphos behaves as a tridentate ligand, thus becoming stabilised by the formation of two five-membered chelate rings. The same driving force is probably responsible of the above-described fluxional behaviour of **5** in solution, as well.

The ability of the dangling phosphorus to coordinate to metals giving polinuclear complexes is at present under investigation.

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