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The Role of Anions in Addressing the Outcome of the Reaction of Tetramethylthiourea with *cis*-$Pt^{II}(phos)_2$ Moieties (phos = PPh_3 or ½dppe), Cyclometallation vs. Hydrolysis to Monothiocarbamato, and the Crystal Structure of *trans*-Bis(*N*-dimethylmonothiocarbamato)bis(triphenylphosphane)platinum(II)

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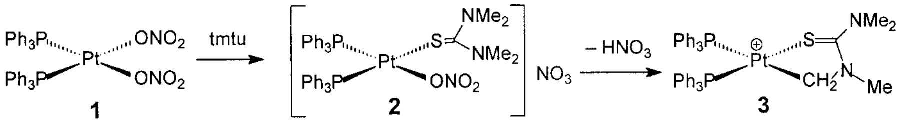
The product of the reaction between tetramethylthiourea (tmtu) and *cis*-$Pt^{II}(phos)_2$ moieties (phos = PPh_3, or ½ dppe) depends on the anionic species present. With NO_3^-, $CF_3CO_2^-$, $CF_3SO_3^-$ and BF_4^-, the cyclometallate cationic complex $[Pt(phos)_2(tmtu^\star\text{-}C,S)]^+$ is obtained (tmtu⋆ is tmtu deprotonated at one methyl group). The acetato and malonato complexes are inactive towards such deprotonation, but, in the presence of water, promote tmtu hydrolysis with formation of *N*-dimethylmonothiocarbamato (mtc) complexes in which mtc is *S*-coordinated. *cis*-$[Pt(PPh_3)_2(mtc)_2]$ isomerises slowly to the *trans* isomer, whose crystal structure is reported.

Introduction

A knowledge of the factors that influence the reactivity of coordinated ligands is of great importance in coordination and organometallic chemistry. Here we wish to report that the proper choice of anionic ligands may affect the outcome of the reaction between tetramethylthiourea (tmtu) and *cis*-$Pt^{II}(phos)_2$ moieties (phos = PPh_3 or ½ dppe).

We have recently found that the reaction of *cis*-$[Pt(PPh_3)_2(NO_3)_2]$ (**1**) with tmtu does not give the disubstituted product *cis*-$[Pt(PPh_3)_2(tmtu)_2]^{2+}$, but that the initially formed *cis*-$[Pt(PPh_3)_2(NO_3)(tmtu)](NO_3)$ (**2**) transforms into the cyclometallated complex $[Pt(PPh_3)_2(tmtu^*\text{-}C,S)](NO_3)$ (**3**) [tmtu*, tetramethylthiourea deprotonated at one methyl group], with formation of nitric acid (Scheme 1).[1] This reaction, performed at room temperature in either chloroform or CH_2Cl_2, was found to be unaffected by both air and water, which, in some experiments, was purposely added to extract the nitric acid formed during the reaction.[1]

Such facile cyclometallation is clearly favoured by the lability of the nitrate ion *cis* to tmtu in **2**; detachment of this ionic ligand produces a vacant coordination site which can interact with a C–H bond of a methyl group of tmtu, activating the bond towards deprotonation.[2,3] The proton is then captured by a "free" (i.e. uncomplexed) NO_3^- ion to give nitric acid.[1] In order to better understand the role of the anion either as a ligand, or as a base, we decided to investigate the reaction of tmtu with a series of other *cis*-$Pt^{II}(PPh_3)_2$ complexes with various anionic ligands and we found that the product of the reaction depends on the nature of the anions present. Thus, while cyclometallation also occurs with *cis*-$[Pt(PPh_3)_2(CF_3CO_2)_2]$ (**4**) and *cis*-$[Pt(PPh_3)_2(CH_3CN)_2]X_2$ (**5a**, X = BF_4^-; **5b**, X = $CF_3SO_3^-$, TfO), the reaction of tmtu with *cis*-$[Pt(PPh_3)_2(AcO)_2]$ (**6**) and $[Pt(PPh_3)_2(malonato)]$ (**7**) follows a completely different route: these anionic ligands promote tmtu hydrolysis, giving rise to the dimethylmonothiocarbamato (mtc) complexes



Scheme 1.

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cis-[Pt(PPh_3)$_2$(mtc)$_2$] (**8**) and *trans*-[Pt(PPh_3)$_2$(mtc)$_2$] (**9**). The Pt^{II}(dppe) complexes behave similarly. We report here these studies, as well as the X-ray structure of *trans*-[Pt(PPh_3)$_2$(mtc)$_2$] (**9**). Although the structure of a phosphane-Pd^{II} complex of mtc has been reported,[4] to the best of our knowledge this is the first X-ray structure of a Pt-mtc derivative. Dialkyldithiocarbamato-Pt complexes are well known,[5] but there are very few reports on Pt-mtc complexes,[4,6] and indeed mtc complexes have been little studied,[7] a possible reason being the unpleasant synthesis of the mtc$^-$ ligand, which requires the use of carbonyl sulfide.[6] The hydrolysis reaction reported here may therefore represent an easy route to Pt-mtc complexes.

Results and Discussion

Cyclometallation versus Hydrolysis: the Role of the Anions

While *cis*-[Pt(PPh_3)$_2$(CF_3CO_2)$_2$] (**4**) is a known compound,[8] BF_4^- and TfO^- have a rather poor complexing ability, therefore we have synthesised the salts of these anions with *cis*-[Pt(PPh_3)$_2$(CH_3CN)$_2$]$^{2+}$, **5a** and **5b**, respectively. Reactions of tmtu with these three complexes, in CH_2Cl_2 solutions, give the corresponding salts of the cationic cyclometallated complex **3**, which were characterised by elemental analyses and by comparison of their NMR spectra with those of the already described nitrate derivative.[1] When the reactions between tmtu and compounds **5** were followed by ^{31}P NMR spectroscopy, we observed, in both cases, the fast formation of a species **10**, which shows two doublets (Table 1), consistent with one phosphane *trans* to an S ligand (δ = 13.7 ppm; J_{Pt-P} = 2890 Hz, compared with, for instance, ref.[9]) and one *trans* to CH_3CN (δ = 7.6 ppm; J_{Pt-P} = 3839 Hz, compared with the data for **5**). The ^1H NMR spectrum displays a peak at δ = 3.30 ppm, which integrates for 12 protons, and a singlet at δ = 2.00 ppm (three protons). We therefore conclude that **10** is *cis*-[Pt(PPh_3)$_2$(CH_3CN)(tmtu)]$^{2+}$. The TfO salt of this intermediate evolves to **3**(TfO) in a few hours, whereas such a conversion is much slower for the BF_4 derivative (>24 h). A fast conversion of **10**(BF_4) to **3**(BF_4) can be achieved by heating the solution at 40 °C or, rather interestingly, also at room temperature by addition of (Et_4N)NO_3 to the solution, which shows the high activity of nitrate anions in the cyclometallation reaction (Scheme 2).

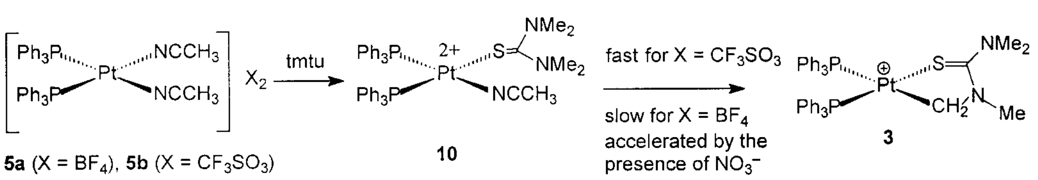
When we investigated *cis*-[Pt(PPh_3)$_2$(AcO)$_2$] (**6**) in the initial runs, we did not use anhydrous conditions, since, as explained in the Introduction, cyclometallation of tmtu is not affected by the presence of water.[1] However, to our surprise, the reaction of **6** with tmtu did not afford **3**, but a mixture, which, according to ^{31}P NMR spectroscopy (Table 1), contains essentially two products **8** and **9** (minor component), with no detectable signal from **3**. Slow diffusion of hexane into a CH_2Cl_2 solution of this mixture gave crystals, which were found to be *trans*-[Pt(PPh_3)$_2$(mtc)$_2$] through X-ray analysis, see below. A $CDCl_3$ solution of these crystals produced a ^{31}P NMR spectrum consistent with that of **9**.

Compounds **8** and **9** were also obtained by reaction of tmtu with the malonato complex **7**.

Table 1. ^{31}P and relevant ^1H NMR spectroscopic data.[a]

Compound	^{31}P NMR	^1H NMR
cis-[Pt(PPh_3)$_2$(NO_3)$_2$], **1**[b]	3.62 (4010)	
cis-[Pt(PPh_3)$_2$(NO_3)(tmtu)]$^+$, **2**[b]	1.70 (3830), 18.95 (3225) (J_{P-P} 19.5)	3.17 (s, 12 H)
cis-[Pt(PPh_3)$_2$(tmtu*)]$^+$, **3**[b]	17.14 (2022), 22.22 (3462) (J_{P-P} 22.8)	3.02 (s, 6 H), 3.08 (s, 3 H), 3.52 (mt, J_{Pt-H} 60, 2 H)
cis-[Pt(PPh_3)$_2$(CF_3CO_2)$_2$], **4**[c]	4.38 (3933)	
cis-[Pt(PPh_3)$_2$(CH_3CN)$_2$]$^{2+}$, **5**	3.27 (3683)	2.00 (s, 3 H)
cis-[Pt(PPh_3)$_2$(AcO)$_2$], **6**	5.72 (3826)	1.34 (s)
[Pt(PPh_3)$_2$(malonato)], **7**	7.9 (3757)	3.42 (s, 2 H)
cis-[Pt(PPh_3)$_2$(mtc)$_2$], **8**[d]	15.7 (3277)	3.21 (s, 12 H)
trans-[Pt(PPh_3)$_2$(mtc)$_2$], **9**	14.9 (3676)	3.20 (s, 12 H)
cis-[Pt(PPh_3)$_2$(CH_3CN)(tmtu)]$^{2+}$, **10**[d]	7.6 (3839), 13.7 (2890) (J_{P-P} 17.0)	3.30 (12 H), 2.00(3 H)
cis-[Pt(PPh_3)$_2$(AcO)(tmtu)]$^+$, **11**[d]	6.82 (3979), 17.2 (3246) (J_{P-P} 19)	2.71 (s, 12 H), 2.22 (s, 3 H)
cis-[Pt(PPh_3)$_2$(AcO)(NO_3)], **12**[d]	6.60 (4250), 8.15 (3921)[e]	1.31 (br., 3 H)
[Pt(dppe)(NO_3)$_2$], **13**[f]	32.94 (3942)	
[Pt(dppe)(tmtu*)]$^+$, **14**	45.4 (3259), 45.9 (1900) (J_{P-P} 7.7)	4.00 (dd, J_{Pt-P} 54.4, 2 H), 3.23 (s, 3 H), 3.14 (s, 6 H)
[Pt(dppe)(AcO)$_2$], **15**	30.99 (3785)	1.71 (s, 6 H)
[Pt(dppe)(mtc)$_2$], **16**	43.04 (3157)	3.37 (s, 12 H)

[a] $CDCl_3$ solutions, δ values in ppm from external H_3PO_4 and Me_4Si. *J* in Hz. ^1H integrations are based on the peaks of the phosphane moieties. [b] Compare ref.[1]. [c] Compare ref.[8]. [d] Recorded in CH_2Cl_2/$CDCl_3$, 1:1. [e] These peaks were too broad to allow a reliable determination of the P–P coupling constant. [f] Compare ref.[9]



Scheme 2.

Structure and Characterization of *trans*-$[Pt(PPh_3)_2(mtc)_2]$ (9)

The structure consists of the packing of $[Pt(PPh_3)_2(mtc)_2]$ molecules with normal van der Waals contacts. An ORTEP[10] view of the complex is shown in Figure 1, while selected bond lengths and angles are reported in Table 2. The metal ion is four-coordinate square planar, with two mutually *trans* phosphane groups and two *trans* mtc anions that are monodentate and coordinated through their sulfur atoms. The planarity around Pt is rigorous, since this atom lies on a crystallographic inversion centre. The mtc ligand is essentially planar, with maximum deviations from the least-squares plane of +0.033(1) Å for S and –0.037(3) Å for C(3). The Pt–P bond length [2.316(1) Å] is comparable with values found in other *trans*-$Pt(PPh_3)_2$ complexes.[11,12] To the best of our knowledge, no Pt-mtc complex has ever been structurally characterised, however, we note that the Pt–S bond length in **9** is in the range of those found in the few instances of monodentate dialkyldithiocarbamate complexes of Pt^{II}.[13] In particular, a compound analogous to **8**, *trans*-$[Pt(PMe_2Ph)_2(dttc\text{-}S)_2]$, displays a very similar Pt–S distance [2.335(2) Å].[14] The dihedral angle between the mtc best plane and the metal coordination plane is 68.0(5)° and can be compared with that of the analogous *trans*-$[Pd(PPh_3)_2$(*N*-dipropylmonothiocarbamato)$_2]$.[4] Bond lengths within the thiocarbamato ligand are also similar.[4]

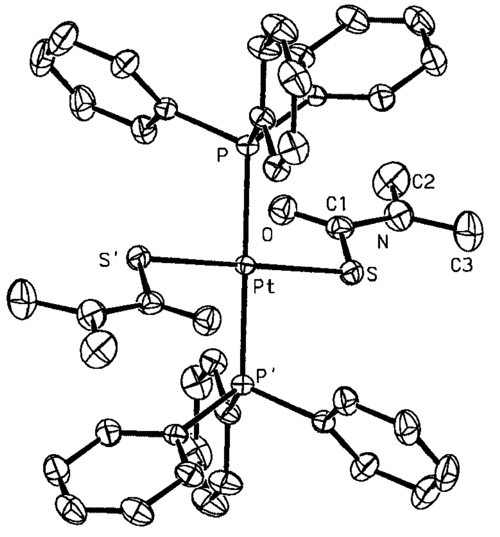


Figure 1. ORTEP view of complex**9**. Ellipsoids are drawn at the 30% probability level.

The NMR spectroscopic data of **9** are reported in Table 1. Note the rather high Pt–P coupling constant, which in *trans*-$Pt^{II}(PPh_3)_2$ complexes is usually in the 2500–3000 Hz range; higher values have, however, also been reported.[12,15] The FAB^+ mass spectrum of **9** (see Experimental section) shows only a weak peak (ca. 5%) corresponding to $[M]^+$; the most abundant peaks are due to $[Pt(PPh_3)_2(SCO)_2]^+$ and $[Pt(PPh_3)_2(mtc)]^+$. This behaviour seems characteristic of these phosphane mtc complexes.

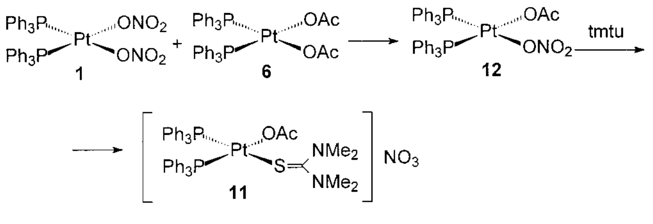
Table 2. Selected bond lengths [Å] and angles [°] for **9**, with estimated standard deviations in parentheses.

Pt–S	2.336(1)	Pt–P	2.316(1)
S–C(1)	1.777(2)	O–C(1)	1.222(3)
N–C(1)	1.375(3)	N–C(2)	1.460(3)
N–C(3)	1.450(4)		
S–Pt–S′	180	S–Pt–P	94.1(1)
S–Pt–P′	85.9(1)	P–Pt–P′	180
Pt–S–C(1)	105.2(1)	C(1)–N–C(2)	117.6(2)
C(1)–N–C(3)	125.0(2)	C(2)–N–C(3)	117.3(3)
S–C(1)–O	123.1(2)	S–C(1)–N	115.6(2)
O–C(1)–N	121.2(2)		

Mechanistic Studies

When the reaction between tmtu and **6** was followed by ^{31}P NMR spectroscopy, we observed the fast formation of two main species, **8** and **11**. The resonances due to **11** diminish with time, and after 4 hours at room-temperature, the spectrum shows only peaks from **8** and **9**. The concentration of **9** increases on standing, although at a very slow rate (weeks); it is therefore likely that isomerisation occurs after hydrolysis. Isolation of the *trans* isomer **9** as a pure sample is due to its lower solubility in the crystallisation procedure.

As for the intermediate **11**, NMR spectroscopic data (see Table 1) suggest the formula *cis*-$[Pt(PPh_3)_2(AcO)(tmtu)](AcO)$. In fact, tmtu is still present as such (i.e. not yet hydrolysed), as shown by the presence in the ^1H NMR spectrum of a peak at δ = 2.71 ppm, which integrates for 12 protons. As for the ^{31}P NMR spectrum, the Pt–P coupling constant of the doublet at δ = 17.2 ppm (3246 Hz) is in accordance with a P atom *trans* to an S ligand,[1,9] while the doublet at δ = 6.82 ppm (J_{Pt-P} = 3979 Hz) is assigned to P *trans* to the acetato moiety (compared with δ = 5.72 ppm, J_{Pt-P} = 3826 Hz in **6**). In order to prove the assignment of **11**, we performed the following experiment. We mixed, in CH_2Cl_2, equimolar quantities of **1** and **6**, obtaining the fast equilibration of these two materials with a new species **12** in the ratio 1:1:3. The two doublets shown in the ^{31}P NMR spectrum of this new species are in agreement with two phosphane groups *trans* to the NO_3 and AcO ligands (Table 1, δ and J_{Pt-P} values of **12** compared with those of **1** and **6**). Since no other ligand is present, **12** must be *cis*-$[Pt(PPh_3)_2(AcO)(NO_3)]$. Upon addition of one mole of tmtu per mole of Pt, we obtained a compound with the same NMR parameters as **11**, as the only species in solution (Scheme 3).



Scheme 3.

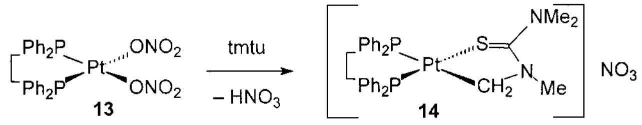
The latter solution is stable (>1 day), i.e. no hydrolysis was observed, even in wet CH_2Cl_2. Because no "free" (i.e. uncomplexed) acetate is present, it is concluded that it is this ion that triggers the hydrolysis reaction. It must be noted that in this experiment, **11** was obtained as the nitrate salt, but no cyclometallation was observed, despite the presence of free NO_3^-, which, according to the results described in a previous section, should promote such a reaction. However, the C–H activation step of the cyclometallation process requires a labile ligand that is *cis* to tmtu.[1–3] In **11**, this position is occupied by an acetato group that is *trans* to a phosphane group, a situation that, because of the antisymbiosis effect,[16] renders a carboxylato ligand rather inert to substitution,[17] as we have recently observed.[18]

Characterisation of **8** presents the problem that it could not be isolated in a pure form, as a result of contamination with **9**. Only after repeated crystallisations could a few milligrams of a pure sample of **8** be obtained, which is just enough for mass and NMR spectroscopy. The ^{31}P NMR parameters of **8** [a singlet with Pt–P coupling constant in the 3200 Hz range (Table 1)] are indicative of a *cis*-PtP_2S_2 coordination set, i.e. two equivalent phosphane groups *trans* to sulfur ligands.[9] Moreover, the peak at δ = 3.21 ppm in the proton spectrum integrates for 12 protons. These facts suggest the formula *cis*-$[Pt(PPh_3)_2(mtc)_2]$ for **8**. A final confirmation of its stoichiometry was obtained by a high resolution ESI^+ spectrum, which showed a peak that corresponds to $[M + Na]^+$ (100%) and whose position differs by only 1 ppm from that computed. Fragmentation is similar to that of **9** (see Experimental Section).

In conclusion, the course of the hydrolysis reaction is summarised in Scheme 4.

Because **8** was always contaminated with the *trans* isomer, and to avoid the problem of *cis–trans* isomerisation, we decided to investigate the dppe derivatives.

First of all we wanted to check whether reaction of $[Pt(dppe)(NO_3)_2]$ (**13**) with tmtu gives, in analogy with **1**, the cyclometallated product $[Pt(dppe)(tmtu^*)](NO_3)$ (**14**). This was indeed obtained, although at a much slower rate than in the case of **1**. Compound **14** was isolated and characterised by elemental analysis, ^1H and ^{31}P NMR spectroscopy (see Table 1). Not only are the Pt–P coupling constants in agreement with a P atom *trans* to a carbon atom and a P atom *trans* to an S ligand, but, more importantly, in the ^1H NMR spectrum, the resonances resulting from tmtu* are also very similar to those of **3**. In particular, the signal centred at 4 ppm, which integrates for 2 protons and displays Pt–H coupling (54.4 Hz), is assigned to Pt–CH_2 (Scheme 5).



Scheme 5.

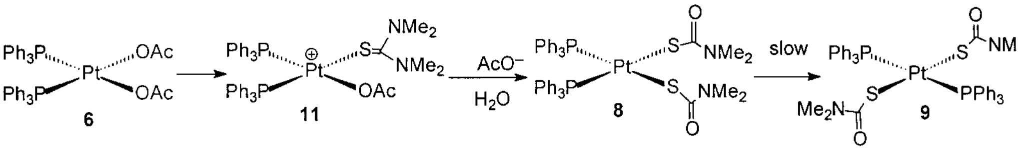
We then moved on to $[Pt(dppe)(AcO)_2]$ (**15**). Reaction of this compound with tmtu led to the isolation of $[Pt(dppe)(mtc)_2]$ (**16**) as a pure product. Besides elemental analysis and mass spectroscopy (see Experimental Section), its identification is confirmed by NMR spectroscopy (Table 1): a ^1H singlet which integrates for 12 protons and one ^{31}P singlet with J_{Pt-P} in accordance with a P atom *trans* to an S atom. On the basis of comparing the Pt–P coupling constants, and by remembering that in the case of the dppe derivatives such constants are usually about 100 Hz lower than those of the analogous PPh_3 complexes,[19] we can confirm the assignment of the structure *cis*-$[Pt(PPh_3)_2(mtu)_2]$ to **8**.

The above results show that the course of the reaction between these Pt–phosphane complexes and tmtu depends on the nature of the anion and the lability of the ligand in the position *cis* to tmtu. Thus, even in the presence of water, no hydrolysis of tmtu was observed with the nitrato and trifluoroacetato complexes as well as with compounds **5a** and **5b**; the only product is the cyclometallated species. On the contrary, with the acetato and malonato derivatives, cyclometallation seems to be inhibited, and, in the presence of water, tmtu is hydrolysed and the mtc complexes **8**, **9** and **16** are formed. To better clarify these points we performed the following experiments.

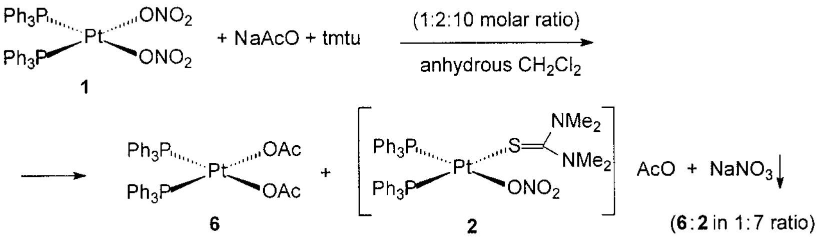
First, under strictly anhydrous conditions, no reaction was observed between tmtu and **6**, which was recovered unchanged after 4 hours. Addition of water, or allowing humidity to enter the reaction vessel by opening it, produced the monothiocarbamato complexes **8** and **9**, showing that water not only hydrolyses tmtu, but also, rather interestingly, that it has an active role in labilising the Pt–acetato bonds.

Second, again under anhydrous conditions, we mixed, in CH_2Cl_2, **1**, tmtu and NaAcO in the molar ratio 1:2:10. This led to the precipitation of $NaNO_3$ and to the formation of a 1:7 mixture of **6** and the acetato salt of **2** (Scheme 6).

The formation of **2** was easily recognised by NMR spectroscopy, since its nitrate salt is already known, as it was the intermediate species that was detected during the cyclometallation reaction of tmtu with **1**.[1] While this mixture is stable for more than one day, it slowly transforms into **11**.



Scheme 4.



Scheme 6.

However, before such a transformation takes place, not only does no hydrolysis occur (no water is present), but also no cyclometallation is observed. This experiment confirms that the latter reaction is promoted by the presence of "free" nitrate and not by acetate; the promotion by free nitrate must be ruled out under these conditions as $NaNO_3$ is insoluble in CH_2Cl_2. When this experiment was repeated using wet CH_2Cl_2, tmtu was hydrolysed, as expected.

Conclusions

We have shown that the interaction of tmtu with the *cis*-Pt^{II}(phos)$_2$ moieties can follow two different reaction paths according to the nature of the anions present. Thus NO_3^-, $CF_3CO_2^-$, BF_4^- and TfO$^-$ lead to the cyclometallated products **3** or **14**, whereas AcO$^-$ and malonate are inactive and, in the presence of water, promote tmtu hydrolysis to give the mtc complexes **8**, **9** and **16**. The two reaction routes are not competitive: no hydrolysis occurs with the former anions and no cyclometallation is observed with the acetato and malonato complexes. As to the origin of the different behaviour, we note the following points.

Cyclometallation requires intermediate cationic complexes, such as **2** or **10**, in which *S*-coordinated tmtu is *cis* to a labile ligand (here NO_3, CF_3CO_2, CH_3CN). Dissociation of these ligands gives rise to a vacant coordination site in the position *cis* to tmtu, which through a σ C–H interaction with the metal centre is a key step in the C–H activation process.[2,3] On the contrary, an acetato group *cis* to tmtu and *trans* to a phosphane group, as in **11**, is less prone to substitution because of the antisymbiosis effect.[16–18] In the latter cationic complex, a methyl group of *S*-coordinated tmtu cannot interact with Pt and tmtu is activated towards nucleophilic attack. However, the function of the "free" anion is less clear; in particular, it is not obvious why deprotonation of a tmtu methyl group (whatever its intimate mechanism) is easily accomplished by NO_3^- and not by AcO$^-$ (see the stability of the acetate salt of **2** in Scheme 6). We propose two possible explanations. First, the relative strengths of protic acids in $CHCl_3$ or CH_2Cl_2 cannot be compared with those in aqueous solutions. For instance, spectroscopic evidence suggests that HNO_3 is a weak acid (and hence NO_3^- a strong base) in chlorinated solvents, even in the presence of water.[20] Thus NO_3^- can easily capture a proton, favouring deprotonation of a CH_3 group. However, the reason why "free" NO_3^- does not induce hydrolysis in the presence of water remains unclear. A second point is that in non-ionising solvents, such as $CHCl_3$ and CH_2Cl_2, the anions are not "free", but presumably strongly associated with the cationic complexes that are the intermediate species in both C–H activation (**2**) and hydrolysis (**11**). The different reaction routes reported here may also depend on the degree and the nature of these ion pairs, which, at the present stage, are difficult to rationalise.

Formation of the *trans* isomer **9** deserves a final comment. In all the hydrolysis runs of tmtu with either **6** or **7**, the *cis* isomer **8** was found to be more abundant, but a small amount of **9** was always present. Formation of such *trans* isomers is not surprising. Not only has the analogous Pd complex this geometry,[4] but also it has been reported that complexes with a somewhat similar coordination set, i.e. [Pt(phos)$_2$(ER)$_2$] (E = S, Se, Te), crystallise with a *trans* geometry[21] or the initially obtained *cis* complex slowly rearranges to the *trans* isomer, which has been calculated to be more stable.[22] It is tempting to think that the formation of **9** may be associated with the rather large $J_{\text{Pt–P}}$ value, an indication of a large σ contribution to the Pt–P interaction, which probably originates from the poor σ-donor ability of S-coordinated mtc groups. Thus, formation of this isomer may arise from a subtle balance between the *trans* and *cis* influence.

Experimental Section

Elemental analyses were performed at the Microanalytical Laboratory, the University of Milano. ^{1}H and ^{31}P{^{1}H} NMR spectra (Table 1) were recorded on a Bruker Advance DRX 300 at 300 and 121 MHz respectively; δ values (ppm) are vs. external Me_4Si and H_3PO_4. Mass spectra were recorded with a VCA Analytical 7070 EQ (FAB$^+$, from nitrobenzyl alcohol, with xenon as the FAB source) and with an ICR-FTMS APEX II with a 4.7-T magnet, Bruker Daltonics (ESI$^+$, CH_2Cl_2/methanol, 1:1). Isotope cluster abundance was checked by computer simulation.

All chemicals were reagent grade. Except where otherwise stated, solvents were used as received.

The syntheses of [Pt(phos)$_2$(NO$_3$)$_2$] have been described previously.[5] *cis*-[Pt(PPh$_3$)$_2$(CH$_3$CN)$_2$](BF$_4$)$_2$, *cis*-[Pt(PPh$_3$)$_2$(CH$_3$CN)$_2$](CF$_3$SO$_3$)$_2$ and *cis*-[Pt(PPh$_3$)$_2$(CF$_3$CO$_2$)$_2$] have been prepared according to literature procedures.[9,23] cis-Pt[(PPh$_3$)$_2$(AcO)$_2$] (**6**), [Pt(PPh$_3$)$_2$(malonato)] (**7**) and [Pt(dppe)(AcO)$_2$] (**15**) were obtained in 75% yields, by a modification of literature methods,[8] using excess sodium acetate or malonate instead of the corresponding silver salts.

Cyclometallation of tmtu with the Acetonitrile Complexes

3(BF$_4$): A CH$_2$Cl$_2$ solution (20 mL) of **5a** (0.120 g, 0.123 mmol) and tmtu (0.016 g, 0.123 mmol) was refluxed for 4 h. The solution was concentrated to 2 mL under reduced pressure, and addition of ethyl acetate gave 0.087 g of the product (75%). $C_{41}H_{41}BF_4N_2P_2PtS$ (937.68): calcd. C 52.5, H 4.4, N 3.0%; found C 52.8, H 4.7, N 3.2%.

3(TfO): This was obtained in a manner similar to that described above from **5a** (0.155 g) and tmtu (0.019 g), but the reaction was performed at room temperature. Yield: 69.4% (0.110 g). $C_{42}H_{41}F_3N_2O_3P_2PtS_2$ (999.94): calcd. C 50.5, H 4.1, N 2.8%; found C 50.2, H 4.3, N 3.0%.

***cis*-[Pt(PPh$_3$)$_2$(AcO)(tmtu)]$^+$ (11):** An equimolar amount of tmtu (0.006 g) was added to a solution of [Pt(PPh$_3$)$_2$(NO$_3$)$_2$] (0.035 g, 0.041 mmol) and [Pt(PPh$_3$)$_2$(AcO)$_2$] (0.035 g, 0.041 mmol) in CH$_2$Cl$_2$ (20 mL). After 6 h at room temperature, the solution was concentrated under reduced pressure. Addition of diisopropyl ether gave a white product. Yield: 0.053 g (65.3%). $C_{43}H_{45}N_3O_5P_2PtS$ (972.93): calcd. C 53.1, H 4.7, N 4.3%; found C 52.8, H 4.6, N 4.3%. The presence of coordinated acetate and ionic nitrate was confirmed by IR spectroscopy (KBr pellets): $\tilde{\nu}$ = 1595 (ν_{asym} coordinated carboxylate), 1384 (sharp, ionic NO$_3^-$) cm^{-1}.

***trans*-[Pt(PPh$_3$)$_2$(mtc)$_2$] (9):** A CH$_2$Cl$_2$ solution (20 mL) of [Pt(PPh$_3$)$_2$(AcO)$_2$] (0.060 g, 0.0717 mmol) and tmtu (0.019 g, 0.144 mmol) was left at room temperature for 6 h. After two weeks diffusion of *n*-hexane gave crystals (10 mg) suitable for X-ray investigation. FAB-MS: *m/z* (%) = 927 (5) [M]$^+$, 839 (50) [M – 2 NMe$_2$]$^+$, 823 (100) [M – mtc]$^+$, 719 (100) [M – 2 mtc]$^+$.

***cis*-[Pt(PPh$_3$)$_2$(mtc)$_2$] (8):** The CH$_2$Cl$_2$/hexane solution obtained above, after filtration of **9**, was evaporated to 2 mL and filtered. Addition of diisopropyl ether to the filtrate gave a white precipitate, which was found by ^{31}P NMR spectroscopy to consist of **9** with an impurity of **8**. Repeated crystallizations gave a few milligrams of pure **8** (^{31}P NMR evidence). FAB-MS: *m/z* (%) = 927 (5) [M]$^+$, 839 (80) [M – 2 NMe$_2$]$^+$, 823 (80) [M – mtc]$^+$, 719 (100) [M – 2 mtc]$^+$. ESI-MS: *m/z* (%) = 950 (100) [M + Na]$^+$, 928 (5) [M + 1]$^+$, 839 (5) [M – 2 NMe$_2$]$^+$, 823 (5) [M – mtc]$^+$. High resolution ESI-MS: calcd. 950.1706 [M + Na]$^+$; found 950.1712.

[Pt(dppe)(tmtu*)]NO$_3$ (14): This compound was obtained by refluxing a solution of [Pt(dppe)(NO$_3$)$_2$] (0.050 g, 0.07 mmol) and tmtu (0.009 g, 0.07 mmol) for two days. The white product was obtained by addition of diisopropyl ether. Yield: 0.033 g (60%). $C_{31}H_{35}N_3O_3P_2PtS$ (786.72): calcd. C 47.3, H 4.5, N 5.3%; found C 47.0, H 4.9, N 5.6%. FAB-MS: *m/z* = 724 [M – NO$_3$]$^+$.

[Pt(dppe)(mtc)$_2$] (16): A solution of [Pt(dppe)(AcO)$_2$] (0.055 g, 0.077 mmol) in CH$_2$Cl$_2$ (20 mL) and tmtu (0.021 g, 0.155 mmol) was left at room temperature for 4 h and concentrated under reduced pressure. The product was obtained by addition of diisopropyl ether. Yield: 0.054 g (86.8%). $C_{32}H_{36}N_2O_2P_2PtS_2$ (801.80): calcd. C 47.9, H 4.5, N 3.5%; found C 47.5, H 4.3, N 3.8%. FAB-MS: *m/z* (%) = 713 (100) [M – 2 NMe$_2$]$^+$, 697 (20) [M – mtc]$^+$, 591 (5) [M – 2 mtc]$^+$. ESI-MS: *m/z* (%) = 824 (5) [M + Na]$^+$, 713 (100) [M – 2 NMe$_2$]$^+$, 697 (50) [M – mtc]$^+$.

Reaction of 1 with tmtu and Sodium Acetate: Sodium acetate (0.039 g 0.476 mmol) was added to a solution of [Pt(PPh$_3$)$_2$(NO$_3$)$_2$] (0.040 g, 0.048 mmol) and tmtu (0.013 g, 0.055 mmol) in CH$_2$Cl$_2$ (20 mL). The resulting slurry was vigorously stirred for 4 h at room temperature, and the solvent was evaporated completely under reduced pressure. The ^{31}P NMR spectrum of a CDCl$_3$ solution of the residue showed the presence of the monothiocarbamato complexes.

Reactions under Anhydrous Conditions: The following reactions were performed under an atmosphere of dry nitrogen, using reagents which had been dried under vacuum for 24 h. CH$_2$Cl$_2$ was distilled over CaH$_2$ immediately before use.

Reaction of *cis*-[Pt(PPh$_3$)$_2$(AcO)$_2$] (6) with tmtu: tmtu (0.013 g, 0.10 mmol) was added to a solution of **6** (0.042 g, 0.05 mmol) in anhydrous CH$_2$Cl$_2$ (20 mL). The solution was left for 6 h at room temperature under a nitrogen atmosphere. The solvent was evaporated to dryness under vacuum and redissolved in CDCl$_3$. ^{31}P NMR spectroscopy showed the presence of only the starting material.

Reactivity of 1 with tmtu and Sodium Acetate: Dry sodium acetate (0.042 g, 0.512 mmol) was added to a CH$_2$Cl$_2$ solution (20 mL) of [Pt(PPh$_3$)$_2$(NO$_3$)$_2$] (0.043 g, 0.051 mmol) and tmtu (0.0134 g, 0.103 mmol). The slurry was stirred vigorously for 4 h at room temperature under a nitrogen atmosphere, and the solvent was then evaporated completely under vacuum. ^{31}P NMR spectroscopy of a CDCl$_3$ solution of the residue showed the presence of a mixture of [Pt(PPh$_3$)$_2$(AcO)$_2$] (**6**) and [Pt(PPh$_3$)$_2$(NO$_3$)(tmtu)]$^+$ (**2**).

X-ray Data Collection and Structure Determination: Crystal data are summarised in Table 3. The diffraction experiment was carried out with a Bruker SMART CCD area-detector diffractometer at 296 K, using Mo-K_α radiation (λ = 0.71073) with a graphite crystal monochromator in the incident beam. No crystal decay was ob-

Table 3. Crystallographic data.

Compound	**9**
Formula	$C_{42}H_{42}N_2O_2P_2PtS_2$
M	927.98
Colour	colourless
Crystal system	triclinic
Space group	$P\bar{1}$
a [Å]	10.087(1)
b [Å]	10.411(1)
c [Å]	11.455(1)
α [°]	99.12(1)
β [°]	114.88(1)
γ [°]	104.04(1)
U [Å^3]	1011.3(2)
Z	1
F(000)	464
D_c [g cm^{-3}]	1.524
T [K]	296
Crystal dimensions [mm]	0.28 × 0.32 × 0.41
μ (Mo-$K\alpha$) [cm^{-1}]	37.2
Min. and max. transmission	
Factors	0.754–1.000
Scan mode	ω
Frame width [°]	0.30
Time per frame [sec]	10
No. of frames	4900
Detector-sample distance [cm]	4.00
θ range	3–27
Reciprocal space explored	full sphere
No. of reflections (total; independent)	23827, 4411
R_{int}	0.0213
Final R_2 and R_{2w} indices[a] (F^2, all reflections)	0.030, 0.038
Conventional R_1 index [$I>2\sigma(I)$]	0.015
Reflections with $I>2\sigma(I)$	4323
No. of variables	232
Goodness of fit[b]	0.94

[a] $R_2 = [\Sigma(|F_o^2 - kF_c^2|)/\Sigma F_o^2]$, $R_{2w} = [\Sigma w/(F_o^2 - kF_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$. [b] $[\Sigma w(F_o^2 - kF_c^2)^2/(N_o - N_v)]^{1/2}$, where $w = 4F_o^2/\sigma(F_o^2)^2$, $\sigma(F_o^2) = [\sigma^2(F_o^2) + (pF_o^2)^2]^{1/2}$, N_o is the number of observations, N_v the number of variables, and *p*, the ignorance factor, = 0.02.

served, therefore no time-decay correction was needed. The collected frames were processed with the software SAINT,[24] and an empirical absorption correction was applied (SADABS)[25] to the collected reflections. Calculations were performed using the Personal Structure Determination Package,[26] and the physical constants tabulated therein.[27] The structure was solved by direct methods (SHELXS)[28] and refined by full-matrix least-squares using all reflections and minimising the function $\Sigma w(F_o^2 - kF_c^2)^2$ (refinement on F^2). All the non-hydrogen atoms were refined with anisotropic thermal factors. The hydrogen atoms were placed in their ideal positions (C–H = 0.97 Å), with the thermal parameter B 1.10 times that of the carbon atom to which they are attached, and were not refined. In the final Fourier map, the maximum residual was 0.76(6) $e\text{Å}^{-3}$ at 0.82 Å from Pt. CCDC-272407 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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[1] S. Fantasia, M. Manassero, A. Pasini, *Inorg. Chem. Commun.* **2004**, *7*, 97–100.
[2] U. Fekland, K. I. Goldberg, *Adv. Inorg. Chem.* **2003**, *54*, 259–320.
[3] R. H. Crabtree, *J. Organomet. Chem.* **2004**, *689*, 4083–4091.
[4] G. Besenyei, E. Herdtweck, S. Holly, D. Maennig, H. Noerth, L. I. Simandi, P. Viski, *Inorg. Chem.* **1988**, *27*, 3201–3201.
[5] For instance: a) R. Colton, T. A. Stephenson, *Polyhedron* **1984**, *3*, 231–234; b) G. Exarchos, S. D. Robinson, J. W. Steed, *Polyhedron* **2001**, *20*, 2951–2963; c) R. Colton, J. Ebner, *Inorg. Chem.* **1989**, *28*, 1559–1563.
[6] a) E. M. Krankovits, R. J. Magee, M. J. O'Connor, *Aust. J. Chem.* **1973**, *26*, 1645–1652; b) K. R. M. Springsteen, D. L. Greene, B. J. McCormick, *Inorg. Chim. Acta* **1977**, *23*, 13–18.
[7] a) J. G. M. van der Linden, W. Blommerde, A. H. Dix, F. W. Pijpers, *Inorg. Chim. Acta* **1977**, *24*, 261–267; b) R. D. Bereman, D. M. Baird, J. R. Dorfman, J. Bordner, *Inorg. Chem.* **1982**, *21*, 2365–2368; c) B. J. McCormick, R. Bereman, D. Baird, *Coord. Chem. Rev.* **1984**, *54*, 99–130.
[8] A. L. Tan, P. M. N. Low, Z.-Y. Zhou, W. Zheng, B.-M. Wu, T. C. W. Mak, T. S. A. Hor, *J. Chem. Soc., Dalton Trans.* **1996**, 2207–2214.
[9] A. Pasini, S. Rizzato, D. De Cillis, *Inorg. Chim. Acta* **2001**, *315*, 196–204.
[10] C. K. Johnson, *ORTEP*, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tn, **1976**.
[11] For instance: a) N. M. Boag, K. Mohan Rao, N. J. Terril, *Acta Crystallogr., Sect. C* **1991**, *47*, 1064–1065; b) A. C. Dema, C. M. Lukehart, *Inorg. Chim. Acta* **1997**, *264*, 193–198; c) D. Steinborn, S. Becke, C. Bruhn, F. W. Heinemann, *J. Organomet. Chem.* **1998**, *556*, 189–196; d) M. Basato, A. Biffis, G. Martinati, C. Tubaro, A. Venzo, P. Ganis, F. Benetollo, *Inorg. Chim. Acta* **2003**, *355*, 399–403.
[12] a) N. Mintcheva, Y. Nishihara, A. Mori, K. Osakada, *J. Organomet. Chem.* **2001**, *629*, 61–67; b) U. Abram, D. Belli Dell'Amico, F. Calderazzo, L. Marchetti, J. Straehle, *J. Chem. Soc., Dalton Trans.* **1999**, 4093–4098; c) W. V. Konze, B. L. Scott, G. J. Kubas, *Chem. Commun.* **1999**, 1807–1808.
[13] a) P. C. Christidis, P. J. Rentzeperis, *Acta Crystallogr., Sect. B* **1979**, *35*, 2543–2547; b) R. Colton, M. F. Mackay, V. Tedesco, *Inorg. Chim. Acta* **1993**, *207*, 227–232.
[14] I. J. B. Lin, H. W. Chen, J. P. Fackler Jr, *Inorg. Chem.* **1978**, *17*, 394–401.
[15] E. Enzmann, M. Eckert, W. Ponikwar, K. Polborn, S. Schneiderbauer, M. Beller, W. Beck, *Eur. J. Inorg. Chem.* **2004**, 1330–1340.
[16] J. Kuyper, *Inorg. Chem.* **1979**, *18*, 1484–1489.
[17] a) L. Battan, S. Fantasia, M. Manassero, A. Pasini, M. Sansoni, *Inorg. Chim. Acta* **2005**, *358*, 555–564 and references cited therein; b) L. Battan, M. Manassero, A. Pasini, *Inorg. Chem. Commun.* **2001**, *4*, 606–609.
[18] R. G. Pearson, *Chemical Hardness*, Wiley VCH, **1977**, p. 15.
[19] P. S. Pregosin, R. W. Kunz, *^{31}P and ^{13}C NMR of Transition Metal Complexes*, Springer-Verlag, **1979**.
[20] a) E. S. Stoyanov, T. P. Vorob'yova, I. V. Smirnov, *J. Struct. Chem.* **2003**, *44*, 365–375; b) E. S. Stoyanov, personal communication.
[21] a) T. B. Rauchfuss, J. S. Shu, D. M. Roundhill, *Inorg. Chem.* **1976**, *15*, 2096–2101; b) V. K. Jain, S. Kannan, E. R. T. Tiekink, *J. Chem. Res. (S)* **1994**, 85; V. K. Jain, S. Kannan, E. R. T. Tiekink, *J. Chem. Res. (M)* **1994**, 501.
[22] M. S. Hannu-Kuure, J. Komulainen, R. Oilunkaniemi, R. S. Laitinen, R. Suontamo, M. Ahlgren, *J. Organomet. Chem.* **2003**, *666*, 111–120.
[23] a) R. Bertani, R. A. Michelin, M. Mozzon, A. Sassi, M. Basato, A. Biffis, G. Martinati, M. Zecca, *Inorg. Chem. Commun.* **2001**, *4*, 281–284; b) R. Bertani, M. Biasiolo, K. Darini, R. A. Michelin, M. Mozzon, F. Visentin, L. Zanotto, *J. Organomet. Chem.* **2002**, *642*, 32–39.
[24] SAINT Reference manual, Siemens Energy and Automation, Madison, W1, **1994–1996**.
[25] G. M. Sheldrick, *SADABS, Empirical Absorption Correction Program*, University of Göttingen, **1997**.
[26] B. A. Frenz, *Comput. Phys.* **1988**, *2*, 42–47.
[27] *Crystallographic Computing 5*, Oxford University Press, Oxford, U. K., **1991**, ch. 11, p. 126.
[28] G. M. Sheldrick, *SHELXS 86, Program for the Solution of Crystal Structures*, University of Göttingen, Germany, **1985**.

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