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The first alkynethiolate derivatives of bis(substituted cyclopentadienyl)titanium(IV) and their role in the synthesis of heterobimetallic compounds. Crystal structures of $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC{\equiv}CBu^t)_2]$ and $[(\eta^5\text{-}C_5H_4SiMe_3)(SC{\equiv}CBu^t)Ti(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SC{\equiv}CBu^t)\text{-}Pt(C_6F_5)_2]$ †

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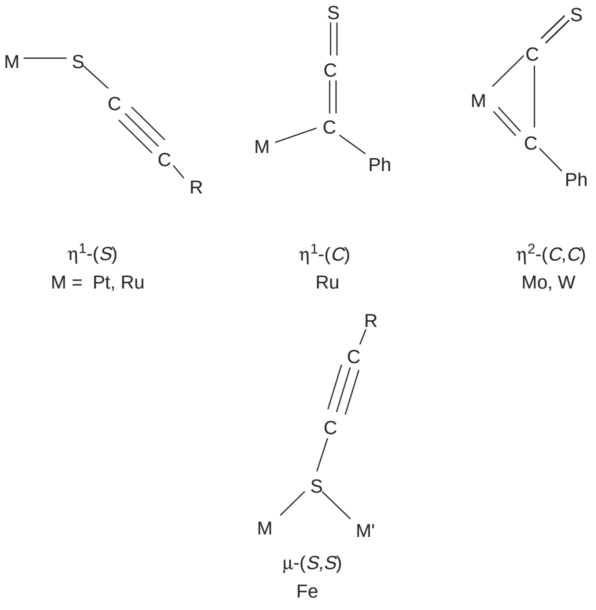
The first thioalkyne derivatives of functionalised titanocene of formula $[Ti(\eta^5\text{-}C_5H_4R')(\eta^5\text{-}C_5H_4R'')(SC{\equiv}CR)_2]$ ($R = Bu^t$, $R' = R'' = SiMe_3$ **1a**; R = Ph, $R' = R'' = SiMe_3$ **1b**; $R = Bu^t$, $R' = SiMe_3$, $R'' = PPh_2$ **2a**; $R = Bu^t$, $R' = R'' = PPh_2$ **3a**) have been prepared by reaction of $[Ti(\eta^5\text{-}C_5H_4R')(\eta^5\text{-}C_5H_4R'')Cl_2]$ and $LiSC{\equiv}CR$ in diethyl ether. Complexes **1a** and **2a** have been used as precursors in the synthesis of Ti–M (M = d^6 or d^8 metal) heteronuclear complexes showing different co-ordination modes. All compounds have been characterised by elemental analysis and ^1H, ^{31}P, ^{19}F and ^{13}C NMR and infrared spectroscopy. The crystal structures of two complexes have been solved.

Introduction

The synthesis and study of early–late heterobimetallic compounds is an active subject of research in organometallic chemistry.[1] One of the reasons for this interest is related to some catalytic processes in view of the potential of this type of compound to promote activation of small molecules (*e.g.* CO).[2] Owing to the propensity of sulfur to form M(μ-SR)M′ bridges, an appropriate synthetic pathway to such species consists on the use of thiolate derivatives of group 4 metallocenes as metalloligands. Stephan and co-workers[3] have made an important contribution in this area by using different thiolate derivatives of titanocene in their reactions with d^{10} transition metal species. In the last years we have studied the reactions between d^6 and d^8 metal fragments and $[Ti(\eta^5\text{-}C_5H_4R)_2(SR')_2]$ (R = H, $SiMe_3$ or PPh_2; R′ = aryl or alkyl group), yielding bi- and tri-nuclear compounds stabilised by double homo $(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)_2$ and $(\mu\text{-}SR)_2$ or hetero $(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SR)$ bridging systems.[4]

On the other hand, the ability of alkynyl ligands to bind several metal centres through σ and π bonds is now firmly established.[5] In particular in this area we and others have also reported the synthesis of different early–late binuclear doubly alkynyl bridged complexes.[6,8] These complexes have been studied in order to gain understanding of the factors that govern the preferred geometries of the C≡C groups because of their relevance in C–C coupling alkynide processes,[7] as well as C–C bond cleavage on butadiynes.[8]



Scheme 1

By contrast with the amount of work devoted to thiolate and alkynide bridged heterobimetallics and their mononuclear precursors, reports on related alkynethiolates are exceedingly rare. Interestingly the few examples that have been published show a quite versatile co-ordination behaviour (Scheme 1). For instance, Weigand *et al.* have reported[9] not only the syntheses of several alkyne thiolate mononuclear complexes of Ru^{II} and Pt^{II} with these ligands acting as η¹-(*S*) bonded ligands (M–SC≡CR′), but also the ability of the phenylalkynethiolate to act as an η¹-(*C*) bonded thioketenyl, [Ru]=C(Ph)–C=S, terminal group.[9a] Recently, the co-ordination as an alkyne thioketenyl η²-(*C*,*C*) with the ligand acting as a three electron donor has been also demonstrated,[10] but, as far as we are aware, only a diiron carbonyl complex $[Fe_2(CO)_6(\mu\text{-}C{\equiv}CPh)(\mu\text{-}SC{\equiv}CPh)]$ containing a sulfur alkynethiolate bridging group μ-(*S*,*S*) has been reported.[11] In the context of these groups it should be noted

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† Dedicated to Professor Pascual Royo on the occasion of his 60th birthday.

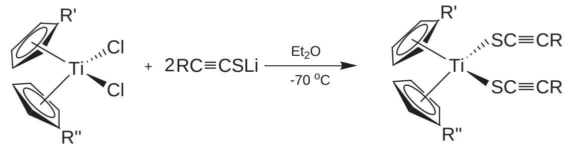
that some additional work has been developed with the isomeric thioacetylide ligands C≡CSR.[12]

In this paper we report on the preparation and properties of several mononuclear alkynethiolate titanocene complexes $[Ti(C_5H_4R')(C_5H_4R'')(SC{\equiv}CR)_2]$ **1**–**3** and describe their reactivity towards several d^6 $[Mo(CO)_4(nbd)]$ and $[Mo(CO)_3(NCMe)_3]$ and d^8 *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pt or Pd) metal complexes containing labile ligands. The syntheses of homo bis(μ-alkynethiolate) **4a**–**6b** and hetero bis(μ-alkynethiolate, μ-cyclopentadienyldiphenylphosphine) bridged derivatives **7**, **8**, **9** and the solid-state structures of $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC{\equiv}CBu^t)_2]$ **1a** and $[(\eta^5\text{-}C_5H_4SiMe_3)(SC{\equiv}CBu^t)Ti(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-}C_5H_4PPh_2)(\mu\text{-}SC{\equiv}CBu^t)Pt(C_6F_5)_2]$ **8** are presented.

Results and discussion

Mononuclear derivatives

The formation of metallocene alkynethiolate titanium(IV) derivatives $[Ti(\eta^5\text{-}C_5H_4R')(\eta^5\text{-}C_5H_4R'')(SC{\equiv}CR)_2]$ **1a**–**3a** was accomplished by treatment of $[Ti(\eta^5\text{-}C_5H_4R')(\eta^5\text{-}C_5H_4R'')Cl_2]$ (R′ = R″ = SiMe$_3$; R′ = SiMe$_3$, R″ = PPh$_2$, R′ = R″ = PPh$_2$) with lithium alkynethiolate reagents LiSC≡CR[13] (2 equivalents) at very low temperature (−70 °C) in diethyl ether [eqn. (1)]. After conventional work-up complexes **1**–**3** were isolated as green microcrystalline solids and their spectroscopic (IR, ^{1}H, ^{13}C and ^{31}P NMR) and analytical data unequivocally confirm the structural proposal shown in eqn. (1) with the alkynethiolate ligands η^1-(S) bonded. Further confirmation was obtained from the X-ray diffraction study of compound **1a**.



(1)

	R'	R''	R
1a	SiMe$_3$	SiMe$_3$	Bu^t
1b	SiMe$_3$	SiMe$_3$	Ph
2a	SiMe$_3$	PPh$_2$	Bu^t
3a	PPh$_2$	PPh$_2$	Bu^t

It should be noted that initial attempts to carry out the former reaction at room temperature, following similar reaction conditions to those reported for ruthenium(II) and platinum(II) complexes,[9] failed to yield the alkynethiolate derivatives. The substitution of SiMe$_3$ by PPh$_2$ groups on the cyclopentadienyl rings reduces considerably the stability of these systems. Thus, whereas complexes **1a**,**1b** and **2a** show satisfactory elemental analysis, the instability of **3a** in solution and in the solid state precludes a good analysis. In the same line we have previously shown that the stability of mixed $[Ti(\eta^5\text{-}C_5H_4SiMe_3)(\eta^5\text{-}C_5H_4PPh_2)X_2]$ (X = Cl or SPh) derivatives is considerably higher than that of analogous $[Ti(\eta^5\text{-}C_5H_4PPh_2)_2X_2]$.[14]

The most noticeable fact in the IR spectra of complexes **1**–**3** is the presence of a weak absorption in the 2129–2145 cm^{-1} region corresponding to the C≡C stretching mode, clearly indicating that the acetylenic fragments are not involved in co-ordination. Their NMR data (^{1}H and ^{13}C) indicate that only one of the two expected isomers (*syn* or *anti*) is present in solution (see Experimental section). In the ^{1}H NMR spectra the resonances due to cyclopentadienyl protons, two for **1a**, **1b** and **3a** (δ 6.40–6.62, 6.01–6.53) and four for complex **2a** (6.54, 6.38, 6.34, 6.11) due to the presence of two different substituted rings, are shifted upfield in relation to the dichloride starting precursors. This effect can be accounted for the lowering in the electronegativity on going from the chloride to the alkynethiolate ligand. As expected, singlet signals are observed for the Bu^t or SiMe$_3$ groups in all complexes. The presence of these groups is also confirmed by their characteristic ^{13}C NMR resonances which appear in the expected range. Particularly evident are the acetylenic carbon resonances (δ 80.8, 117.5 **1a**; 93.0, 107.3 **1b**; 80.2, 117.8 **2a**) which occur in a similar region to that previously reported for other η^1-(*S*) bonded alkynethiolate (M–SC≡CR)[9] or alkynyl (M–C≡CR)[6,8] compounds. Complexes **1a** and **1b** show only three cyclopentadienyl carbon resonances while the mixed derivative $[Ti(\eta^5\text{-}C_5H_4SiMe_3)(\eta^5\text{-}C_5H_4PPh_2)(SC{\equiv}CBu^t)_2]$ **2a** exhibits five resonances for each substituted C$_5$H$_4$ ring suggesting that the five carbon atoms are inequivalent probably due to molecular steric strains. The shielding of the ^{31}P resonances displayed by complexes **2a** (δ −15.2) and **3a** (δ −15.5) is typical of this type of compound.[4a]

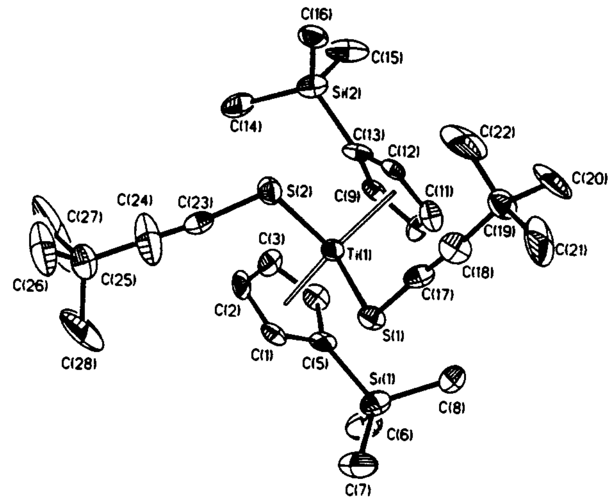


Fig. 1 View of molecular structure of $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC{\equiv}CBu^t)_2]$ **1a**.

Table 1 Selected bond lengths (Å) and angles (°) of complex **1a** (molecule 1)

Ti(1)–S(1)	2.451(4)	C(17)–C(18)	1.174(13)
Ti(1)–S(2)	2.451(4)	C(23)–C(24)	1.144(14)
S(1)–C(17)	1.688(11)	Ti(1)–cent(1)	2.050
S(2)–C(23)	1.712(12)	Ti(1)–cent(2)	2.038
S(2)–Ti(1)–S(1)	92.30(13)	S(1)–C(17)–C(18)	177.5(12)
cent(1)–Ti(1)–cent(2)	130.9	C(17)–C(18)–C(19)	173.3(13)
S(2)–C(23)–C(24)	174.0(13)	C(23)–C(24)–C(25)	169(2)
Ti(1)–S(1)–C(17)	107.7(4)	Ti(1)–S(2)–C(23)	114.2(3)

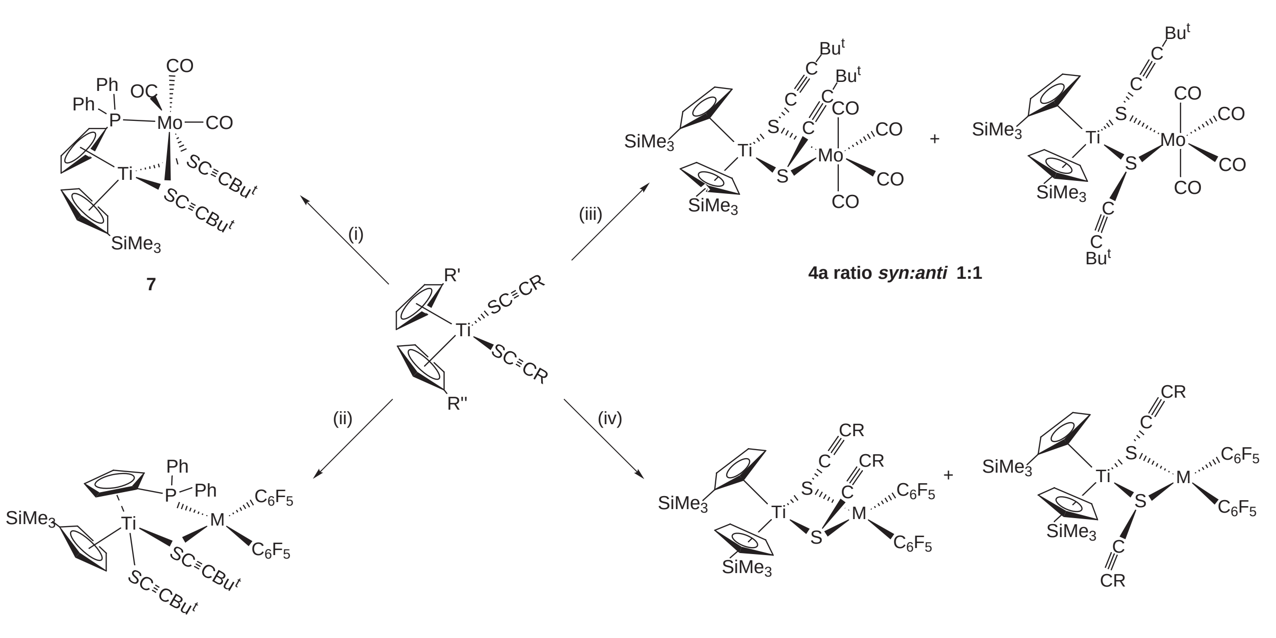
Crystal structure of $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC{\equiv}CBu^t)_2]$ 1a

This compound crystallises with two crystallographically independent molecules, which have essentially the same structure, in the asymmetric unit. Discussion will therefore be limited to only one of them. The monomeric structure of **1a** is shown in Fig. 1 and selected bond distances and angles are listed in Table 1. The compound shows a distorted tetrahedral arrangement around the titanium atom made up of the two centroids of trimethylsilylcyclopentadienyl rings, which adopt a staggered disposition, and the two thiolate ligands. The S(1)–Ti(1)–S(2) angle of 92.30(13)° as well as the Ti(1)–S(1,2) [2.451(4) Å], Ti(1)–centroid(1) [2.050(2) Å] and Ti(1)–centroid(2) [2.038(3) Å] distances are in the range reported for analogous compounds $[Ti\{\eta^5\text{-}C_5H_4P(S)Ph_2\}_2(SPh)_2]$,[14b] $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC_6F_5)_2]$[14a] and $[Ti(\eta^5\text{-}C_5H_5)_2(SMe)_2]$.[3e] Once again the *endo* (*anti*) conformation shown by this titanium(IV) derivative confirms the relationship between the type of isomer and the S(1)–Ti–S(2) angle. The bond lengths S–C [1.688(11), 1.712(12) Å] and C≡C [1.174(13), 1.144(14) Å] and angles Ti–S–C [107.4(7), 114.2(3)], S–C–C [177.5(12), 174.0(12)] and C–C–C [173.3(13), 169(2)] found within the alkynethiolate fragments show no unusual features, being quite similar to those found in complexes $[Pt(PPh_3)_2\{SC{\equiv}CC(Me)\}_2]$[9b] and $[Fe_2(CO)_6(\mu\text{-}C{\equiv}CPh)(\mu\text{-}SC{\equiv}Ph)]$[11] which to our knowledge are the only examples of thioalkyne derivatives of transition metals structurally characterised.

Heterobinuclear derivatives

We have previously shown that titanocene thiolate derivatives $[Ti(\eta^5\text{-}C_5H_4R')_2(SR)_2]$ (R′ = H, $SiMe_3$ or PPh_2) can act as either bi- [R′ = H or $SiMe_3$(*S*,*S*), PPh_2(*P*,*P*)] or tetra-dentate [R′ = PPh_2, bis(*P*,*S*) or *P*,*P*; *S*,*S*] ligands towards the d^6 $Mo(CO)_4$ and d^8 $M(C_6F_5)_2$ (M = Pd or Pt) metal fragments.[4] The substitution of arene- or alkene-thiolates by alkynethiolates on the mononuclear titanocene supplies an additional co-ordination position. We have reported several examples illustrating the ability of bis(alkynyl) transition metal complexes $[M'L_n(C{\equiv}CR)_2]$ (M′ = Pt,[15a–d] Ir[15e] or Ti[6a]) to bond "*cis*-$M(C_6F_5)_2$" (M = Pt or Pd) metal fragments through η^2-acetylenic bonding interactions. Therefore, we considered it of interest to explore the reactivity of the novel bis(alkynethiolate) derivatives **1**–**3** towards the same substrates: $[Mo(CO)_4(nbd)]$ and *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pt or Pd, thf = tetrahydrofuran), respectively.

The results of this study are summarised in Scheme 2. Treatment of $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC{\equiv}CR)_2]$ with either $[Mo(CO)_4(nbd)]$ (excess) or *cis*-$[M(C_6F_5)_2(thf)_2]$ (1 equivalent) in toluene at room temperature (for **1a** and M = Pt in CH_2Cl_2) results in the formation of neutral bis(thiolato)bridged heterobinuclear complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CR)_2ML_n]$ [ML_n = $Mo(CO)_4$ **4a**, $Pt(C_6F_5)_2$ **5a**, **5b**, or $Pd(C_6F_5)_2$ **6a**, **6b**] in moderate to high yield (60% **4a**–88% **6b**). Complex **4a** is isolated as a green solid after chromatographic purification. Complexes **5a** (orange) and **6b** (red-garnet) are precipitated as solids by treatment of the residues with *n*-heptane and *n*-hexane respectively, while **5b** and **6a** can be isolated as orange solids only by removing the solvent. These latter compounds are extremely soluble even in hydrocarbon solvents such as *n*-hexane, pentane or *n*-heptane. In spite of many attempts we have not been able to obtain suitable crystals for X-ray analysis of any of these dinuclear compounds **4**–**6**, however their spectroscopic data are consistent with the *S*,*S* co-ordination mode of the difunctional metallocene $[Ti](SC{\equiv}CR)_2$ chelating ligands. Thus, their IR spectra show a medium $\nu(C{\equiv}C)$ absorption in the characteristic region of non-co-ordinated alkynes.[13b] Compared with the precursors (**1a** 2129 cm^{-1} and **1b** 2134 cm^{-1}) the stretching frequency $\nu(C{\equiv}C)$ for **5** and **6** is shifted to higher wavenumbers (2168 **5a**, 2165, **5b**, **6b**; 2166 cm^{-1} **6a**) suggesting that co-ordination of the sulfur lone pair to platinum or palladium probably reduces sulfur π-donor interactions with the acetylenic fragment. In marked contrast the solution IR spectrum of the Mo–Ti complex **4a** shows the $\nu(C{\equiv}C)$ at 2072 cm^{-1}. The relative lowering of $\nu(C{\equiv}C)$ (≈57 cm^{-1}) is considerably smaller than those previously reported for co-ordinated thioalkynes,[16] *i.e.* $[S\{(\eta^2\text{-}C{\equiv}CPh)Co_2(CO)_6\}_2]$[16a] 1592 *vs.* $S(C{\equiv}CPh)_2$ 2180 cm^{-1} and $[\{Cu(O_3SCF_3)_2S(C{\equiv}CBu^t)_2]$[16b] 1988 *vs.* $S(C{\equiv}CBu^t)_2$ 2200 cm^{-1}, suggesting that acetylenic fragments are not co-ordinated to Mo. The NMR data are consistent with the presence of the dinuclear species in the two isomeric forms *syn* and *anti* shown in Scheme 2. This structural feature, which arises from the relative orientation of the alkyne groups on the sulfur atoms, is not unusual and in many cases equilibrium studies find the two conformers to be of similar thermodynamic stability. In fact, a few $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}SR)_2Mo(CO)_4]$ compounds have been reported as *endo* (*anti*/*syn*) stereochemically non-rigid mixtures in solution.[17] We have previously found that the heterobimetallic Ti–Pt and Ti–Pd $[(\eta^5\text{-}C_5H_4R')_2Ti(\mu\text{-}SR)_2M(C_6F_5)_2]$ (M = Pt or Pd, R′ = H or $SiMe_3$, R = Ph or C_6F_5) systems adopt both in the solid state (X-ray; M = Pd, R′ = $SiMe_3$, R = Ph) and in solution an *endo* (*syn*) arrangement with respect to the central TiS_2M core.[4b] The higher preference for the *anti* isomer found for these Ti–M mixed derivatives, related to the ones mentioned before, could be attributed to the bulkiness of the alkyne fragment on these



M=Pt **8**
M=Pd **9**

	R	M	ratio *syn*:*anti*
5a	Bu^t	Pt	0.9:1
5b	Ph	Pt	1:1
6a	Bu^t	Pd	5:1
6b	Ph	Pd	10:1

Scheme 2 (i) $[Mo(CO)_3(NCMe)_3]$, toluene, room temperature (r.t.); (ii) $[M(C_6F_5)_2(thf)_2]$ (M = Pt or Pd), toluene, −20 °C; (iii) $[Mo(CO)_4(nbd)]$, toluene, r.t.; (iv) $[M(C_6F_5)_2(thf)_2]$ (M = Pt or Pd), toluene, r.t. (for **5a**, CH_2Cl_2).

μ-SC≡CR bridging ligands. Similar steric considerations have previously been suggested to rationalise the shift of the equilibrium in favour of the *anti* isomer.[18] The preference for the *syn* isomer is slightly higher for the phenyl derivatives **6b** and **5b** than for the *tert*-butyl complexes **6a** and **5a** respectively. The reason for the fact that the *syn* conformation seems to be more thermodynamically favoured on palladium than platinum mixed-metal complexes is less clear.

According to the presence of an ≈1 : 1 *syn* : *anti* mixture, the Ti–Mo complex **4a** exhibits in its proton spectrum two singlet resonances (δ 1.23, 1.20) due to Bu^t groups and, at high field, two signals of equal intensity (δ 0.44, 0.33) assigned to the non-equivalent $SiMe_3$ groups in the *syn* isomer and, a more intense signal at δ 0.39 which belongs to the equivalent $SiMe_3$ groups in the *anti* isomer. The expected three distinct cyclopentadienyl sets of resonances are observed slightly upfield shifted (δ 6.31–5.27) with respect to those seen for **1** (δ 6.46, 6.38) indicating an increase of electron density on the Ti. This spectroscopic feature has been previously observed in related bis(alkyl) and aryl bridging thiolate Ti–Mo compounds.[17] The proton spectrum is temperature dependent. Thus, on raising the temperature all signals broaden, and at +50 °C a single sharp Bu^t (δ 1.24) and broad $SiMe_3$ (δ 0.41) resonances are observed while in the cyclopentadienyl region only two very broad humps are barely discernible suggesting that both isomers are interconverting on the NMR timescale. When the temperature is lowered the high-field region (Bu^t, $SiMe_3$ resonances) does not change indicating a similar *syn* : *anti* ratio (1.1 : 1) but, however, the signals in the cyclopentadienyl region clearly broaden. In the lowest temperature spectrum (−50 °C) ten distinct proton resonances [δ 6.30 (2 H), 6.22 (2 H), 6.12, 5.84, 5.67 (1 H each), 5.52 (2 H), 5.26 (4 H), 5.12, 4.88, 4.79 (1 H each)] are seen implying rigid formulations with the lack of a symmetry plane passing through Ti and Mo atoms at low temperature. This fact could be tentatively related to hindrance of the rotation of either the bulky C≡CBu^t groups around the C(sp)–S bonds or the substituted η^5-$C_5H_4SiMe_3$ rings.

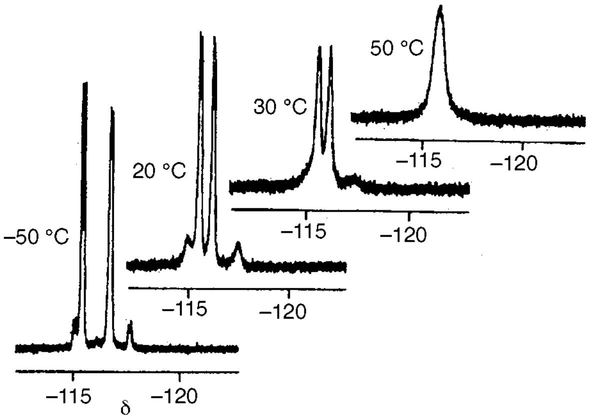


Fig. 2 Variable temperature ^{19}F NMR spectra (F_{ortho} region) of [(η^5-$C_5H_4SiMe_3)_2Ti(\mu$-SC≡CPh$)_2Pd(C_6F_5)_2$] **6b** (*syn* and *anti*).

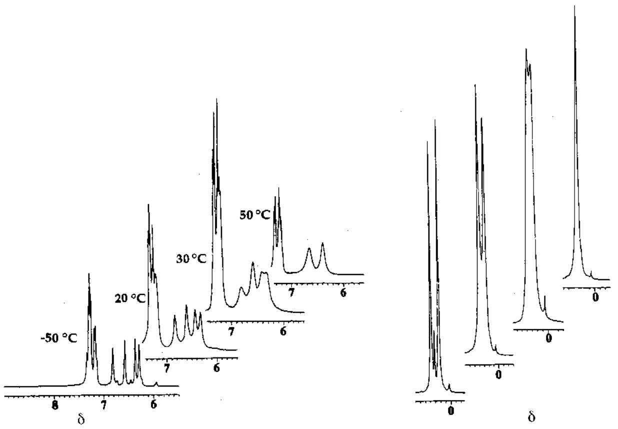


Fig. 3 Proton NMR spectra of the complex [(η^5-$C_5H_4SiMe_3)_2Ti(\mu$-SC≡CPh$)_2Pd(C_6F_5)_2$] **6b** (*syn* and *anti*) at different temperatures.

As was previously found in related aryl (SPh, SC_6F_5) thiolate *syn* isomers [(η^5-$C_5H_4SiMe_3)_2Ti(\mu$-SR$)_2M(C_6F_5)_2$] (M = Pt or Pd), the heterobinuclear Ti–Pt complexes **5** are relatively more rigid in solution than the Ti–Pd ones **6**. Thus, both titanium–platinum complexes **5** display in their low (−50 °C) and room temperature (20 °C) ^{19}F NMR spectra the expected two different sets (AFMRX systems) of rigid C_6F_5 fluorine resonances (one set assigned to each isomer), and similar spectra, but with a less defined pattern, were also observed at the highest accessible temperature (+50 °C). No significant modification of the ratio of both isomers was observed in the range of temperature explored. Similar results were observed from the variable-temperature ^1H NMR spectra. Only at high temperature (+50 °C) the cyclopentadienyl and $SiMe_3$ (also Bu^t groups for **5a**) resonances of both isomers become broad (one $SiMe_3$ is observed for **5b** but coalescence of C_5H_4 signals is not reached) suggesting that the rate of interconversion *syn*–*anti* is still slow on the NMR timescale. By contrast, the ^1H and ^{19}F NMR spectra of the titanium–palladium complexes **6** at +50 °C show the presence of only one set of resonances for the C_6F_5, $C_5H_4SiMe_3$ and Bu^t groups (this latter in the case of **6a**). Selected ranges of the variable temperature ^{19}F (F_{ortho}) and ^1H ($C_5H_4SiMe_3$) spectra of **6b** are shown in Figs. 2 and 3. As can be observed when the temperature is lowered the broad F_{ortho} resonance (Fig. 2) is resolved into four distinct resonances with very different 1 : 10 : 10 : 1 ratio. The signals with lower intensity which exhibit higher $\delta(F^2)$, $\delta(F^6)$ values (at −50 °C, −115.8; −117.6) are unequivocally assigned to the *anti* isomer in accordance with the proton data (Fig. 3). The proton spectrum at low temperature (−50 °C) clearly reveals the presence of the two non-equivalent $C_5H_4SiMe_3$ groups, which is consistent with that expected for the *syn* isomer (major isomer, δ 6.81, 6.57, 6.36 and 6.28 CH; δ 0.38, 0.22 $SiMe_3$). The remaining signals of lower intensity (δ 6.77, 6.45, 6.21 and 5.92 CH; 0.31 $SiMe_3$) are therefore attributed to the *anti* isomer. When the temperature is increased the signals broaden and, finally, collapse to only two broad ones for the cyclopentadienyl resonances and one signal for the $SiMe_3$ at *ca.* +50 °C. This pattern suggests fast interconversion of both isomers on the NMR timescale at this high temperature. Similar behaviour was observed for complex **6a**, the most remarkable difference being the different *syn* : *anti* (≈5 : 1) ratio found at low temperature. The ^{13}C NMR spectra of all complexes have also been recorded (**5**, **6** at −50 °C, due to their low stability in solution, and room temperature for **4a**, see Experimental section for data). A *syn* : *anti* mixture in approximately the expected ratio is observed for all complexes, particularly, for the $SiMe_3$ and Bu^t (**5a**, **6a**) resonances. Unfortunately, they are not very informative in the C≡C region. Only for **5b** the expected four alkyne carbon resonances which appear slightly upfield shifted in relation to the starting material are clearly identified. For **6b** the acetylenic carbon resonances of the major isomer (*syn*) are also shifted (δ 103.5, 81.6 *vs.* 107.3, 93.0 **1b**) and, a small signal at δ 99.2 can tentatively assigned to the minor *anti* isomer. For the remaining complexes, only one (**4a**) or two signals (**5a**, **6**) in the δ 67.78–75.5 range can be assigned.

According to previous results[4c] the preference for coordination through the phosphorus atom is evidenced by using the mixed-ligand mononuclear complex [Ti(η^5-$C_5H_4SiMe_3$)(η^5-$C_5H_4PPh_2$)(SC≡C$Bu^t)_2$] **2a** as precursor. Thus (Scheme 2), by treatment of **2a** with [$Mo(CO)_4$(nbd)] in toluene, at room temperature, a single heterodimetallic complex **7** was obtained in very low yield (12%). The IR spectrum (toluene solution) of the isolated material showed, in addition to a band at

2070 cm^{-1} assignable to $\nu(\text{C}{\equiv}\text{C})$, a clear CO 1956vs, 1895m, 1879s pattern attributable to a *fac*-Mo(CO)_3 unit suggesting that the organometallic **2a** fragment is acting as a tridentate (*S*,*S*,*P*) ligand to the Mo. Further evidence follows from the elemental analysis and the spectroscopic properties. Moreover, when $[\text{Mo(CO)}_3(\text{NCMe})_3]$ was used instead of $[\text{Mo(CO)}_4(\text{nbd})]$ the reaction proceeded, as expected, in a cleaner way and complex $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\text{Ti}(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-SC}{\equiv}\text{CBu}^t)_2\text{-Mo(CO)}_3]$ **7** was obtained in a higher yield (53%). A similar behaviour has recently been observed by us when using related trifunctional ligand systems $[\text{Ti}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)\{\eta^5\text{-C}_5\text{H}_4\text{P(E)-PPh}_2\}(\text{SPh})_2]$ (E = O or S) and $[\text{W(CO)}_4(\text{nbd})_2]$.[19] It seems that the three potential donor atoms (*S*, *S* and *P*) are well suited for the stabilisation of the *fac*-Mo(CO)_3 fragment. The NMR data reveal that only one of the two expected isomers (*syn* and *anti*) is present in solution. A *syn* orientation is tentatively suggested on the basis of the ^{1}H and ^{13}C NMR spectra which display magnetically equivalent $\text{SC}{\equiv}\text{CBu}^t$ ligands. Thus, the ^{1}H NMR spectrum exhibits, in addition to four cyclopentadienyl proton resonances at δ 6.23, 5.17 and 5.61, 5.49 assignable to different $\text{C}_5\text{H}_4\text{PPh}_2$ and $\text{C}_5\text{H}_4\text{SiMe}_3$ rings, respectively, a single sharp Bu^t signal at δ 1.20. The SiMe_3 protons are observed at δ 0.41. A similar pattern was observed in the −50 to +50 °C temperature range, suggesting the absence of any dynamic process. In the ^{13}C NMR spectrum the proposed formulation is mainly supported by the observation of only one set of acetylenic carbon resonances (δ 111.4 and 75.4) and a clear singlet signal at δ 31.1 due to methyl carbon resonances of the equivalent Bu^t groups. Furthermore, in accordance with the *P*,*S*,*S*, co-ordination suggested, the ^{31}P NMR spectrum shows the phosphorus resonances (δ 39.7) strongly shifted to low field ($\Delta = +54.9$) relative to the starting material (δ −15.2 **2a**).

Similarly, as shown in Scheme 2, treatment of complex **2a** with 1 equivalent of *cis*-$[\text{M}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$ (M = Pt or Pd) in toluene at low temperature (−20 °C) affords the heterodinuclear derivatives $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{SC}{\equiv}\text{CBu}^t)\text{Ti}(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-C}_5\text{H}_4\text{PPh}_2)\text{-}(\mu\text{-SC}{\equiv}\text{CBu}^t)\text{M}(\text{C}_6\text{F}_5)_2]$ (M = Pt **8** or Pd **9**). These complexes, isolated as violet microcrystalline solids, are moderately air-stable in the solid state, but in solution they decompose in a few hours. The dimetallic formulation with an heteromixed bridging system is consistent with their spectroscopic data (IR, NMR) and confirmed by an X-ray diffraction study on the Ti–Pt complex **8** (see below).

The presence of non-co-ordinated alkyne fragments is inferred from the IR spectra. Thus, both complexes show $\nu(\text{C}{\equiv}\text{C})$ absorptions assignable to the alkynethiolate ligands which lie approximately in the same region as for the corresponding mononuclear derivative [2157w, 2141m **8**; 2158w, 2141m **9** *vs.* 2145 cm^{-1} **2a**]. Moreover, co-ordination of the phosphorus atom is evidenced from their ^{31}P NMR spectra, which show a singlet resonance (δ 5.14 **8**, 10.93 **9**) shifted to higher frequency relative to that of **2a**. For both complexes the signal is somewhat broad probably due to unresolved long-range phosphorus–fluorine couplings and, as expected, for **8** the signal is flanked by 195-platinum satellites [^1J(Pt–P) = 2361 Hz]. The ^{1}H NMR spectra (at −50 °C and at room temperature) exhibit, in addition to phenyl resonances, two singlets at δ 1.20, 1.11 for **8** and 1.22, 1.11 for **9** and another singlet at δ 0.13 due to the methyl moieties of the inequivalent *tert*-butylalkynethiolate and free $\text{C}_5\text{H}_4\text{SiMe}_3$ ligands, respectively. Seven proton signals (one of them with double intensity) are seen in the cyclopentadienyl region indicating magnetically non-equivalent halves on both substituted cyclopentadienyl rings. The ^{19}F NMR spectra are not temperature dependent either, showing the presence of inequivalent C_6F_5 rings, for which the platinum co-ordination plane is not a mirror plane (AFMRX systems, see Experimental section).

A single crystal X-ray structural determination of complex **8** (Fig. 4) confirmed that the mononuclear precursor acts as a *P*,*S* bidentate ligand towards the "*cis*-$\text{Pt}(\text{C}_6\text{F}_5)_2$" fragment. The complex crystallises together with one molecule of toluene and 0.5 of hexane. Selected bond lengths and angles are collected in Table 2. The titanium atom is pseudo-tetrahedrally surrounded by two cyclopentadienyl ligands and the sulfur atoms of the two $\text{SC}{\equiv}\text{CBu}^t$ ligands. The platinum centre exhibits a distorted "square-planar" geometry formed by the C_{ipso} atoms of two mutually *cis* C_6F_5 groups, a sulfur atom of a μ-$\text{SC}{\equiv}\text{CBu}^t$ ligand and a phosphorus atom of the bridging $\text{C}_5\text{H}_4\text{PPh}_2$ group. The centroid(1)–Ti–centroid(2) angle of 133.5° as well as the titanium–centroid distances (2.039 and 2.049 Å) are in the usual range found for related complexes such as $[\{(\text{Mo(CO)}_4\}_2\{\mu\text{-}(\text{PPh}_2\text{C}_5\text{H}_4)_2\text{Ti}(\text{SPh})_2\}]$ (2.065 Å)[4e] or $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\mu\text{-SPh})_2\text{Pd}(\text{C}_6\text{F}_5)_2]$ [2.07(2), 2.05(1) Å][4b] with the cyclopentadienyl rings exhibiting an *antiperiplanar* (staggered) disposition. As was expected the two titanium to sulfur linkages are very different, the shortest corresponding to the unco-ordinated $\text{SC}{\equiv}\text{CBu}^t$. The bond between the metal to the sulfur of the terminal thioalkyne ligand [Ti–S(2) 2.366(4) Å] is slightly shorter than that observed in **1a** [2.451(4) Å] but in the range found for other mononuclear titanocene dithiolates such as $[\text{Ti}(\eta^5\text{-C}_5\text{H}_5)_2(\text{SEt})_2]$ [2.398(3) and 2.387(3) Å].[20] The other sulfur atom S(1) is bridging between titanium and platinum. The Ti–S(1) bond distance [2.532(4) Å] is substantially longer than the corresponding Pt–S(1) bond length [2.360(3) Å] and both slightly longer than those previously observed in the trimetallic complex $[(\text{OC})_4\text{Mo}(\mu\text{-PPh}_2\text{C}_5\text{H}_4)_2\text{-Ti}(\mu\text{-SPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$[4c] [Ti–S 2.305(1), 2.456(2); Pt–S 2.256(1), 2.347(1) Å]. However, these distances lie in the range of those for other thiolate-bridged containing titanium or platinum centres.[3,4,21,22] The Pt–P bond distance of 2.277(3) Å (and also the Pt–S) is comparable with that found in $[\text{Pt}(\text{SC}_5\text{H}_9\text{N-Me}_2)(\text{dppe})]$.[22] The S(1)–Ti–S(2) angle of 89.39(12)° is slightly

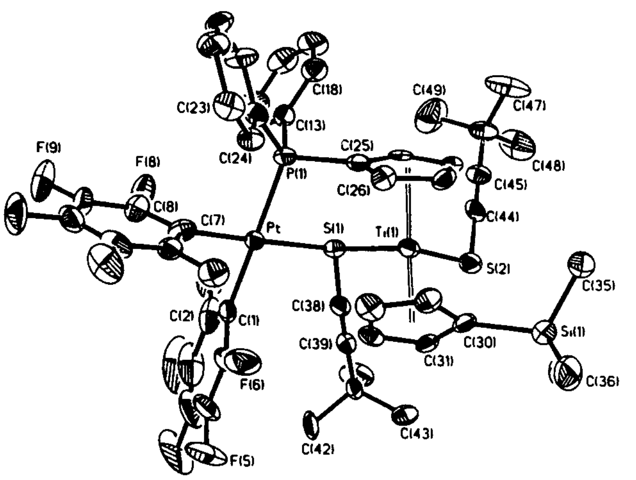


Fig. 4 Molecular structure of $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)(\text{SC}{\equiv}\text{CBu}^t)\text{Ti}(\mu\text{-}\eta^5{:}\kappa\text{-}P\text{-C}_5\text{H}_4\text{PPh}_2)(\mu\text{-SC}{\equiv}\text{CBu}^t)\text{Pt}(\text{C}_6\text{F}_5)_2]$ **8**.

Table 2 Selected bond lengths (Å) and angles (°) for complex **8**

Pt–C(7)	2.023(13)	S(1)–C(38)	1.700(12)
Pt–P(1)	2.277(3)	S(2)–C(44)	1.668(12)
Pt–C(1)	2.039(12)	Ti–cent(1)	2.039
Pt–S(1)	2.360(3)	Ti–cent(2)	2.049
Ti–S(2)	2.366(4)	C(38)–C(39)	1.19(2)
Ti–S(1)	2.532(4)	C(44)–C(45)	1.20(2)
Ti···Pt	3.817(3)		
C(1)–Pt–P(1)	175.7(4)	C(39)–C(38)–S(1)	175.3(11)
Ti–S(1)–C(38)	106.6(4)	C(38)–C(39)–C(40)	178.2(13)
C(1)–Pt–S(1)	94.5(3)	C(45)–C(44)–S(2)	179.3(11)
C(7)–Pt–S(1)	178.1(4)	S(1)–Ti–cent(1)	102.0
P(1)–Pt–S(1)	83.92(11)	S(1)–Ti–cent(2)	109.7
Pt–S(1)–Ti	102.51(12)	C(7)–Pt–C(1)	87.0(5)
S(2)–Ti–S(1)	89.39(12)	C(7)–Pt–P(1)	94.6(4)
Ti–S(2)–C(44)	111.1(4)	C(44)–C(45)–C(46)	178.2(13)

smaller than that seen in **1a** [92.30(13)°] and those observed in related mononuclear titanocene bis(thiolate) complexes $[Ti(\eta^5-C_5H_4SiMe_3)_2(SC_6F_5)_2]$ [100.6(1)°],[14a] $[Ti(\eta^5-C_5H_5)_2(SR)_2]$ [R = Ph (99.4°),[23] or Et (93.8°)[20]] or titanocene thiolate bridged $[(\eta^5-C_5H_4SiMe_3)_2Ti(\mu-SPh)_2Pd(C_6F_5)_2]$[4b] [95.7(2)°] complexes. The internal angles at platinum and at bridging sulfur [P(1)–Pt–S(1) 83.92(11)° acute and Pt–S(1)–Ti 102.51(12)° obtuse] are in accordance with the very long Pt···Ti distance [3.817(3) Å] found. The acetylenic fragments, $C\equiv CBu^t$, are located on the same side of the S(1)–Ti(1)–S(2) plane adopting an *endo* (*syn*) conformation. Their structural data, C≡C bonds [C(38)–C(39) 1.19(2), C(44)–C(45) 1.20(2) Å] and bond angles [S(1)–C(38)–C(39) 175.3(11); C(38)–C(39)–C(40) 178.2(13), S(2)–C(44)–C(45) 179.3(11), C(44)–C(45)–C(46) 178.2(13)°], are in the usual range and deserve no further comment.

As was mentioned before, complex $[Ti(\eta^5-C_5H_4PPh_2)_2(SC\equiv CBu^t)_2]$ **3a** is very unstable both in the solid state and in solution. In preliminary experiments it was treated with $[Mo(CO)_4(nbd)]$ (1 equivalent) in toluene either at room or lower (−40 °C) temperature, but unfortunately the reaction failed, giving just decomposition products and, therefore, no more experiments were made with this precursor.

In summary, bis(alkynethiolate)titanium complexes $[Ti(\eta^5-C_5H_4R')(\eta^5-C_5H_4R'')(SC\equiv CR)_2]$ **1**–**3** have been prepared from $[Ti(\eta^5-C_5H_4R')(\eta^5-C_5H_4R'')Cl_2]$, by using classical metal–halogen exchange reactions with $LiSC\equiv CR$ reagents. In spite of the presence of two potential bifunctionalities, the lone pair at the sulfur atom and the acetylenic moiety on each $SC\equiv CR$, the mononuclear $[Ti(\eta^5-C_5H_4SiMe_3)_2(SC\equiv CR)_2]$ (R = Bu^t **1a** or Ph **1b**) complexes serve only as bidentate (*S*,*S*) metalloligands when treated with d^6 $[Mo(CO)_4(nbd)]$ or d^8 *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pt or Pd) substrates. The co-ordination of the acetylenic fragments cannot be forced even in presence of an excess of these latter reagents, reactions which lead to the same doubly thiolate-bridged early–late heterodimetallic products **4**–**6** (see Experimental section). The NMR data reveal that in all cases the products are isolated as a *syn*:*anti* mixture of isomers with a clear thermodynamic preference for the *syn* conformation in the palladium mixed-metal complexes (≈1:1 for Ti–Mo **4a** and Ti–Pt **5** *vs.* 5:1 **6a**, 10:1 **6b**). The variable NMR data confirm that both isomers interconvert on the NMR timescale at the highest accessible temperature (+50 °C) (**4a** and **6** fast **5** slow).

Similar to previous observations, a favoured co-ordination through phosphine ligands with these late transition metals is evidenced by the fact that the mixed ligand complex $[Ti(\eta^5-C_5H_4SiMe_3)(\eta^5-C_5H_4PPh_2)(SC\equiv CBu^t)_2]$ **2a** acts as bidentate *P*,*S* when treated with *cis*-$[M(C_6F_5)_2(thf)_2]$ (M = Pt or Pd) yielding **8** and **9**, respectively and, as a tridentate organometallic metallo ligand toward $[Mo(CO)_4(nbd)]$ or $[Mo(CO)_3(NCMe)_3]$, giving $[(\eta^5-C_5H_4SiMe_3)Ti(\mu-\eta^5:\kappa-P-C_5H_4PPh_2)(\mu-SC\equiv CBu^t)_2Mo(CO)_3]$ **7**.

Experimental

Reactions were carried out under an atmosphere of argon by means of conventional Schlenk techniques.[24] Solvents were purified according to standard procedures.[25] The complexes $[Ti(\eta^5-C_5H_4SiMe_3)_2Cl_2]$,[26] $[Ti(\eta^5-C_5H_4SiMe_3)(\eta^5-C_5H_4PPh_2)Cl_2]$,[14b] $[Ti(\eta^5-C_5H_4PPh_2)_2Cl_2]$,[27] $[Mo(CO)_4(nbd)]$,[28] $[Mo(CO)_3(NCMe)_3]$[29] and *cis*-$[M(C_6F_5)_2(thf)_2]$[30] (M = Pt or Pd) were prepared as previously published. All other reagents were used as obtained commercially. Microanalyses were determined with Perkin-Elmer 2400 and 240-B microanalysers. Infrared spectra (KBr) were recorded on Perkin-Elmer 1600 FT and FT-IR 1000 spectrophotometers, NMR spectra on Bruker AMX-300 or ARX-300 with chemical shifts reported in ppm relative to external standards ($SiMe_4$ for ^1H and ^{13}C, $CFCl_3$ for ^{19}F and H_3PO_4 for ^{31}P) and mass spectra (FAB+) on a VG Autospec spectrometer.

Syntheses

$[Ti(\eta^5-C_5H_4SiMe_3)(SC\equiv CBu^t)_2]$ 1a. To a diethyl ether solution (20 cm^3) of $LiBu^n$ (1.66 cm^3, 2.66 mmol) cooled at −20 °C was added $Bu^tC\equiv CH$ (0.32 cm^3, 2.66 mmol). After 10 min of stirring S_8 (0.085 g, 0.33 mmol) was introduced in the Schlenk and the cooling bath was removed. The mixture was stirred for 45 min at room temperature and subsequently added dropwise to another diethyl ether solution (25 cm^3) of $[Ti(\eta^5-C_5H_4SiMe_3)_2Cl_2]$ (0.50 g, 1.27 mmol) cooled at −70 °C. The bright green solution obtained was kept under nitrogen with continuous stirring for 1 h while the temperature slowly reached −10 °C. The solvent was evaporated to dryness, the residue then extracted with pentane and filtered through a pad of Celite. The resulting solution was concentrated and cooled to −20 °C to yield dark green needles of complex **1a** (0.63 g, 85%) (Found: C, 61.13; H, 8.03. $C_{28}H_{44}S_2Si_2Ti$ requires C, 61.28; H, 8.08%); $\tilde{\nu}_{max}/cm^{-1}$ 2129 (C≡C). MS: *m*/*z* 548 $\{(\eta^5-C_5H_4SiMe_3)_2Ti(SC\equiv CBu^t)_2]^+$, 8}, 435 $\{[(\eta^5-C_5H_4SiMe_3)_2(SC\equiv CBu^t)]^+$, 100} and 322 $\{[(\eta^5-C_5H_4SiMe_3)_2Ti]^+$, 60%}. ^1H NMR ($CDCl_3$): δ 6.46 (t, 4 H, $C_5H_4SiMe_3$), 6.38 (t, 4 H, $C_5H_4SiMe_3$), 1.35 (s, 18 H, Bu^t) and 0.24 (s, 18 H, $SiMe_3$). ^{13}C-$\{^1H\}$ NMR ($CDCl_3$): δ 123.3 (s, C^1 of C_5H_4), 122.0 (s, $C^{2,5}$ of C_5H_4), 119.4 (s, $C^{3,4}$ of C_5H_4), 117.5 (s, C≡C), 80.8 (s, C≡C), 31.8 (s, Bu^t) and 0.17 (s, $SiMe_3$).

$[Ti(\eta^5-C_5H_4SiMe_3)_2(SC\equiv CPh)_2]$ 1b. This compound was obtained following the above procedure starting from $[Ti(\eta^5-C_5H_4SiMe_3)_2Cl_2]$ (0.45 g, 0.76 mmol) and $LiSC\equiv CPh$ (1.60 mmol). After 1.5 h of stirring the resulting diethyl ether solution was concentrated and filtered through a pad of Celite. Crystallisation from a saturated diethyl ether solution at −20 °C afforded dark green crystals of compound **1b** (85%) (Found: C, 65.03; H, 6.09. $C_{32}H_{36}S_2Si_2Ti$ requires C, 65.28; H, 6.16%); $\tilde{\nu}_{max}/cm^{-1}$ 2134 (C≡C). MS: *m*/*z* 588 $\{[(\eta^5-C_5H_4SiMe_3)_2Ti(SC\equiv CPh)_2]^+$, 4}, 455 $\{[(Ti(SC\equiv CPh)]^+$, 100} and 322 $\{[(\eta^5-C_5H_4SiMe_3)_2Ti]^+$, 95%}. ^1H NMR ($CDCl_3$): δ 7.41–7.37 (m, 4 H, Ph), 7.23–7.19 (m, 6 H, Ph), 6.62 (t, 4 H, $C_5H_4SiMe_3$), 6.53 (t, 4 H, $C_5H_4SiMe_3$) and 0.28 (s, 18 H, $SiMe_3$). ^{13}C-$\{^1H\}$ NMR ($CDCl_3$): δ 138.8–126.9 (s, C_6H_5), 124.3 (s, C^1 of C_5H_4), 122.2 (s, $C^{2,5}$ of C_5H_4) 119.7 (s, $C^{3,4}$ of C_5H_4), 107.3 (s, C≡C), 93.0 (s, C≡C) and 0.16 (s, $SiMe_3$).

$[Ti(\eta^5-C_5H_4SiMe_3)(\eta^5-C_5H_4PPh_2)(SC\equiv CBu^t)_2]$ 2a. This compound was obtained following the same procedure as for **1a** but the final residue was extracted with heptane (73% yield). The precursors used were $[Ti(\eta^5-C_5H_4SiMe_3)(\eta^5-C_5H_4PPh_2)Cl_2]$ (0.37 g, 0.56 mmol) and $LiSC\equiv CBu^t$ (1.17 mmol) (Found: C, 66.82; H, 6.90. $C_{37}H_{45}PS_2SiTi$ requires C, 67.25; H, 6.86%); $\tilde{\nu}_{max}/cm^{-1}$ 2145 (C≡C). MS: *m*/*z* 660 $\{[(\eta^5-C_5H_4SiMe_3)(\eta^5-C_5H_4PPh_2)Ti(SC\equiv CBu^t)_2]^+$, 30}, 547 $\{[(\eta^5-C_5H_4SiMe_3)(\eta^5-C_5H_4PPh_2)Ti(SC\equiv CBu^t)]^+$, 100} and 432 $\{[(\eta^5-C_5H_4SiMe_3)(\eta^5-C_5H_4PPh_2)Ti]^+$, 50%}. ^1H NMR ($CDCl_3$): δ 7.41–7.37 (m, 4 H, Ph), 7.23–7.19 (m, 6 H, Ph), 6.54 (m, 2 H, $C_5H_4PPh_2$), 6.38 (t, 2 H, $C_5H_4SiMe_3$), 6.34 (t, 2 H, $C_5H_4SiMe_3$), 6.11 (m, 2 H, $C_5H_4PPh_2$), 1.31 (s, 18 H, Bu^t) and 0.17 (s, 9 H, $SiMe_3$). ^{31}P-$\{^1H\}$ NMR: δ −15.2 (s, $C_5H_4PPh_2$). ^{13}C-$\{^1H\}$ NMR ($CDCl_3$): δ 133.8–128.5 (s, C_6H_5), 124.5, 123.5, 123.4, 121.8, 121.5, 120.3, 120.1, 120.0, 119.9, 119.1 (s, C_5H_4), 117.8 (s, C≡C), 80.2 (s, C≡C), 31.7 (s, Bu^t) and 0.11 s, $SiMe_3$).

$[Ti(\eta^5-C_5H_4PPh_2)_2(SC\equiv CBu^t)_2]$ 3a. The synthesis was performed as described for complex **1a** starting from $[Ti(\eta^5-C_5H_4PPh_2)_2Cl_2]$ (0.45 g, 0.73 mmol) and $LiSC\equiv CBu^t$ (1.53 mmol). After 30 min of stirring the resulting diethyl ether solution was concentrated and filtered through a pad of Celite. The solvent was evaporated to dryness affording **3a** as a green solid (70%). $\tilde{\nu}_{max}/cm^{-1}$ 2129 (C≡C). ^1H NMR ($CDCl_3$): δ 7.27–7.17 (m, 10 H, Ph), 6.40 (t, 4 H, $C_5H_4PPh_2$), 6.01 (m, 4

H, $C_5\mathit{H}_4PPh_2$) and 1.33 (s, 18 H, Bu^t). $^{31}P\text{-}\{^1H\}$ NMR: δ −15.5 (s, $C_5H_4PPh_2$). The ^{13}C NMR spectrum could not be recorded due to the low stability in solution.

$[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2Mo(CO)_4]$ 4a (*syn* and *anti*). To a solution of $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC{\equiv}CBu^t)_2]$ **1a** (0.20 g, 0.36 mmol) in toluene (25 cm^3) was added $[Mo(CO)_4(nbd)]$ (0.32 g, 1.08 mmol) and the mixture stirred at room temperature for 30 h. The solvent was removed *in vacuo* and the solid obtained purified by chromatography on silica gel 100. Elution with hexane–toluene (3:1) afforded a green-blue band of complex **4a** (0.16 g, 60%) (*syn*:*anti* ratio ≈1:1). Identical results were obtained starting from **1a** and 1 equivalent of $[Mo(CO)_4(nbd)]$, but in that case longer periods of stirring (≈72 h) were necessary (Found: C, 50.51; H, 5.73. $C_{32}H_{44}MoO_4S_2Si_2Ti$ requires C, 50.79; H, 5.86%). $\tilde{\nu}_{max}/cm^{-1}$ 2072 (C≡C); (toluene solution) 2019s, 1929s, 1915vs (CO). MS: *m*/*z* 756 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2Mo(CO)_4]^+$, <5}, 728 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2Mo(CO)_3]^+$, <5%}, 700 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2Mo(CO)_2]^+$, <5}, 672 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2\text{-}Mo(CO)]^+$, <5}, 644 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2Mo]^+$, 15}, 435 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC{\equiv}CBu^t)]^+$, 50} and 322 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti]^+$, 100%}. ^1H NMR ($CDCl_3$): at −50 °C, δ 6.30 (2 H), 6.22 (2 H, 6.12, 5.84, 5.67 (1 H each), 5.52 (2 H), 5.26 (4 H), 5.12, 4.88, 4.79 (1 H each) (C_5H_4 *syn*, *anti* isomers), 1.20s, 1.17s (Bu^t), 0.37 (s, $SiMe_3$, *anti* isomer), 0.42s, 0.22s ($SiMe_3$, *syn* isomer); at 20 °C, 6.31 (s, br, 2 H, C_5H_4, *syn* isomer), 6.21 (s, br, 2 H, C_5H_4, *syn* isomer), 5.55 (s, br, 6 H, C_5H_4, *anti* and *syn* isomers), 5.36 (s, br, 2 H, C_5H_4, *syn* isomer), 5.27 (s, br, 4 H, C_5H_4, *anti* isomer), 1.23 (s, Bu^t), 1.20 (s, Bu^t), 0.39 (s, 18 H, $SiMe_3$, *anti* isomer), 0.44, 0.33 (s, $SiMe_3$, *syn* isomer), (ratio *syn*:*anti* ≈1:1); at +50 °C, cyclopentadienyl region very broad (≈6.2, 5.4 br), 1.24 (s, Bu^t), 0.41 (s, br, $SiMe_3$). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): δ 217.9 (s, CO equatorial, *syn* isomer), 217.2 (s, CO equatorial, *anti* isomer), 204.7 (s, CO axial, *syn* isomer), 203.1 (s, CO axial, *anti* isomer), 201.7 (s, CO axial, *syn* isomer), 129.3br, 123.4br, 116.8, 114.5, 113.3, 112.4, 106.2, 102.2, 101.2 (s, C_5H_4, C≡C), 75.9 (s, C≡C), 31.1 [s, $C(\mathit{C}H_3)_3$], 28.9 (s, $\mathit{C}Me_3$) and 0.14 (s, $SiMe_3$).

$[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2Pt(C_6F_5)_2]$ 5a (*syn* and *anti*). A deep green solution of $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC{\equiv}CBu^t)_2]$ (0.098 g, 0.178 mmol) in CH_2Cl_2 (10 cm^3) was treated with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.120 g, 0.178 mmol) and, immediately, turned red-brown. The mixture was stirred for 5 min and then the solvent was removed *in vacuo*. Addition of *n*-heptane (≈5 cm^3) to the residue afforded an orange-brown solid (0.153 g, 80% yield) identified as a mixture of *syn* and *anti* isomers of $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2Pt(C_6F_5)_2]$ **5a**. When the reaction was carried out in a molar ratio 1:2 using complex **1a** (0.010 g, 0.019 mmol) and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.025 g, 0.037 mmol) in $CDCl_3$ (0.6 cm^3) and monitored by ^1H and ^{19}F NMR spectroscopy at 20 °C the complex **5a** was observed (major component) in addition to decomposition products (Found: C, 44.50; H, 3.70; S, 5.95. $C_{40}F_{10}H_{44}PtS_2Si_2Ti$ requires C, 44.57; H, 4.11; S, 5.48%). $\tilde{\nu}_{max}/cm^{-1}$ 2168m (C≡C), 800vs, (br) $(C_6F_5)_{X\text{–}sens}$. MS: *m*/*z* 1077 (M^+, 28), 964 ($[M - SC{\equiv}CBu^t]^+$, 32), 940 ($[M - C_5H_4SiMe_3]^+$, 25), 910 ($[M - C_6F_5]^+$, 94), 631 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC{\equiv}CBu^t)Pt]^+$, 58}, 475 $\{[(\eta^5\text{-}C_5H_4SiMe_3)(C_5H_4)Ti(SC{\equiv}CBu^t)_2]^+$, 100}, 435 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2\text{-}Ti(SC{\equiv}CBu^t)]^+$, 70} and 322 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti]^+$, 100%}. ^1H NMR ($CDCl_3$): at 20 °C, δ 6.46, 6.29, 6.23, 6.13, 5.94, 5.87, 5.73 (s, ratio 1:1:1:1:2:1:1, C_5H_4, *syn* and *anti* isomers), 1.21 (s, Bu^t), 1.14 (s, Bu^t), 0.39 (s, $SiMe_3$, *syn* isomer), 0.33 (s, $SiMe_3$, *anti* isomer), 0.25 (s, $SiMe_3$, *syn* isomer), (*syn*:*anti* 0.9:1); approximately the same spectra is observed at −50 °C; at +50 °C, the signals are broad, 6.5, 6.3, 6.2, 5.98, 5.90, 5.80 (br, C_5H_4), 1.21, 1.17 (br, Bu^t), 0.35 (br, $SiMe_3$ *anti* and *syn* isomers), 0.28 ($SiMe_3$, *syn* isomer). ^{19}F NMR [$CDCl_3$, $^3J(Pt\text{–}F_o)$/Hz in parentheses]: at −50 °C, δ 117.94 [dm (417)], −118.07 [dm (≈355)], −118.6 [dm (≈465)], −119.4 [dm (392)] (F_o *syn* and *anti* isomers), −161.3 (t, F_p, *anti* isomer), −161.5 (t, F_p, *syn* isomer), −164.2 (m, F_m, *syn* and *anti* isomers) (*syn*:*anti* 0.9:1); at 20 °C, −117.6 [dm, overlapping of two F_o (≈411, ≈337)], −118.6 [dm (≈455)], −119.3 [dm (≈385 Hz)] (ratio 2:1:1, F_o, *syn* and *anti*), −162.0m, −162.25m (ratio 0.9:1, F_p, *syn* and *anti*), −164.5, −165.0 (m, ratio 2:2, F_m, *syn* and *anti*); at +50 °C, −117.5 [br (358)], −118.6 [d, br (446)], −119.2 [d, br (391)] (ratio 2:1:1, F_o, *syn* and *anti*), −162.3 (m, br, overlapping of two F_p, *syn* and *anti*), −164.6 (m, br), −165.3m, (ratio 1:1, F_m, *syn* and *anti*). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): at −50 °C, δ 148.05, 144.96, 138.5, 135.3, 123.3, 116.05 (br, C_6F_5), 130.1, 122.1, 120.8, 120.2, 120.0, 119.6, 113.1, 112.5, 109.6, 107.0 (s, C_5H_4 and C≡C), 67.98s, 67.78s (C≡C, *syn* and *anti* isomers), 30.3 [s, $C(\mathit{C}H_3)_3$], 29.1 (s, $\mathit{C}Me_3$), 28.9 (s, $\mathit{C}Me_3$), 0.0 (s, *syn* isomer), −0.14 (s, *anti* isomer) and −0.39 (s, *syn* isomer) [$Si(CH_3)_3$].

$[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CPh)_2Pt(C_6F_5)_2]$ 5b (*syn* and *anti*). A solid mixture of $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(SC{\equiv}CPh)_2]$ (0.131 g, 0.223 mmol) and *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.150 g, 0.223 mmol) was treated with toluene (5 cm^3). Immediately the resulting brown-red solution was concentrated *in vacuo*, giving an orange-red residue, identified as $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CPh)_2Pt(C_6F_5)_2]$ **5b** (0.174 g, 70% yield) (*syn*:*anti* ratio at −50 °C, 1:1). When the reaction in a molar ratio 1:2 {0.010 g, 0.0170 mmol of complex **1b** and 0.023 g, 0.034 mmol of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ in 0.6 cm^3 of $CDCl_3$} was monitored by NMR spectroscopy at 20 °C considerable decomposition took place, with **5b** being the major product. After longer periods (≈3 h) more decomposition was observed (Found: C, 47.47; H, 3.38; S, 5.31. $C_{44}F_{10}H_{36}PtS_2Si_2Ti$ requires C, 47.27; H, 3.24; S, 5.73%). $\tilde{\nu}_{max}/cm^{-1}$ 2165m (C≡C), 801vs, (br) $(C_6F_5)_{X\text{–}sens}$. MS: *m*/*z* 1117 (M^+, 10), 619 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC{\equiv}CPh)\text{-}(C_6F_5) - 3H]^+$, 14}, 457 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(SC{\equiv}CPh) + 2H]^+$, 56} and 322 $\{[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti]^+$, 100%}. ^1H NMR ($CDCl_3$): at −50 °C, δ 7.37–7.20 (Ph), 6.59, 6.46, 6.41, 6.37, 6.12, 6.09, 6.03, 5.91 (s, identical ratio, C_5H_4, *syn* and *anti* isomers), 0.43 (s, $SiMe_3$, *syn* isomer), 0.36 (s, $SiMe_3$, *anti* isomer), 0.28 (s, $SiMe_3$, *syn* isomer) (*syn*:*anti* ≈1:1); at 20 °C, 7.37–7.16 (Ph), 6.61, 6.48, 6.41, 6.17, 6.12, 6.10, 5.95 (s, ratio 1:1:2:1:1:1:1, C_5H_4, *syn* and *anti* isomers), 0.43 (s, $SiMe_3$, *syn* isomer), 0.38 (s, $SiMe_3$, *anti* isomer), 0.30 (s, $SiMe_3$, *syn* isomer) (*syn*:*anti* ≈1:1); at +50 °C, 7.36–7.15 (Ph), 6.60sh, 6.45br, 6.14br, 6.01sh (C_5H_4) and 0.39 (s, br, $SiMe_3$). ^{19}F NMR [$CDCl_3$, $^3J(Pt\text{–}F_o)$/Hz in parentheses]: at −50 °C, δ −117.8 [d (430), 2F], −118.5 [d (451), 2F], −118.97 [d (365), 2F] −120.0 [d (398), 2F] (F_o, *syn* and *anti* isomer), −160.6, −161.5 (t, F_p, *syn* and *anti* isomer), −163.3, −164.0 (m, F_m, *syn* and *anti* isomer) (*syn*:*anti* 1:1); at 20 °C, −117.6 [d (408), 2F], −118.6 [dm, overlapping of two F_o (≈458, ≈389), 4F], −119.8 [d (392), 2F], (F_o, *syn* and *anti* isomer), −161.3, −161.7 (t, F_p, *syn* and *anti* isomer), −163.8, −164.6 (m, F_m, *syn* and *anti* isomer) (*syn*:*anti* ≈1:1); at +50 °C, −117.5, −118.3, −118.5, −118.98 (br, F_o), −161.6, −161.9 (br, F_p), −164.0, −164.9 (br, F_m) (*syn* and *anti* isomer). $^{13}C\text{-}\{^1H\}$ NMR ($CDCl_3$): at −50 °C, δ 148.2, 145.2, 138.7, 138.2, 135.4–134.0, 116.6, 113.8 (br, C_6F_5), 138.2, 131.3–112.5 (s, C_6H_5, C_5H_4), 99.3s, 96.4s (C≡C *syn* and *anti* isomers), 79.7s, 79.5s (C≡C *syn* and *anti* isomers), −0.0 (s, *syn* and *anti* isomer) and −0.35 (s, *syn* isomer) [$Si(CH_3)_3$].

$[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(\mu\text{-}SC{\equiv}CBu^t)_2Pd(C_6F_5)_2]$ 6a (*syn* and *anti*). This product was prepared in a similar way to complex **5b** by using the appropriate starting precursors, $[Ti(\eta^5\text{-}C_5H_4\text{-}SiMe_3)_2(SC{\equiv}CBu^t)_2]$ (0.141 g, 0.256 mmol) and *cis*-$[Pd(C_6F_5)_2(thf)_2]$ (0.150 g, 0.256 mmol). It was isolated by removing the solvent *in vacuo*, (yield 0.16 g 63%) (mixture of *syn* and *anti* isomers, ratio ≈5:1 at −50 °C). When an excess of *cis*-$[Pd(C_6F_5)_2(thf)_2]$ was employed {1:2 molar ratio; 0.012 g, 0.021 mmol of **1a** and 0.025 g, 0.043 mmol of *cis*-$[Pd(C_6F_5)_2(thf)_2]$ in 0.6 cm^3 of $CDCl_3$} a mixture of **6a** and *cis*-[Pd(C$_6$F$_5$)$_2$(thf)$_2$] was observed by NMR spectroscopy (Found: C, 48.08; H, 4.21; S, 6.32. C$_{40}$F$_{10}$H$_{44}$PdS$_2$Si$_2$Ti requires C, 48.56; H, 4.48; S, 6.48%). $\tilde{\nu}_{max}$/cm^{-1} 2166m (C≡C), 786s, 778s (C$_6$F$_5$)$_{\text{X-sens}}$. MS: *m*/*z* 1011 ([*M* + Na]$^+$, 2), 541 {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(SC≡CBu^t)Pd]$^+$, 7}, 492 {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Pd(SC≡CBu^t) − H]$^+$, 7}, 435 {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(SC≡CBu^t)]$^+$, 53} and 322 {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti]$^+$, 100%}. ^{1}H NMR (CDCl$_3$): at −50 °C, δ 6.45, 6.39, 6.07, 6.00 (s, C$_5$H$_4$, *syn* isomer), 6.31, 5.72 (C$_5$H$_4$, *anti* isomer), 1.23 (s, Bu^t, *syn* isomer), 1.14 (s, Bu^t, *anti* isomer), 0.37 (s, SiMe$_3$, *syn* isomer), 0.27 (s, SiMe$_3$, *anti* isomer), 0.19 (s, SiMe$_3$, *syn* isomer) (*syn*:*anti* 5:1); at 20 °C, 6.48, 6.43, 6.11, 6.07 (s, ratio 1:1:1:1, C$_5$H$_4$, *syn* isomer), 6.30, 5.81 (br, C$_5$H$_4$, *anti* isomer), 1.26 (s, Bu^t, *syn* isomer), 1.22 (sh, Bu^t, *anti* isomer), 0.37 (s, SiMe$_3$, *syn* isomer), 0.30 (s, SiMe$_3$, *anti* isomer) and 0.23 (s, SiMe$_3$, *syn* isomer); at +50 °C, 6.42, 6.11 (br, C$_5$H$_4$), 1.25, (s, Bu^t) and 0.31 (s, SiMe$_3$). ^{19}F NMR (CDCl$_3$): at −50 °C, δ −115.2 (d, *anti* isomer), −115.5 (d, *syn* isomer), −115.9 (dm, *syn* isomer), −117.0 (d, *anti*) (F$_o$, ratio *syn*:*anti* 5:1), −160.7 (t, overlapping of two F$_p$, *syn* and *anti* isomer), −163.1, −163.8 (br, F$_m$, *syn* and *anti* isomer); at 20 °C, −114.9 (d, *anti* isomer), −115.5 (m, overlapping of two F$_o$, *syn* isomer) −116.8 (d, *anti* isomer) (F$_o$, *syn*:*anti* 3:1), −161.4 (t, F$_p$), −163.8, −164.5 (m, F$_m$, *syn* and *anti* isomer); at +50 °C, −115.3 (br, F$_o$), −161.7 (t, F$_p$), −164.1, −164.7 (br, F$_m$). ^{13}C-{^{1}H} NMR (CDCl$_3$): at −50 °C, δ 147.7, 144.7, 138.5–137.1, 135.3–133.8, 120.4 (br, C$_6$F$_5$), 129.4–110.0 (s, C$_5$H$_4$, C≡C), 70.0 (s, C≡C, *anti* isomer), 69.8 (s, C≡C, *syn* isomer), 30.4 [s, C(*C*H$_3$)$_3$, *syn* isomer], 29.3 [s, C(*C*H$_3$)$_3$, *anti* isomer], 29.1 (s, *C*Me$_3$, *syn* isomer), 27.6 (s, *C*Me$_3$, *anti* isomer), −0.17 [s, Si(CH$_3$)$_3$, *syn* isomer], −0.27 [s, Si(CH$_3$)$_3$, *anti* isomer] and −0.52 [s, Si(CH$_3$)$_3$, *syn* isomer].

[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(μ-SC≡CPh)$_2$Pd(C$_6$F$_5$)$_2$] 6b (*syn* and *anti*). The reaction was performed as described for complex **5a** in toluene (5 cm^3) starting from [Ti(η^5-C$_5$H$_4$SiMe$_3$)$_2$(SC≡CPh)$_2$] (0.150 g, 0.255 mmol) and *cis*-[Pd(C$_6$F$_5$)$_2$(thf)$_2$] (0.149 g, 0.255 mmol). In this case **6b** was precipitated as a red-garnet solid by adding *n*-hexane (3 cm^3) (0.23 g, 88% yield) (*syn*:*anti* at −50 °C, 10:1). When the reaction was carried out in a 1:2 molar ratio in 0.6 cm^3 of CDCl$_3${0.013 g, 0.021 mmol of **1b** and 0.025 g, 0.043 mmol of *cis*-[Pd(C$_6$F$_5$)$_2$(thf)$_2$]} a mixture of **6b** and *cis*-[Pd(C$_6$F$_5$)$_2$(thf)$_2$] was observed by NMR spectroscopy (Found: C, 50.79; H, 3.61; S, 5.91. C$_{44}$F$_{10}$H$_{36}$PdS$_2$Si$_2$Ti requires C, 51.34; H, 3.52; S, 6.23%). $\tilde{\nu}_{max}$/cm^{-1} 2165m (C≡C), 789vs, 778vs (C$_6$F$_5$)$_{\text{X-sens}}$. MS: *m*/*z* 861 {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(SC≡CPh)$_2$Pd(C$_6$F$_5$)]$^+$, 15}, 619 {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(SC≡CPh)(C$_6$F$_5$) − 3H]$^+$,14},457 {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(SC≡CPh) + 2H]$^+$, 15} and 322 {[(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti]$^+$, 100%}. ^{1}H NMR (CDCl$_3$): at −50 °C, δ 7.29 (m), 7.17 (m) (Ph), 6.81, 6.57, 6.36, 6.28 (br, C$_5$H$_4$, *syn* isomer), 6.77, 6.45, 6.21 and 5.92 (C$_5$H$_4$, *anti* isomer), 0.38 (s, SiMe$_3$, *syn* isomer), 0.31 (s, SiMe$_3$, *anti* isomer), 0.22 (s, SiMe$_3$, *syn* isomer) (*syn*:*anti*, 10:1); at 20 °C, 7.27 (m, Ph), 6.83, 6.59, 6.42, 6.31 (br, C$_5$H$_4$), 0.39 (s, SiMe$_3$), 0.26 (s, SiMe$_3$) (*syn* and *anti* isomer); at +50 °C, 7.33 (d), 7.23 (m) (Ph), 6.66 (vbr), 6.39 (vbr) (C$_5$H$_4$) and 0.34 (s, SiMe$_3$). ^{19}F NMR (CDCl$_3$): at −50 °C, δ −115.8 (d, *anti* isomer), −115.4 (d, *syn* isomer), −116.7 (d, *syn* isomer), −117.6 (d, *anti* isomer) (F$_o$, *syn*:*anti* 10:1), −160.1 (t, F$_p$, *anti* isomer), −160.4 (t, F$_p$, *syn* isomer), −162.2, −163.5 (m, F$_m$, *syn* and *anti* isomer); at 20 °C, −114.8 (br, *anti* isomer), −115.5 (d, *syn* isomer), −116.1 (br, *syn* isomer), −117.4 (br, *anti* isomer) (F$_o$, *syn*:*anti* ≈7:1), −161.0 (t, F$_p$, *syn* and *anti* isomer), −162.9 (br), −164.2 (m, br) (F$_m$, *syn* and *anti* isomer); at +50 °C, −115.9 (br, F$_o$), −161.2 (t, F$_p$), −162.3 (br) and −163.6 (br, F$_m$). ^{13}C-{^{1}H} NMR (CDCl$_3$): at −50 °C, δ 148.4, 147.6, 138.7, 138.1–137.2, 135.5, 134.9–133.8, 121.09, 118.2 (br, C$_6$F$_5$), 131.16, (s, C$_o$, C$_6$H$_5$), 128.7, 128.4, 128.2 (s, C$_m$, C$_6$H$_5$), 125.2, 123.4, 123.1, 122.6 (s, C$_6$H$_5$, C$_5$H$_4$, *syn*), 103.5 (s, C≡C *syn* isomer), 81.6 (s, C≡C *syn* isomer), small signals seen at 121.1 and 99.2 (C≡C) tentatively attributed to the *anti* isomer, −0.13 [s, Si(CH$_3$)$_3$, *anti* isomer], −0.17 (s) and −0.39 (s) [Si(CH$_3$)$_3$, *syn* isomer].

[(η^5-C$_5$H$_4$SiMe$_3$)Ti(μ-η^5:κ-*P*-C$_5$H$_4$PPh$_2$(μ-SC≡CBu^t)$_2$Mo(CO)$_3$] 7. To a toluene solution (25 cm^3) of [Ti(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)(SC≡CBu^t)$_2$] **2a** (0.20 g, 0.30 mmol) was added [Mo(CO)$_3$(NCMe)$_3$] (0.11 g, 0.36 mmol). After 3 h of stirring at room temperature the solvent was evaporated to dryness and the solid residue chromatographed on silica gel 100. A violet band was eluted by hexane–toluene (1:1) and its recrystallisation from heptane at −20 °C yielded **7** as a dark violet solid (0.13 g, 53%). Complex **7** can also be obtained in very low yield (12%) using **2a** (0.23 g, 0.34 mmol) and [Mo(CO)$_4$(nbd)] (0.12 g, 0.42 mmol) as precursors (Found: C, 56.51; H, 5.25. C$_{40}$H$_{45}$MoO$_3$PS$_2$SiTi requires C, 57.14; H, 5.39%). $\tilde{\nu}_{max}$/cm^{-1} 2070 (C≡C); (toluene solution) 1956vs, 1895m, 1879s (CO). MS: *m*/*z* 840 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti(μ-SC≡CBu^t)$_2$Mo(CO)$_3$]$^+$, <5}, 784 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti(μ-SC≡CBu^t)$_2$Mo(CO)]$^+$, <5}, 756 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti(μ-SC≡CBu^t)$_2$Mo]$^+$, 100}, 547 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti(μ-SC≡CBu^t)]$^+$, 15} and 434 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti]$^+$, 65%}. ^{1}H NMR (CDCl$_3$): δ 7.61–7.52 (m, 4 H, Ph), 7.33–7.28 (m, 6 H, Ph), 6.23 (s, br, 2 H, C$_5$*H*$_4$PPh$_2$), 5.61 (s, br, 2 H, C$_5$*H*$_4$SiMe$_3$), 5.49 (s, br, 2 H, C$_5$*H*$_4$SiMe$_3$), 5.17 (s, br, 2 H, C$_5$*H*$_4$PPh$_2$), 1.20 (s, 18 H, Bu^t) and 0.41 (s, 9 H, SiMe$_3$); similar spectra were obtained at low (−50 °C) and high (+50 °C) temperature. ^{31}P-{^{1}H} NMR: δ 39.7 (s, C$_5$H$_4$PPh$_2$). ^{13}C-{^{1}H} NMR (CDCl$_3$): δ 213.8 (s, CO), 133.3–128.4 (s, C$_6$H$_5$), 124.3–100.7 (s, C$_5$H$_4$), 111.4 (s, C≡C), 75.4 (s, C≡C), 31.1 [s, C(*C*H$_3$)$_3$], 28.9 [*C*(CH$_3$)$_3$] and 0.30 (s, SiMe$_3$).

[(η^5-C$_5$H$_4$SiMe$_3$)(SC≡CBu^t)Ti(μ-η^5:κ-*P*-C$_5$H$_4$PPh$_2$)(μ-SC≡CBu^t)Pt(C$_6$F$_5$)$_2$] 8. To a toluene solution (20 cm^3) of complex **2a** (0.120 g, 0.18 mmol) at −20 °C was added *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$] (0.122 g, 0.18 mmol). The cooling bath was then removed and the mixture stirred for 15 min. The resulting violet solution was subsequently filtered through a pad of Celite and concentrated (*ca.* 10 cm^3). Addition of *n*-hexane (10 cm^3) afforded complex **8** as a violet crystalline solid (0.150, 70%) (Found: C, 49.85; H, 3.85. C$_{49}$H$_{45}$F$_{10}$PPtS$_2$SiTi requires C, 49.46; H, 3.81%). $\tilde{\nu}_{max}$/cm^{-1} 2157w, 2141m (C≡C), 800vs, 786vs (C$_6$F$_5$)$_{\text{X-sens}}$. MS: *m*/*z* 1077 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti(SC≡CBu^t)Pt(C$_6$F$_5$)$_2$]$^+$, 22}, 661 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti(SC≡CBu^t)$_2$]$^+$, 55}, 548 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti(SC≡CBu^t)]$^+$, 100} and 434 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti]$^+$, 50%}. ^{1}H NMR (CDCl$_3$): at −50 °C, δ 7.63 (m), 7.39–7.18 (m) (Ph), 7.01 (s, 2 H), 6.78, 6.68, 6.48, 6.16, 6.08, 5.90 (s, 1 H each) (C$_5$H$_4$), 1.20 (s, 9 H, Bu^t), 1.11 (s, 9 H, Bu^t) and 0.13 (s, 9 H, SiMe$_3$); a similar pattern was observed at 20 °C with some of the C$_5$H$_4$ signals slightly displaced. ^{19}F NMR [CDCl$_3$, ^{3}*J*(Pt–F$_o$)/Hz in parentheses]: at 20 °C, δ −116.6 [m (343), 1F], −117.7 [dm (455), 1F], −118.7 [d (414), 1F], −120.0 [m, br (326), 1F] (F$_o$), −162.7, −163.4 (t, F$_p$), −164.2 (m, 1F), −164.5 (m, 1F), −164.9 (m, 2F) (F$_m$); a similar pattern was observed at −50 °C. ^{31}P-{^{1}H} NMR (CDCl$_3$): δ 5.14 [s, C$_5$H$_4$PPh$_2$, ^{1}*J*(Pt–P) = 2361 Hz].

[(η^5-C$_5$H$_4$SiMe$_3$)(SC≡CBu^t)Ti(μ-η^5:κ-*P*-C$_5$H$_4$PPh$_2$(μ-SC≡CBu^t)Pd(C$_6$F$_5$)$_2$] 9. The synthesis was performed as described for complex **8** starting from **2a** (0.15 g, 0.22 mmol) and *cis*-[Pd(C$_6$F$_5$)$_2$(thf)$_2$] (0.13 g, 0.22 mmol) (45%) (Found: C, 53.89; H, 4.19. C$_{49}$H$_{45}$F$_{10}$PPdS$_2$SiTi requires C, 53.44; H, 4.12%). $\tilde{\nu}_{max}$/cm^{-1} 2158w, 2141m (C≡C), 786vs, 776vs (C$_6$F$_5$)$_{\text{X-sens}}$. MS: *m*/*z* 540 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti(SC≡CBu^t)Pd − H]$^+$, 42} and 434 {[(η^5-C$_5$H$_4$SiMe$_3$)(η^5-C$_5$H$_4$PPh$_2$)Ti]$^+$, 52%}. ^{1}H NMR (CDCl$_3$): at −50 °C, δ 7.52–7.18 (m, Ph), 7.03, 7.00, 6.89, 6.71, 6.39 (s, 1 H each), 6.00 (s, 2 H), 5.86 (s, 1 H) C$_5$H$_4$), 1.22 (s, 9 H, Bu^t), 1.11 (s, 9 H, Bu^t) and 0.13 (s, 9 H, SiMe$_3$); a similar pattern was observed at 20 °C. ^{19}F NMR

Table 3 Crystal data and structure refinement for [Ti(η^5-$C_5H_4SiMe_3$)$_2$(SC≡CBu^t)$_2$] **1a** and [(η^5-$C_5H_4SiMe_3$)(SC≡CBu^t)Ti(μ-η^5 : κ-*P*-$C_5H_4PPh_2$)(μ-SC≡CBu^t)Pt(C_6F_5)$_2$] **8**

	1a	**8**
Empirical formula	$C_{28}H_{44}S_2Si_2Ti$	$C_{57}H_{60}F_{10}PPtS_2SiTi$
M	548.83	1307.22
a/Å	11.470(6)	12.904(2)
b/Å	14.170(7)	14.069(1)
c/Å	21.405(11)	18.090(2)
α/°	94.04(3)	70.18(1)
β/°	104.40(3)	71.42(1)
γ/°	106.26(4)	74.91(1)
U/Å^3	3198(3)	2885.6(6)
Z	4	2
D_c/Mg m^{-3}	1.140	1.505
F(000)	1176	1312
μ/mm^{-1}	0.487	2.749
Crystal size/mm	0.46 × 0.13 × 0.08	0.34 × 0.30 × 0.12
θ Range for data collection/°	2.05 to 23.53	2.10 to 25.00
hkl Index ranges	−12 to 12, −15 to 15, 0–24	−14 to 1, −15 to 15, −20 to 20
Reflections collected	9746	10495
Independent reflections	9454 [R(int) = 0.1162]	9885 [R(int) = 0.0788]
Data/restraints/parameters	6527/0/547	8882/0/685
Goodness of fit on F^2	0.967	1.049
$R1$, $wR2$ Final indices [$I > 2\sigma(I)$]	0.0902, 0.1122	0.0672, 0.1538
(all data)	0.2820, 0.1703	0.1217, 0.2064
Largest difference peak and hole/e Å^{-3}	0.655 and −0.665	2.599 and 1.748

Details in common: λ 0.71073 Å; triclinic, space group $P\bar{1}$; full-matrix least-squares refinement on F^2; $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{\frac{1}{2}}$; goodness of fit = $[\Sigma w(F_o^2 - F_c^2)^2/(N_{obs} - N_{param})]$; $w = [\sigma^2(F_o) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2, 0 + 2F_c^2)]/3$.

($CDCl_3$): at 20 °C, δ −114.1 (d, 1F), −115.05 (d, 1F), −115.6 (d, 1F), −117.5 (m, 1F) (F_o), −161.95, −161.99 (overlapping of two triplets, 2F_p), −163.4 (m), −163.7 (m) (3F), −164.1 (m, 1F) (F_m); a similar pattern was observed at −50 °C. ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 10.93 (s, $C_5H_4PPh_2$).

X-Ray crystallography

Complex 1a. Crystals of compound **1a** suitable for X-ray analysis were grown from a saturated pentane solution at −20 °C. A deep brown needle-shaped crystal was fixed with epoxy on top of a glass fiber and transferred to the cold stream of the low temperature device of a Siemens STOE/AED2 automated four circle diffractometer. Crystal data and structure refinement parameters are listed in Table 3. Data were collected at 200 K by the θ–2θ method. Three check reflections measured at regular intervals showed no loss of intensity at the end of data collection. An empirical absorption correction based on ψ scans was applied (maximum and minimum transmission factors = 0.913, 0.841). The structure was solved by the Patterson method. All non-hydrogen atoms were located in succeeding Fourier difference syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were added at calculated positions and assigned isotropic displacement parameters equal to 1.2 or 1.5 times the U_{iso} value of their respective apparent carbon atoms. Two molecules of the compound were found per asymmetric unit. There was no electron density higher than 1 e Å^{-3} in the final map.

Complex 8·0.5 *n*-hexane·toluene. Suitable crystals of complex **8**·0.5 *n*-hexane·toluene were obtained by slow diffusion of hexane into a toluene solution of **8** at 20 °C. A dark red crystal was mounted in inert oil on top of a glass fiber and transferred to the cold stream of the low temperature device of a Siemens P4 automated four circle diffractometer. Crystal data and structure refinement parameters are listed in Table 3. Cell constants were calculated from 50 well centered reflections with 2θ angles ranging from 23 to 26°. Data were collected at 173 K by the θ–2θ method. Three check reflections measured at regular intervals showed no significant loss of intensity at the end of data collection. The data were treated (maximum and minimum transmission factors 0.983 and 0.680) and the structure solved and refined as above. Regions of electron density located at non-bonding distances were modelled as interstitial solvent and refined with anisotropic displacement parameters. In total, there were a quarter of a molecule of *n*-hexane and a molecule of toluene per formula unit. Three carbon atoms, refined at half occupancy, were found for the hexane molecule, three other carbon atoms being generated by symmetry. The toluene molecule was found in two regions, with half occupancy in each and with the molecule disordered over a symmetry center. There were four peaks of electron density higher than 1 e Å^{-3} in the final map, three located very close to the platinum atom having no chemical meaning and the other in the solvent area.

All calculations were carried out using the program SHELXL 93.[31]

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