Synthesis, Crystal Structure and Solution Behaviour of Palladium(II) Complexes with Tetrazenido or Amido Ligands and Potentially Tridentate Ligands

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$Pd(DBA)_2$ reacts with the azide $C_6F_5N_3$ in the presence of terpy* to form the tetrazenido palladium(II) complex [(η^2-terpy*)Pd{η^2-$N_4(C_6F_5)_2$}] **1**, whereas with TsN_3 the amido complex [(η^3-terpy*)Pd(NHTs)]$^+$ is obtained. Another synthetic route involving abstraction of chloride ions from [(L)PdCl]Cl and transmetallation with KNHTs yields the complexes [(η^3-L)Pd(NHTs)](BF_4) (**4**: L = terpy*; **5**: L = triphos). Compounds **1**, **4** and **5** have been characterized in the solid state by single-crystal X-ray analysis as mononuclear, square-planar complexes. ^{1}H and ^{19}F NMR spectroscopy reveal that **1** is a fluxional molecule. Rotation of both C_6F_5 rings is hindered, with energy barriers of 53.9 kJ·mol^{-1} (293 K) and 60.7 kJ·mol^{-1} (325 K). Additionally, the lateral pyridines and the C_6F_5 rings exchange through an oscillatory process where one terminal pyridine enters the coordination sphere while the other leaves it. The corresponding energy barrier (74.9 kJ·mol^{-1} at 298 K) has been determined from selective inversion NMR experiments.

Introduction

The covalent bond between a late transition metal of the second or third series and nitrogen has received much attention recently. It is frequently involved in important steps of stoichiometric or catalytic reactions; for instance, palladium amido complexes are involved in the formation of C−N bonds.[1] It has long been considered that the high reactivity of the metal−nitrogen bond is a consequence of the mismatch between the soft metal and the hard nitrogen atom, although this interpretation has been put in question.[2]

The synthesis and reactivity of polynuclear palladium(II) complexes with bridging imido ligands has been reported.[2] On the contrary, mononuclear palladium imido complexes have never been fully characterized,[3] although they have frequently been postulated as transient intermediates in reactions such as the palladium-catalyzed carbonylation of nitroaromatics.[4] Thus, it would be desirable to stabilize and isolate such species. In principle, imido complexes could be obtained from azides, or from the deprotonation of an amido complex. Yet the reaction of organic azides with zerovalent group 10 metals leads instead to tetrazenido, amido or azido complexes, or to polymers.[5,6a,6b,7] It has nevertheless been proposed that transient mononuclear imido intermediates should be involved in the formation of the tetrazenido complexes.

We have been interested lately in the use of tridentate ligands in the coordination chemistry of palladium.[8] Such ligands have been found to stabilize reactive organometallic species,[9] and it could be expected that they might stabilize those imido compounds. In addition, a bridged complex should be avoided in favour of a mononuclear complex, provided that only one coordination site remains in a tetracoordinate palladium complex.

We report here the synthesis and characterization of new palladium tetrazenido and amido complexes obtained from the reaction of Pd^0 with organic azides or the reaction of Pd^{II} complexes with potassium tosylamide, in the presence of the potentially tridentate ligands 4,4′,4"-tri(*tert*-butyl)-2,2′:6′,2"-terpyridine (terpy*)[10] or bis(2-diphenylphosphanylethyl)phenylphosphane (triphos).

Results and Discussion

Tetrazenido Palladium Complexes

The reaction of palladium(0) bis(dibenzylideneacetone) $Pd(DBA)_2$ with an excess of terpy* and pentafluorophenyl azide in toluene at room temperature leads to the η^2-terpy* tetrazenido palladium(II) complex **1** (Scheme 1). The yield is moderate (39%), mainly owing to the difficulty of separa-

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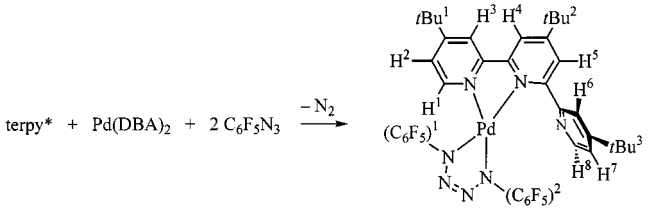
tion from other by-products; however, the yield of the synthesis of tetrazenido or tetrazadiene metal complexes from organic azides is usually lower than 50%.[5] If an equimolar amount of terpy* and azide are used in the synthesis, complex **1** is still obtained as the only product, although with a lower yield. To the best of our knowledge, the only other palladium tetrazenido complex reported to date was prepared by another synthetic route.[5a]



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Scheme 1. Synthesis of the tetrazenido palladium complex **1**

Compound **1** is soluble in organic solvents like THF, CH_2Cl_2, toluene or even pentane. In general, the complex is not stable in solution, and it slowly decomposes at room temperature in chloroform or methanol, yielding pentafluorophenyl azide and pentafluoroaniline according to ^{19}F NMR analysis. This kind of transformation has been reported for rhodium, iridium or platinum tetrazenido complexes upon treatment with an acid.[11]

The molecular structure of **1** is depicted Figure 1, and selected bond lengths and angles are given in Table 1. Two crystallographically independent, but closely similar, molecules of **1** and two molecules of diisopropyl ether are present within the asymmetric unit; only one molecule of **1** is discussed in the following section. The ORTEP drawing shows a palladium atom coordinated by a bidentate bis(pentafluorophenyl)tetrazenido ligand and a bidentate terpy* ligand. The complex is square planar, but slightly distorted toward a tetrahedral geometry. Pd1, N4, N5, N6, and N7 are nearly coplanar within ±0.03 Å, and their mean plane makes an angle of 19.9(1)° with the N1−Pd1−N2 plane; N1 is located 0.597(3) Å below the mean plane and N2 0.242(3) Å above. The palladium atom deviates from the plane of the coordinating pyridines, as shown by the Pd1−N1−C5−C10 torsion angle of −19(1)°. Those distortions, which arise from steric interactions between terpy* and the tetrazenido ligand, are minimized by the roughly parallel positioning of the uncoordinating pyridine plane and the adjacent pentafluorophenyl plane. Both planes are ca. 3 Å distant one from the other, which is consistent with some π-stacking. The N2−C14−C19−N3 torsion angle is much larger [156.9(9)°] than that found in other η^2-terpy metal complexes;[8a,12,13] the other rotamer, i.e. where this torsion angle would be close to 0°, is not observed in the unit cell. As a consequence of the minimized steric interactions between the two ligands, the difference between the Pd1−N1 and the Pd1−N2 bond lengths (0.02 Å) is small.

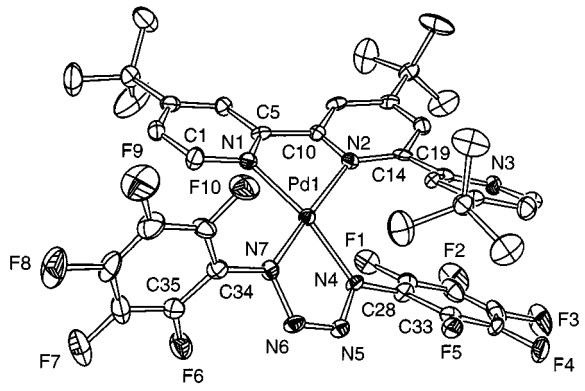


Figure 1. ORTEP drawing of **1** showing 30% probability thermal ellipsoids and the atom-numbering scheme; hydrogen atoms and $i Pr_2O$ are omitted for clarity

Table 1. Selected bond lengths [Å] and bond angles [°] for complex **1**

Pd1−N1	2.052(9)	N4−C28	1.39(1)
Pd1−N2	2.073(9)	N4−N5	1.39(1)
Pd1−N4	1.988(8)	N5−N6	1.25(1)
Pd1−N7	1.986(8)	N6−N7	1.41(1)
		N7−C34	1.39(1)
N1−Pd1−N2	78.9(4)	Pd1−N2−C10	111.2(7)
N1−Pd1−N4	162.9(4)	Pd1−N2−C14	130.4(8)
N1−Pd1−N7	104.0(4)	Pd1−N4−C28	131.7(7)
N2−Pd1−N4	103.4(4)	Pd1−N4−N5	116.6(6)
N2−Pd1−N7	172.7(4)	Pd1−N7−C34	132.7(8)
N4−Pd1−N7	75.9(4)	Pd1−N7−N6	117.2(6)
Pd1−N1−C1	128.4(8)	N4−N5−N6	116.1(9)
Pd1−N1−C5	112.3(7)	N5−N6−N7	114.0(9)

Like the tetrazenido palladium complex $[Pd(PEt_3)_2(N_4Ph_2)]$ described by Trogler et al.,[5a] the N4−N5 and N6−N7 bond lengths [1.39(1) and 1.41(1) Å, respectively] correspond to single bonds, whereas the N5−N6 bond length [1.25(1) Å] is characteristic of a double bond. However, the Pd1−N4 and Pd1−N7 bonds are shorter than in Trogler's complex [1.988(8) and 1.986(8) Å, respectively], which can be related to the lower *trans* influence of pyridines compared to phosphorus ligands. The pentafluorophenyl rings are tilted, as shown by the torsion angles N6−N7−C34−C35 [−54(1)°] and N5−N4−C28−C33 [−43(1)°]. This is another characteristic of the tetrazenido form in contrast to the tetrazadiene form.[5c]

The room-temperature NMR spectrum of **1** is characteristic of an unsymmetrical, bidentate terpy* ligand (Figure 2), and is in agreement with the X-ray structure. The protons of the noncoordinating pyridine are all deshielded in comparison with the equivalent protons of the lateral coordinating pyridine, although the tendency is generally the reverse in η^2-terpy metal complexes.[8,12,14] The latter protons, in particular H^1 and H^2, lie in the anisotropy cone of the pentafluorophenyl ring A, with chemical shifts as low as $\delta = 6.40$ (H^2). In contrast, H^6 is strongly deshielded at $\delta = 10.12$. This may be the effect of a weak agostic CH···Pd

interaction or of the paramagnetic anisotropy of the metal atom;[15] the X-ray structure indicates that H^6 is located ca. 2.7 Å above the palladium atom. The deshielding effect of the nitrogen that is located close to H^5, i.e. N3 on the solid-state structure (vide supra), must also explain the difference between the chemical shifts of H^5 and H^4 ($\Delta\delta$ = 1.14 ppm).[12b]

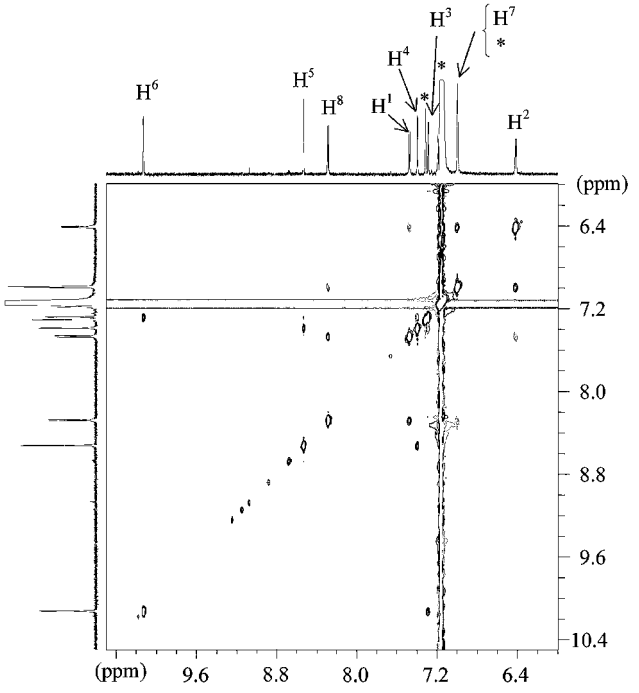
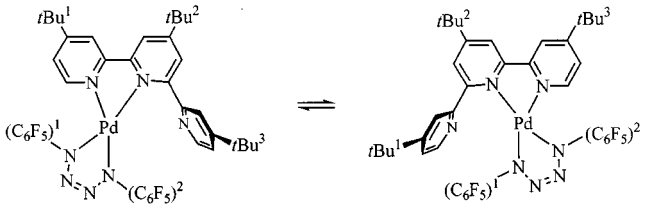


Figure 2. Section of the phase-sensitive $^1H-^1H$ ROESY spectrum of complex **1** (C_6D_6, 298 K, 500 MHz), showing exchange cross-peaks (positive, darker lines) and NOE cross peaks (negative, lighter lines); see Scheme 2 for hydrogen labelling; the asterisks correspond to the solvent

The ^1H-^1H ROESY spectrum shows negative (NOE) cross-peaks that allow us to assign unambiguously the proton signals. In particular, H^3 presents a strong NOE cross-peak with H^4. This was expected since they lie in close proximity, both coordinating pyridines being coplanar. The absence of an NOE interaction between H^5 and H^6 is consistent with the N2−C14−C19−N3 dihedral angle found in the X-ray structure (vide supra).

Exchange (positive) cross-peaks for the H^1/H^8, H^2/H^7, H^3/H^6 and H^4/H^5 pairs (Figure 2), and for the tBu^1/tBu^3 pair are observed in the ROESY spectrum. This fluxionality can be interpreted by the well-known oscillatory mechanism of (η^2-terpy) metal complexes (Scheme 2).[12,14,16] This mechanism is also supported by a ^{19}F-^{19}F NOESY spectrum recorded at room temperature in C_6D_6, which shows that the *para* fluorines of rings A and B exchange with one another. In order to determine the exchange rate of this fluxional mechanism, we ran a selective inversion-recovery NMR experiment.[17] The recovery of the tBu^1 and tBu^3 protons was followed as a function of time after the selective inversion of tBu^1 (Figure 3); the initial decrease in intensity of the tBu^3 signal reflects the chemical exchange. We determined from these NMR spectroscopic data the exchange rate at 298 K as $k = 0.47 \pm 0.05$ s^{-1}, which corresponds to $\Delta G^{\ddagger} = 74.9 \pm 0.3$ kJ·mol^{-1}. The experiment was confirmed by the selective inversion of the tBu^3 protons, leading in turn to an alteration of the intensity of the tBu^1 signal and to the same value of k. This $\Delta G^{\ddagger}_{298}$ value is, to the best of our knowledge, the highest known for an η^2-terpy palladium complex; this is probably linked with the bulkiness of the tetrazenido ligand.



Scheme 2. Fluxional behaviour of complex **1**

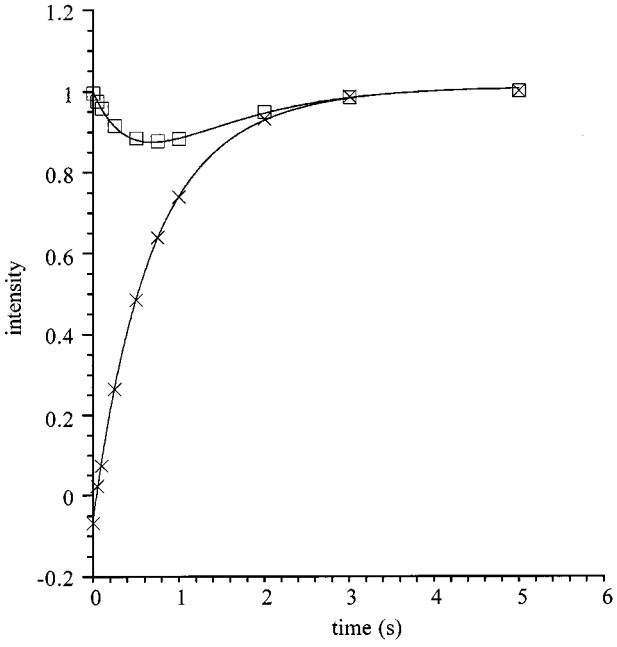


Figure 3. Result of the selective inversion-recovery of the tBu^1 protons of complex **1** at 298 K: evolution vs. time of the intensity of the tBu^1 signal at δ = 0.81 (×) and the tBu^3 signal at δ = 1.46 (square)

The low-temperature ^{19}F NMR spectrum of complex **1** in deuterated chloroform displays ten distinct signals between δ = −170 and −145 (Figure 4). Therefore at this temperature both the oscillatory mechanism and the rotation of the pentafluorophenyl rings around the carbon−nitrogen bonds are frozen; the complex is present as a single conformer, very probably the one which was observed by X-ray crystallography. Upon raising the temperature, we first observe the coalescence of one pair of *meta* signals at δ = −163.52/−162.61 (T_c = 285 K) and one pair of *ortho* signals at δ = −147.62/−145.90 (T_c = 293 K). The same value of $\Delta G^{\ddagger}$ was calculated for both pairs of exchanging signals, i.e. 54.0 kJ·mol^{-1}. Above 272 K, another set

of *ortho* (δ = −151.43/−146.98) and *meta* (δ = −166.06/−164.66) signal pairs starts to coalesce. The complete coalescence into one signal is not reached for any of them at the boiling temperature of the solvent; yet T_c can be estimated for the *meta* signals at 325 K, with a corresponding $\Delta G^{\ddagger} = 60.7\ kJ{\cdot}mol^{-1}$. All those coalescences are obviously the effect of the rotation of the pentafluorophenyl rings. As the rotation of $(C_6F_5)^2$ must be more restricted than the rotation of $(C_6F_5)^1$ because of the proximity of the uncoordinated pyridine, we can assign the values of $53.9\ kJ{\cdot}mol^{-1}$ to ring 1 and of $60.7\ kJ{\cdot}mol^{-1}$ to ring 2. Thus all the signals of the low-temperature ^{19}F NMR spectrum could be assigned. We note that, in general, the fluorines borne by ring 2 are more shielded than the equivalent fluorines of ring 1.

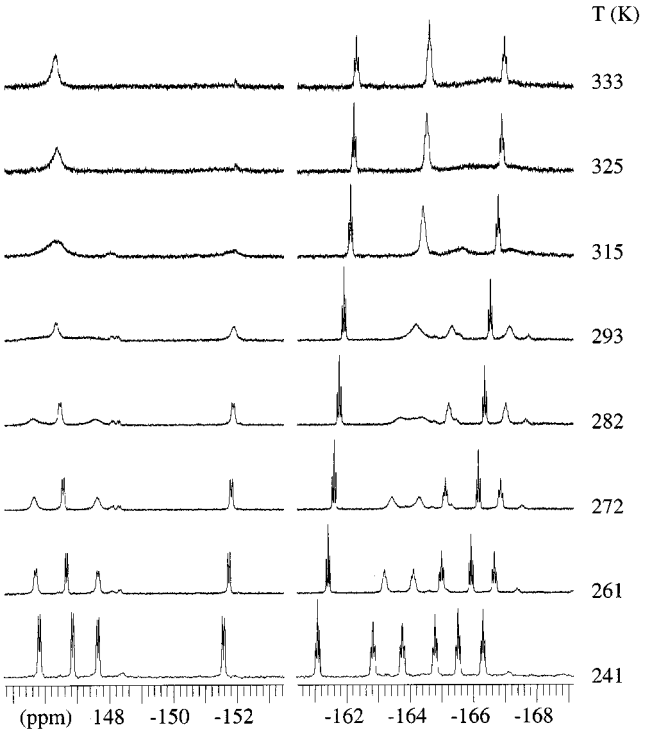
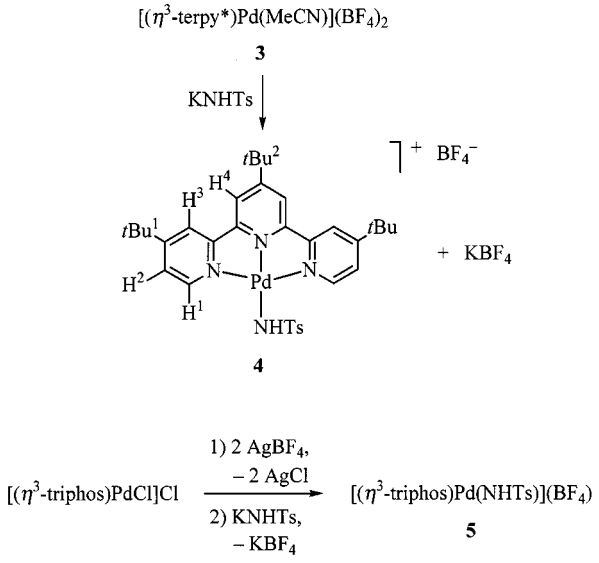


Figure 4. ^{19}F NMR spectra of complex **1** ($CDCl_3$, 376.5 MHz) in the range 241−333 K; see Exp. Section for the complete assignment

the solvent. We therefore had to prepare this cationic amido complex by another synthetic pathway in order to characterize it completely.

The amido complexes **4** and **5** were prepared in very good yield from potassium tosylamide (Scheme 3), since it had been shown that potassium anilide is an efficient reagent for the preparation of palladium amido complexes.[18] The terpy* palladium(II) precursor **3** bearing a labile CH_3CN ligand could be synthesized from terpy* and $[Pd(CH_3CN)_4](BF_4)_2$, following the method described with terpy.[19] An alternative pathway consisted of preparing [(η³-terpy*)PdCl]Cl (**2**) from terpy* and $[Pd(PhCN)_2Cl_2]$, and then removing the chloride anions with silver tetrafluoroborate. The ^1H NMR characteristics of **4** are exactly the same as those of the product obtained from $Pd(DBA)_2$, terpy* and TsN_3. Complex **5** was obtained in a one-pot reaction from [(η³-triphos)PdCl]Cl, removing first the chloride ions with a silver salt at room temperature and then allowing the palladium complex to react at −78° C with the amide anion. Other palladium or platinum sulfonamido complexes have been reported in the literature,[6] but **4** and **5** are, to the best of our knowledge, the first cationic ones reported to date.



Scheme 3. Synthesis of the amido complexes **4** and **5**

Amido Palladium Complexes

Following the reaction conditions that led to complex **1**, we replaced pentafluorophenyl azide by tosyl azide. It is worth noting that $[Pd(PPh_3)_4]$ reacts with tosyl azide to give, presumably, a polymeric triphenylphosphane derivative of Pd^0.[5b] In spite of our best efforts, the product of the reaction of $Pd(DBA)_2$ with TsN_3 and terpy* could not be completely purified. However, its NMR features reveal one tosylamido moiety and a symmetrical terpy* ligand, suggesting the expected tridentate coordination. In addition, its FAB^+-MS spectrum shows a peak at $m/z = 677.1$ that corresponds to a $[(terpy^*)Pd(NHTs)]^+$ cation. We suppose that the NH proton originates from some residual water in

Complexes **4** and **5** are not air-sensitive, but **5** slowly decomposes in solution at room temperature. Their relative stability is probably connected with the electron-withdrawing tosyl fragment; it has been suggested that amido palladium complexes are stabilized by substituents that can accommodate π-donation from the nitrogen lone pair.[18] The ^1H NMR N*H* signals appear at δ = 3.61 (**4**) and δ = 2.55 (**5**), and are therefore in the same region as for reported palladium or platinum sulfonamido complexes.[6]

The molecular structures of complexes **4** and **5** are depicted in Figure 5 and 6, and selected bond lengths and angles are given Table 2 and 3. Both of them consist of slightly distorted square-planar $[(\eta^3\text{-L})Pd(NHTs)]^+$ cationic

complexes, where L is either terpy* (**4**) or triphos (**5**), and noncoordinating tetrafluoroborate anions. Complex **4** co-crystallizes with two molecules of water each with an occupancy ratio of 50% and 25%. In the case of complex **5**, the asymmetric unit contains two crystallographically independent molecules of **5** and one acetonitrile; those molecules are practically equivalent and only one is discussed.

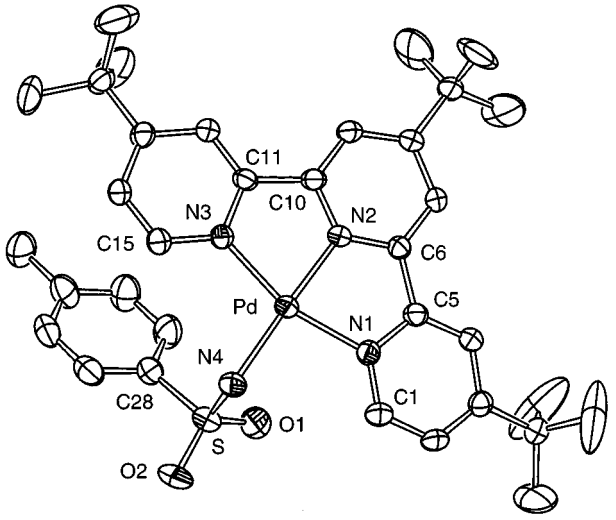


Figure 5. ORTEP drawing of **4** showing 30% probability thermal ellipsoids and the atom-numbering scheme; hydrogen atoms, BF_4^- and H_2O are omitted for clarity

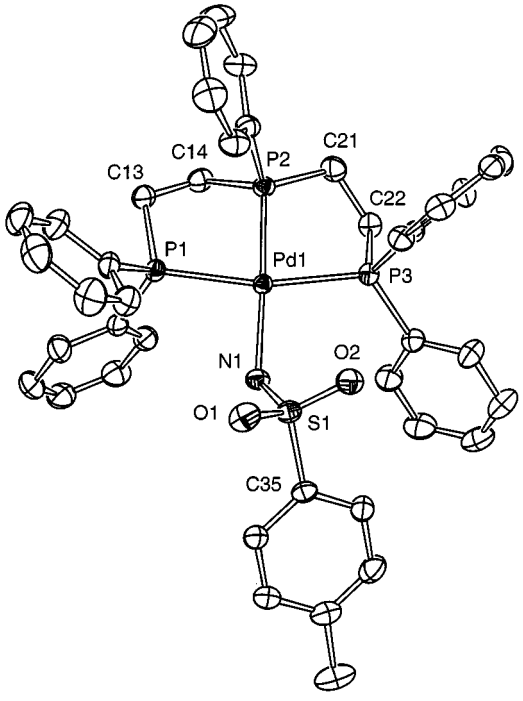


Figure 6. ORTEP drawing of **5** showing 30% probability thermal ellipsoids and the atom-numbering scheme; hydrogen atoms, BF_4^- and CH_3CN are omitted for clarity

For both complexes, the characteristics of the (η^3-L)Pd fragments are very close to those of related terpy[20] or triphos[21] complexes, with the short bond angles N−Pd−N [N1−Pd−N2 = 81.0(3)°, N2−Pd−N3 = 80.5(3)°] or P−Pd−P [P1−Pd1−P2 = 82.64(3)°, P2−Pd1−P3 = 82.07(3)°] expected for five-membered metallacycles. The palladium atom lies out of the N_4 mean plane by only 0.0375(2) Å in complex **4**, and out of the NP_3 mean plane by 0.1178(1) Å in complex **5**.

Table 2. Selected bond lengths [Å] and bond angles [°] for complex **4**

Pd−N1	2.023(7)	Pd−N4	2.027(7)
Pd−N2	1.935(6)	N4−S	1.604(9)
Pd−N3	2.022(7)	S−C28	1.78(1)
N1−Pd−N2	81.0(3)	Pd−N1−C5	113.2(5)
N1−Pd−N3	161.5(3)	Pd−N2−C6	118.4(5)
N1−Pd−N4	96.5(3)	Pd−N2−C10	118.6(6)
N2−Pd−N3	80.5(3)	Pd−N3−C11	114.3(5)
N2−Pd−N4	176.4(3)	Pd−N3−C15	128.3(6)
N3−Pd−N4	101.9(3)	Pd−N4−S	117.1(4)
Pd−N1−C1	128.1(6)	N4−S−C28	107.4(5)

Table 3. Selected bond lengths [Å] and bond angles [°] for complex **5**

Pd1−P1	2.3416(7)	Pd1−N1	2.084(2)
Pd1−P2	2.2293(7)	N1−S1	1.592(2)
Pd1−P3	2.3309(7)	S1−C35	1.778(3)
P1−Pd1−P2	82.64(3)	Pd1−P1−C13	107.12(4)
P1−Pd1−P3	163.32(3)	Pd1−P2−C14	106.15(5)
P1−Pd1−N1	94.96(7)	Pd1−P2−C21	112.06(6)
P2−Pd1−P3	82.07(3)	Pd1−P3−C22	102.29(4)
P2−Pd1−N1	174.84(7)	Pd1−N1−S1	123.50(5)
P3−Pd1−N1	99.72(7)	N1−S1−C35	105.4(1)

Concerning the sulfonamido fragments, the palladium−nitrogen bond length [**4**: 2.027(7) Å; **5**: 2.084(2) Å] is typical of a single bond; it is somewhat longer in **5** than in **4** because of the *trans* influence of the phosphane. In fact, the Pd−N bond in palladium amido complexes is generally a single bond,[6,18] as long as no ligand-to-metal π-donation is possible in d^8 metal complexes.[22] The nitrogen−sulfur bond is rather short [**4**: 1.604(9) Å; **5**: 1.592(2) Å], whereas the N−S bond length measured on a tungsten tosylamido complex is larger [1.641(5) Å].[23] This is indicative of a delocalization of the nitrogen lone pair onto the adjacent electron-withdrawing SO_2 function as in other palladium sulfonamido complexes.[6] We observe a higher value for the Pd1−N1−S1 angle in **5** [123.50(5)°] than for the Pd−N4−S angle in **4** [117.1(4)°]; the phenyl substituents borne by triphos exert a steric influence that may be the origin of this difference.

In complex **4**, the Pd−N−S plane is roughly perpendicular to the coordination plane, with an angle of 87.7(1)° with the N_4 plane, although in complex **5** the angle with the P_3N plane is somewhat smaller [60.39(5)°]. Those large angles can stem from a minimized interaction between the nitrogen lone pair and the filled *d*-orbitals of palladium,[24]

and/or from a reduced steric strain between the tridentate ligand and the tosylamido ligand.

In addition, the tetrafluoroborate anion is disordered in the X-ray structure of **4**. We can, however, observe that some of the fluorine atoms are less than 3 Å distant from N4, suggesting an NH···F hydrogen bond between the complex and BF_4.

Like some other Pd and Rh amido complexes,[2] **4** and **5** could not be deprotonated to imido complexes, despite the electron-withdrawing effect of the tosyl substituent. Most of the reactions with bases like organolithium reagents or LDA led to decomposition and intractable mixtures. The CD_2CN^- anion generated by reaction of butyllithium with CD_3CN substituted the tosylamido ligand in complex **5** according to FAB-MS analysis. Similarly, the reaction of **5** with Cs_2CO_3 in methanol led to a (triphos)Pd(OH)$^+$ cation. We also noted the absence of reactivity of **5** towards CO.

Conclusion

The results described in this paper show that under identical conditions, the reaction of $Pd(DBA)_2$ and terpy* with $C_6F_5N_3$ leads to the tetrazenido complex **1**, whereas with TsN_3 the product is an amido complex. These results contrast with the reported reactions of Pd^0 complexes with azides, which give either bis-azido Pd^{II} complexes[7] or polymeric triphenylphosphane derivatives of Pd^0.[5b] The terpyridine ligand obviously plays a key role in the orientation of the reaction; however, no imido complexes were obtained.

In the product **1**, derived from $C_6F_5N_3$, terpy* binds palladium in a bidentate manner and the complex is fluxional via an oscillatory mechanism. The X-ray structure and NMR properties of **1** also reveal that the rotations of the C_6F_5 rings around the C−N bonds are hindered. In contrast, terpy* is tridentate and the fourth coordination position is occupied by $TsNH^-$ in the product derived from TsN_3. We suspect that steric interactions between the large, tetrahedral sulfonamide function and the pendant pyridine of terpy* would be too important to make a tosyl analogue of **1** stable.

Experimental Section

General: All experiments were carried out at room temperature under a nitrogen or argon atmosphere, using a vacuum line or Vacuum Atmospheres glovebox equipped with Dri-Train HE-493 inert gas purifier, unless otherwise stated. All solvents were dried by standard methods and distilled under nitrogen, except benzonitrile (Fluka) which was used as received. $[Pd(CH_3CN)_4](BF_4)_2$ and $AgBF_4$ were purchased from Strem and used as received. Tosyl azide,[25] pentafluorophenyl azide,[26] potassium tosylamide,[27] 4,4′,4"-tri(*tert*-butyl)-2,2′:6′,2"-terpyridine (terpy*),[10] $Pd(DBA)_2$,[28] $[Pd(PhCN)_2Cl_2]$,[29] [(triphos)PdCl]Cl[30] were prepared following reported procedures.

The NMR spectra were obtained at room temperature (unless otherwise indicated) on Bruker spectrometers. ^1H NMR spectra were recorded at 200.13 MHz (AC-200 instrument), 300.16 MHz (AC-300) or 500.13 MHz (ARX-500) and referenced to $SiMe_4$; the assignments were supported by irradiations and/or 2D analysis. $^{13}C\{^1H\}$ NMR spectra (broadband decoupled) were recorded at 50.32 MHz (AC-200) or 100.62 MHz (AM-400) and referenced to $SiMe_4$; the assignments were supported by DEPT-135° or ^1H-^{13}C HMQC analysis. $^{31}P\{^1H\}$ NMR spectra (broadband decoupled) were recorded at 121.51 MHz (AC-300) and referenced to 85% aqueous H_3PO_4. $^{19}F\{^1H\}$ NMR spectra (broadband decoupled) were recorded at 376.50 MHz (AM-400) and referenced to $CFCl_3$; the assignments were supported by ^{19}F-^{19}F COSY analysis. For variable-temperature spectra, the probe temperature was controlled (±1 K) by a B-VT 2000 unit calibrated with a methanol NMR tube. The $\Delta G^{\ddagger}$ values were calculated with the Eyring equation $\Delta G^{\ddagger} = RT_c\,(22.96 + \ln T_c/\Delta\nu)$ [J·mol^{-1}] where T_c (K) is the temperature of coalescence of two given signals and $\Delta\nu$ (Hz) their difference in chemical shift at low exchange temperature;[31] the error is estimated to be ±1 kJ·mol^{-1}. The phase-sensitive ^1H-^1H ROESY spectrum (mixing time 0.3 s) and the selective inversion-recovery experiments were recorded on the ARX-500 spectrometer, and the phase-sensitive ^{19}F-^{19}F NOESY spectrum on the AM-400 spectrometer (mixing time 0.4 s). The selective inversion-recovery experiments were achieved using a 50 ms Gaussian 180° pulse (5%−truncated waveform) and a 20 s interpulse delay; the curves were fitted either as pairs or all four simultaneously according to Bloch's equations modified for exchange,[32] with a home-written C program using the Powell algorithm from the Numerical Recipes package.[33] The $\Delta G^{\ddagger}$ value was deduced from the equation $\Delta G^{\ddagger} = RT\,(23.76 - \ln k/T)$.[31]

FT-IR spectra were recorded on a Perkin−Elmer 1600 Series spectrometer on KBr pellets.

MS spectra and elemental analyses were carried out by the corresponding facilities at the Centre de Recherche de Chimie, Université Louis Pasteur, Strasbourg.

[(η²-terpy*)Pd{η²-N₄(C₆F₅)₂}] (1): $Pd(DBA)_2$ (1.00 g, 1.74 mmol) was added to a solution of terpy* (1.00 g, 2.49 mmol) in toluene (50 mL) while stirring. A solution of pentafluorophenyl azide (2.00 g, 9.57 mmol) in toluene (10 mL) was added dropwise. After 18 h stirring at room temperature, the colour had turned from reddish-violet to dark-greenish. The solution was filtered and evaporated to dryness, and the residue washed with pentane (4 × 50 mL) and toluene (20 mL). The complex was recrystallized from THF/pentane as an air-stable, dark grey-blue powder (0.61 g, 39%). − $C_{39}H_{35}F_{10}N_7Pd$ (898.14): calcd. C 52.16, H 3.93, N 10.92; found C 51.61, H 3.80, N 10.85. − ^1H NMR (300 MHz, C_6D_6): δ = 0.81 (s, 9 H, *t*Bu^1), 1.04 (s, 9 H, *t*Bu^2), 1.46 (s, 9 H, *t*Bu^3), 6.40 (dd, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 1.7 Hz, 1 H, H^2), 6.99 (dd, $^3J_{HH}$ = 5.1 Hz, $^4J_{HH}$ = 1.7 Hz, 1 H, H^7), 7.27 (d, $^4J_{HH}$ = 1.5 Hz, 1 H, H^3), 7.38 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, H^4), 7.47 (d, $^3J_{HH}$ = 6.1 Hz, 1 H, H^1), 8.28 (d, $^3J_{HH}$ = 5.1 Hz, 1 H, H^8), 8.52 (d, $^4J_{HH}$ = 2.0 Hz, 1 H, H^5), 10.12 (d, $^4J_{HH}$ = 1.7 Hz, 1 H, H^6). − $^{19}F\{^1H\}$ NMR (376.5 MHz, $CDCl_3$, 230 K): δ = −166.06, −164.66 (2 dd app. t, $^3J_{FF}$ = 23 Hz, 2 F, F^{2meta}), −165.26 (dd app. t, $^3J_{FF}$ = 22 Hz, 1 F, F^{2para}), −163.52, −162.61 (2 dd app. t, $^3J_{FF}$ = 23 Hz, 2 F, F^{1meta}), −160.86 (dd app. t, $^3J_{FF}$ = 23 Hz, 1 F, F^{1para}), −151.43, −146.98 (2 d, $^3J_{FF}$ = 24 Hz, 2 F, F^{2ortho}), −147.62, −145.90 (2 d, $^3J_{FF}$ = 22 Hz, 2 F, F^{1ortho}).

Reaction of Pd(DBA)₂ with Terpy* and Tosyl Azide: $Pd(DBA)_2$ (0.500 g, 0.870 mmol) was added to a solution of terpy* (0.698 g, 1.74 mmol) in toluene (50 mL) while stirring. A solution of tosyl

azide (1.20 g, 6.08 mmol) in toluene (5 mL) was added dropwise. After 18 h stirring at room temperature, the colour had turned from reddish-violet to dark brown. The suspension was filtered, and the product collected on a frit as a brown-greenish powder was washed with toluene and dried. − MS (FAB^+, NBA matrix): *m*/*z* (%) = 677.1 (79) [(terpy*)Pd(NHTs)$^+$], 507.1 (100) [(terpy*)Pd$^+$]. − ^{1}H NMR (200 MHz, CD_3CN): δ = 1.42 (s, 18 H, *t*Bu^1), 1.52 (s, 9 H, *t*Bu^2), 2.26 (s, 3 H, Me), 3.61 (br s, 1 H, NH), 7.12 (d, $^3J_{HH}$ = 7.8 Hz, 2 H, H$^{arom\ Ts}$), 7.54 (dd, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, H^2), 7.93 (d, $^3J_{HH}$ = 8.2 Hz, 2 H, H$^{arom\ Ts}$), 8.14 (d, $^3J_{HH}$ = 6.0 Hz, 2 H, H^1), 8.28 (m, 4 H, H^3 + H^4). − ^{13}C{^{1}H} NMR (50 MHz, [D$_6$]DMSO): δ = 20.7 (s, 1 C, Me), 29.8 [s, 6 C, *t*Bu^1, C(*C*H$_3$)$_3$], 30.2 [s, 3 C, *t*Bu^2, C(*C*H$_3$)$_3$], 36.0 [s, 2 C, *t*Bu^1, *C*(CH$_3$)$_3$], 37.0 [s, 1 C, *t*Bu^2, *C*(CH$_3$)$_3$], 121.4 (s, 2 C, C−H^4), 122.2 (s, 2 C, C−H^3), 124.1 (s, 2 C, C−H^2), 125.9, 128.7 (2 s, 2 × 2 C, C−H^{Ts}), 140.1, 143.8 (2 s, 2 × 1 C, C−S + C−Me), 151.7 (s, 2 C, C−H^1), 154.1, 157.0 (2 s, 2 × 2 C, C−N), 166.3 (s, 2 C, C−*t*Bu^1), 167.7 (s, 1 C, C−*t*Bu^2).

[(η^3-terpy*)PdCl]Cl (2): Terpy* (1.20 g, 3.00 mmol) was partly dissolved in 250 mL methanol in a round-bottomed flask, and [Pd(PhCN)$_2$Cl$_2$] (1.15 g, 3.00 mmol) was added to the solution. A clear solution was obtained after 3 h reflux, which was cooled and filtered. Evaporation under reduced pressure led to an orange oil, which was recrystallized from a CH_2Cl_2/Et_2O mixture to yield the complex as a pale yellow powder (1.62 g, 94%). − $C_{27}H_{35}Cl_2N_3Pd{\cdot}H_2O$ (596.92): calcd. C 54.33, H 6.25, N 7.04, Cl 11.88; found C 54.56, H 6.28, N 6.93, Cl 11.86. − MS (ES^+): *m*/*z* (%) = 542.3 (100) [M$^+$ − Cl]. − ^{1}H NMR (300 MHz, $CDCl_3$): δ = 1.54 (s, 18 H, *t*Bu^1), 1.70 (s, 9 H, *t*Bu^2), 7.56 (dd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HH}$ = 2.0 Hz, 2 H, H^2), 8.78 (d, $^3J_{HH}$ = 6.0 Hz, 2 H, H^1), 8.98 (d, $^4J_{HH}$ = 1.8 Hz, 2 H, H^3), 9.06 (s, 2 H, H^4).

[(η^3-terpy*)Pd(CH$_3$CN)](BF$_4$)$_2$ (3). Method A: A solution of terpy* (45 mg, 0.112 mmol) dissolved in benzonitrile (2 mL) was added to a yellow solution of [Pd(CH$_3$CN)$_4$](BF$_4$)$_2$ (50 mg, 0.112 mmol) in benzonitrile (5 mL), after which the colour faded slightly. Addition of 60 mL diethyl ether led to an off-white precipitate which was collected on a frit and washed with diethyl ether (79 mg, 98%). The complex could be recrystallized from CH_3CN/Et_2O. − $C_{29}H_{38}B_2F_8N_4Pd$ (722.66): calcd. C 48.20, H 5.30, N 7.75; found C 48.11, H 5.32, N 7.61. − IR: $\nu_{C\equiv N}$ = 2305, 2333 cm^{-1}. − ^{1}H NMR (300 MHz, CD_3CN): δ = 1.47 (s, 18 H, *t*Bu^1), 1.53 (s, 9 H, *t*Bu^2), 7.77 (dd, $^3J_{HH}$ = 6.1 Hz, $^4J_{HH}$ = 2.1 Hz, 2 H, H^2), 8.30 (s, 2 H, H^4), 8.35 (d, $^4J_{HH}$ = 2.0 Hz, 2 H, H^3), 8.42 (d, $^3J_{HH}$ = 6.1 Hz, 2 H, H^1).

Method B: To a solution of **2** (50 mg, 0.0864 mmol) in acetonitrile (5 mL) was added a solution of $AgBF_4$ (67 mg, 0.344 mmol) in acetonitrile (2 mL). The solution was stirred for 18 h in the dark, and the resulting suspension was filtered. The filtrate was evaporated to dryness and the residue recrystallized from a CH_2Cl_2/CH_3CN mixture to yield the complex (51 mg, 82%).

Table 4. Crystal and refinement data for complexes **1**, **4**, and **5**

	1·*i*Pr$_2$O	**4**·0.75 H$_2$O	**5**·0.5 CH$_3$CN
Formula	$C_{39}H_{35}F_{10}N_7Pd{\cdot}C_6H_{14}O$	$C_{34}H_{43}BF_4N_4O_2PdS{\cdot}0.75\ H_2O$	$C_{41}H_{41}BF_4NO_2P_3PdS{\cdot}0.5\ C_2H_3N$
Mol wt	1000.32	778.53	918.51
Colour	Black	Yellow	Red
Cryst system	Orthorhombic	Monoclinic	Triclinic
a (Å)	33.341(5)	11.4382(9)	10.1424(6)
b (Å)	16.4755(3)	17.749(1)	21.419(1)
c (Å)	16.7758(3)	19.427(1)	21.459(1)
α (deg)			66.471(4)
β (deg)		106.437(6)	82.905(5)
γ (deg)			77.310(5)
V (Å^3)	9215(1)	3782.8(4)	4166.4(5)
Z	8	4	4
D_{calc} (g cm^{-3})	1.44	1.37	1.46
*F*000	4096	1606	1876
Wavelength (Å)	0.71073	0.71073	0.71073
μ (mm^{-1})	0.476	0.602	0.654
Space group	*Pna*2$_1$	$P_12_1/n1$	$P\bar{1}$
Diffractometer	Kappa CCD	Enraf Nonius CAD4	Enraf Nonius CAD4
Crystal dimens (mm)	0.23 × 0.19 × 0.12	0.25 × 0.20 × 0.20	0.40 × 0.40 × 0.40
Temperature (K)	173	294	294
Radiation	Mo-K_α graphite monochromated	Mo-K_α graphite monochromated	Mo-K_α graphite monochromated
Scan mode	phi scans	*θ*/*2θ*	*θ*/*2θ*
hkl limits	0,17/0,19/0,37	0,14/0,22/−24,23	0,12/−26,26/−26,26
θ limits (deg)	2.5/24.48	2.5/26.30	2.5/26.29
No. of data measured	42085	8363	17869
No. of data with $I>3\sigma(I)$	5055	3877	12276
Weighting scheme	$4F_0^2/[\sigma^2(F_0^2) + 0.0004\ F_0^4] + 1.0$	$4F_0^2/[\sigma^2(F_0^2) + 0.0064\ F_0^4]$	$4F_0^2/[\sigma^2(F_0^2) + 0.0064\ F_0^4]$
No. of variables	1152	405	983
R	0.045	0.060	0.041
R_w	0.052	0.088	0.064
Largest peak in final difference (e Å^{-3})	0.653	0.993	1.458
GOF	1.065	1.639	1.335

[(η^3-terpy*)Pd(NHTs)](BF$_4$) (4): A suspension of TsNHK (44 mg, 0.210 mmol) in dichloromethane (6 mL) was added to a suspension of **3** (150 mg, 0.208 mmol) in dichloromethane (7 mL) while stirring. The reagents slowly dissolved while the solution turned yellow. After 18 h stirring at room temperature, the resulting suspension was filtered and the solvent was evaporated to dryness. The complex was recrystallized from THF/Et_2O as an air-stable, yellow powder (125 mg, 79%). – $C_{34}H_{43}BF_4N_4O_2PdS$ (765.01): calcd. C 53.38, H 5.67, N 7.32; found C 53.53, H 5.47, N 7.33.

[(η^3-triphos)Pd(NHTs)](BF$_4$) (5): To a solution of [(triphos)PdCl]Cl (136 mg, 0.191 mmol) in dichloromethane (4 mL) was added a suspension of $AgBF_4$ (74 mg, 0.380 mmol) in dichloromethane (2 mL). The mixture was stirred at room temperature for 30 min. and filtered. The filtrate was cooled to −78° C and a suspension of TsNHK (40 mg, 0.191 mmol) in dichloromethane (1 mL) was added. After stirring at −78° C for 30 min., the temperature was raised to 20° C and the suspension filtered. The solvent was evaporated to dryness and the crude product was obtained as an air-stable, orange powder (160 mg, 93%). The complex was recrystallized from acetonitrile/diethyl ether. – $C_{41}H_{41}BF_4NO_2P_3PdS$ (897.98): calcd. C 54.84, H 4.60, N 1.56; found C 54.96, H 4.65, N 1.85. – IR: ν_{NH} = 3303, 3263 cm^{-1}. – ^{1}H NMR (200 MHz, CD_2Cl_2): δ = 2.1−3.4 (m, 8 H, CH_2), 2.31 (s, 3 H, Me), 2.55 (t, $^3J_{HP}$ = 3.1 Hz, 1 H, NH), 6.84, 6.90 (2 d, $^3J_{HH}$ = 8.7 Hz, 4 H, $H^{arom.\ Ts}$), 7.4−8.0 (m, 25 H, H^{Ph}). – $^{13}C\{^1H\}$ NMR (100 MHz, CD_3CN): δ = 21.4 (s, 1 C, Me), 28.3 (d virtual t, $^1J_{CP}$ = 34 Hz, $|^2J_{CP} + {}^4J_{CP'}|$ = 14 Hz, 2 C, C−PPh), 31.3 (d virtual t, $^2J_{CP}$ = 9 Hz, $|^1J_{CP} + {}^3J_{CP'}|$ = 32 Hz, 2 C, C−PPh_2), 126.1, 129.8 (2 s, 2 × 2 C, C−H^{Ts}), 126.6 (d, $^1J_{CP}$ = 52 Hz, 1 C, $C^{ipso\ PPh}$), 128.1, 129.5 (2 virtual t, $|^1J_{CP} + {}^3J_{CP'}|$ = 47 Hz, 2 × 2 C, $C^{ipso\ PPh}{}_2$), 130.3, 130.4 (2 virtual t, $|^3J_{CP} + {}^5J_{CP'}|$ = 11 Hz, 2 × 4 C, $C^{meta\ PPh}{}_2$), 131.0 (d, $^3J_{CP}$ = 11 Hz, 2 C, $C^{meta\ PPh}$), 133.3, 133.4 (2 s, 2 × 2 C, $C^{para\ PPh}{}_2$), 134.4, 134.7 (2 virtual t, $|^2J_{CP} + {}^4J_{CP'}|$ = 14 Hz, 2 × 4 C, $C^{ortho\ PPh}{}_2$), 134.6 (d, $^2J_{CP}$ = 12 Hz, 2 C, $C^{ortho\ PPh}$), 134.8 (d, $^4J_{CP}$ = 2 Hz, 1 C, $C^{para\ PPh}$), 141.4, 145.6 (2 s, 2 C, C−S + C−Me). – $^{31}P\{^1H\}$ NMR (121.5 MHz, CD_3CN): δ = 49.9 (d, $^2J_{PP}$ = 13 Hz, 2 P, PPh_2), 110.9 (t, $^2J_{PP}$ = 13 Hz, 1 P, PPh).

X-ray Crystallographic Study: Single crystals of **1** were obtained from a saturated diisopropyl ether solution cooled to −20° C. Single crystals of **4** and **5** were obtained with the double-layer method: a water layer was stratified with a saturated solution of **4** in an acetone/water mixture, and a saturated solution of **5** in an acetonitrile/toluene/pentane mixture was stratified with a pentane layer. The crystal data were collected at 173 K for complex **1** and at 294 K for complexes **4** and **5** on a Kappa CCD diffractometer for **1** and on a CAD4-MACH3 for **4** and **5**, using monochromated Mo-K_α radiation (λ = 0.71073 Å). Details of data collection parameters and refinements results are listed in Table 4. The structures were solved using direct methods. After refinement of the non-hydrogen atoms, difference-Fourier maps revealed maxima of residual electron density close to positions expected for hydrogen atoms. Hydrogen atoms were introduced as fixed contributors at calculated positions [C−H = 0.95 Å, B(H) = 1.3B_{eq})]. Final difference maps revealed no significant maxima. All calculations were done using the Nonius OpenMoleN package.[34] Neutral atom scattering factor coefficients and anomalous dispersion coefficients were taken from a standard source.[35]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-156069 (**1**), CCDC-156070 (**4**) and CCDC-156071 (**5**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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