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Co-ordinative ability of the new compounds $[Ti(\eta^5\text{-}C_5H_4R)_2(C{\equiv}CBu^t)_2]$ (R = PPh_2, $Ph_2P{=}O$ or $Ph_2P{=}S$) as precursors in the synthesis of heterodi- and heterotri-nuclear species. Crystal structure of $[ClCu(\mu\text{-}\eta^5{:}\kappa P\text{-}C_5H_4PPh_2)_2Ti(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)_2CuCl]$

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New mononuclear bis(alkyne) derivatives of functionalised titanocene $[Ti(\eta^5\text{-}C_5H_4R)_2(C{\equiv}CBu^t)_2]$ (R = PPh_2 **1**, $Ph_2P{=}O$ **7** or $Ph_2P{=}S$ **8**) have been isolated by reaction of $[Ti(\eta^5\text{-}C_5H_4R)_2Cl_2]$ (R = PPh_2, $Ph_2P{=}O$ or $Ph_2P{=}S$) and $LiC{\equiv}CBu^t$ in diethyl ether. The reactions of the former species with $(CuCl)_n$ and $[Mo(CO)_4(nbd)]$ have been investigated. Novel heterobi- $[L_nM(\mu\text{-}\eta^5{:}\kappa P\text{-}C_5H_4PPh_2)_2Ti(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)_2]$ [ML_n = CuCl **4** or $Mo(CO)_4$ **5**], $[\{\eta^5\text{-}C_5H_4P(E)Ph_2\}_2Ti(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)_2CuCl]$ (E = O **9** or S **10**) and heterotri-nuclear complexes $[L_nM(\mu\text{-}\eta^5{:}\kappa P\text{-}C_5H_4PPh_2)_2Ti(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)_2CuCl]$ [ML_n= CuCl **2** or $Mo(CO)_4$ **6**] have been synthesized. The crystal structure of compound **2** has been solved.

Introduction

In the last years our group has focussed its interest on the synthesis of thiolate derivatives of functionalised titanocenes and their further use as precursors of new early–late heterometallic compounds $[(\eta^5\text{-}C_5H_4R')_2Ti(\mu\text{-}SR)_2M(C_6F_5)_2]$ (R′ = H or $SiMe_3$; R = Ph or C_6F_5),[1] $[(OC)_4Mo(\mu\text{-}\eta^5{:}\kappa P\text{-}C_5H_4PPh_2)_2Ti(\mu\text{-}SPh)_2M(C_6F_5)_2]$ (M = Pd or Pt),[2] $[(C_6F_5)_2Pt(\mu\text{-}\eta^5{:}\kappa P\text{-}C_5H_4PPh_2)_2Ti(SPh)_2]$[3] and $[(\eta^5\text{-}C_5H_4SiMe_3)(SC{\equiv}CBu^t)Ti(\mu\text{-}\eta^5{:}\kappa P\text{-}C_5H_4PPh_2)(\mu\text{-}SC{\equiv}CBu^t)M(C_6F_5)_2]$ (M = Pd or Pt).[4] Different co-ordination situations, such as *P*,*P*; *S*,*S* or *P*,*S*, have been observed in these species. The chemistry of transition metal acetylides is a subject of growing interest in part due to the versatility of C≡CR groups as bridging ligands.[5] In particular for titanocene acetylides, whereas complexes $[(\eta^5\text{-}C_5H_5)_2Ti(C{\equiv}CPh)_2Pt(PR_3)]$ (R = Ph or C_6H_{11})[6] and $[(\eta^5\text{-}C_5H_5)_2Ti(C{\equiv}CBu^t)_2Pt(C_6F_5)_2]$[7] show a symmetrical double bridge $\mu\text{-}\eta^2$ or $\mu\text{-}\eta^1$ alkyne, the compound $[(\eta^5\text{-}C_5H_5)_2Ti(C{\equiv}CBu^t)_2Pt(PPh_3)]$[8] exhibits asymmetric $\mu\text{-}\eta^2$ and $\mu\text{-}\eta^1$ bridges.

Although chelating bis(alkynyl) systems ($\mu\text{-}\eta^2$) can be in-plane (tweezer) or out-of plane (V-shape) bonded to the other metal, data reported on bis(alkynyl) titanocenes reveal that the metal centre M is located in the plane of the 3-titanium-1,4-diyne ligand. Lang and co-workers have carried out interesting studies in this field by using functionalised titanocenes as metalloligands to prepare some heterometallic species showing a tweezer-like interaction, $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2MR]$ (M = Cu or Ag; R = alkyl or aryl),[9] $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2MCl_2]$ (M = Fe, Co or Ni)[10] and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2MX]$ (M = Cu or Ag; X = halide or pseudohalide).[11] In addition, extended Hückel calculations carried out by these authors on some of the above mentioned complexes justify this type of interaction.[9,11]

On the other hand, the co-ordination chemistry of phosphine oxides and sulfides has been a subject of study,[12] however data reported on related phosphoryl- and thiophosphoryl-cyclopentadienyl ligands are scarce.[13] We report here the synthesis of new mononuclear complexes $[Ti(\eta^5\text{-}C_5H_4R)_2(C{\equiv}CBu^t)_2]$ (R = PPh_2, $Ph_2P{=}O$ or $Ph_2P{=}S$) and their reactions as precursors of heterodi- and heterotri-nuclear species. The crystal structure of $[ClCu(\mu\text{-}\eta^5{:}\kappa P\text{-}C_5H_4PPh_2)_2Ti(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)_2CuCl]$ has been determined by a X-ray diffraction study.

Results and discussion

Treatment of $[Ti(\eta^5\text{-}C_5H_4PPh_2)_2Cl_2]$ with 2 equivalents of $LiC{\equiv}CBu^t$ in diethyl ether at −20 °C affords the compound $[Ti(\eta^5\text{-}C_5H_4PPh_2)_2(C{\equiv}CBu^t)_2]$ **1** in high yield. Complex **1** is stable in the solid state but decomposes gradually in solution under an inert atmosphere. The $^{31}P\text{-}\{^1H\}$ NMR spectrum exhibits a signal (δ −15.1) in the same range to that observed for $[Ti(\eta^5\text{-}C_5H_4PPh_2)_2Cl_2]$[14] and $[Ti(\eta^5\text{-}C_5H_4PPh_2)_2(SPh)_2]$.[3] The two resonances that appear in the $^{13}C\text{-}\{^1H\}$ NMR spectrum at δ 138.2 and 115.8, as well as a band at 2069 cm^{-1} in the IR, are consistent with the presence of two equivalent alkyne groups σ co-ordinated to the titanium atom. The ^1H NMR spectrum in the Cp region shows two signals at δ 6.24 and 6.12 corresponding to the four protons of each ring and a singlet at δ 1.14 assigned to the Bu^t group. The lower electronegativity of $C{\equiv}CBu^t$ compared to that of the chloride ligand is responsible for the shifting of the Cp resonances upfield.

The chemistry of Cu^I with phosphines is quite well known, particularly that related to monophosphines.[15] On the other hand, in the last few years several papers have been reported concerning the co-ordination of CuX moieties through C≡CR groups of some alkynyl derivatives of titanocenes.[16] Taking into account these precedents and due to the possibility for $[Ti(\eta^5\text{-}C_5H_4PPh_2)_2(C{\equiv}CBu^t)_2]$ **1** to act as a Lewis base through the PPh_2 and $C{\equiv}CBu^t$ groups, in order to know its co-ordinative preferences we carried out the reaction between complex **1** and CuCl in 1 : 1 stoichiometry, which gave the trinuclear compound $[ClCu(\mu\text{-}\eta^5{:}\kappa P\text{-}C_5H_4PPh_2)_2Ti(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)_2CuCl]$ **2**. The elemental analyses are in agreement with this formulation and in addition the molecular peak observed in the FAB possitive spectrum of **2** reveals the presence of two CuCl fragments in the molecule. The IR spectrum in the solid state shows a ν(C≡C) at 1984 cm^{-1}, shifted to lower frequency after co-ordination to the copper(I) fragment, and two resonances are observed in the ^{13}C-{^{1}H} NMR spectrum for the acetylide carbon atoms at lower field (δ 149.8 and 134.1) in comparison to those of the mononuclear titanium precursor. A broad signal corresponding to the PPh$_2$ groups of complex [ClCu(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$Ti(μ-η^2-C≡CBu^t)$_2$CuCl] **2**, only slightly shifted (δ −17.0) to higher field, is recorded in the ^{31}P-{^{1}H} NMR spectrum. As we will mention later, this result is in contrast with the strong shift that this signal experiences when a molybdenum fragment is co-ordinated to the titanium atom through this PPh$_2$ group, but it is in agreement with data found for other copper phosphine complexes.[17] The ^{1}H NMR spectrum exhibits two multiplets at δ 6.08 and 5.98 and a singlet at δ 1.35 attributable to the protons of Cp and Bu^t groups respectively. The molecular structure of complex **2**, suggested by analytical and spectroscopic data, was confirmed by a X-ray diffraction study.

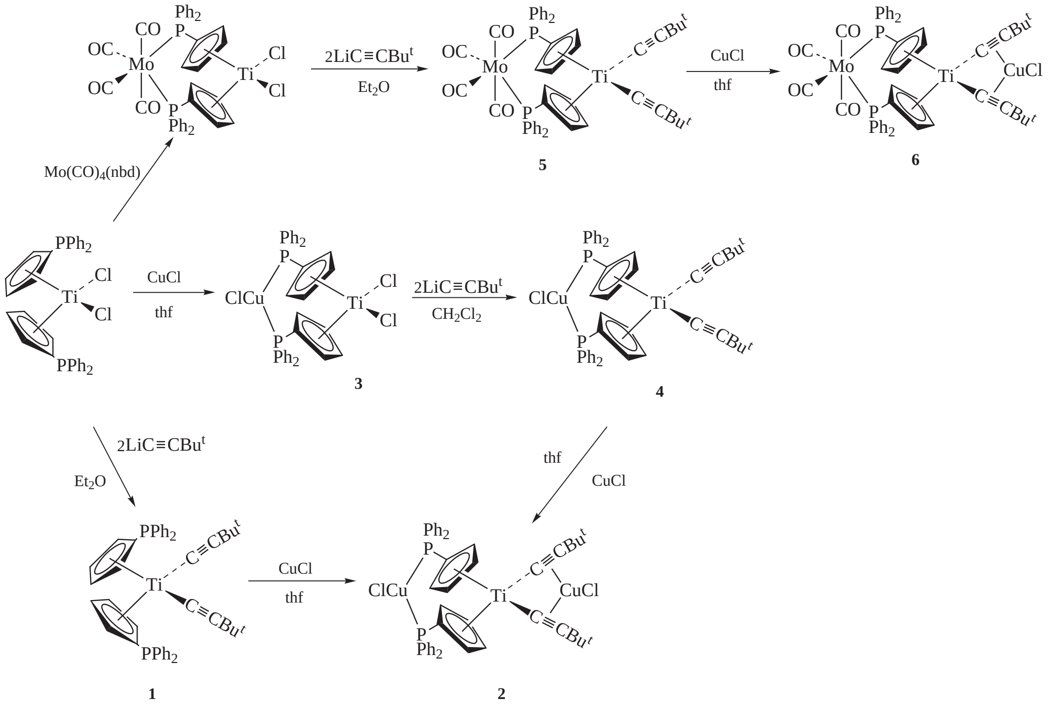
Irrespective of whether the reaction of complex **1** and CuCl was carried out using 1 or 2 equivalents of CuCl only **2** was obtained. This seems to indicate an equal tendency of the CuCl moiety to co-ordinate *P*,*P* or (η^2-C≡C)$_2$, although a recent report[18] on reactions of copper(I) halides and X(C≡CBu^t)$_2$ (X = PPh, S, SO or SO$_2$) ligands showed a co-ordinative preference PhP > C≡C > S.

Keeping in mind the idea of preparing heteronuclear species with only a copper fragment linked to the titanocene, either towards PPh$_2$ or C≡CBu^t groups, we studied the reaction between [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$Cl$_2$] and CuCl in CH$_2$Cl$_2$. Stirring this mixture at room temperature afforded the complex [ClCu(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$TiCl$_2$] **3**. Further reaction of **3** with the stoichiometric amount of LiC≡CBu^t in diethyl ether–dichloromethane (1:3) at −20 °C gave [ClCu(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$Ti(C≡CBu^t)$_2$] **4** (Scheme 1). The last reaction failed when it was carried out using just diethyl ether. We think that the great insolubility of complex **3** in this solvent could be the reason for this result. Complexes **3** and **4** are very unstable in solution, and the last also in the solid state. In fact **4** could not be characterised by analytical data or mass spectroscopy. The compound [ClCu(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$Ti(μ-η^2-C≡CBu^t)$_2$CuCl] **2** was also obtained by addition of an equimolecular amount of CuCl to a solution of **4**.

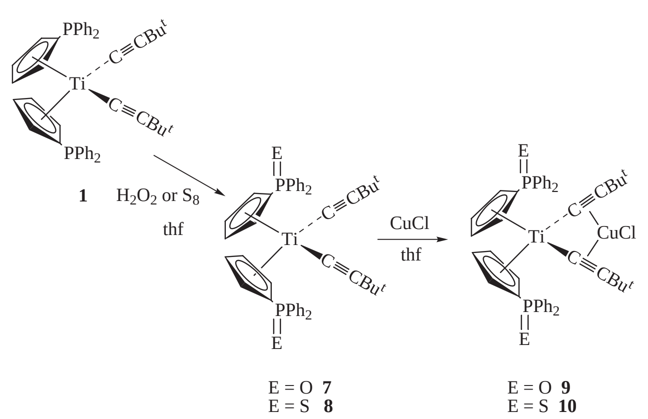
On the other hand, we thought that a possible way to force the co-ordination of the CuCl fragment only through the alkyne groups could be the use of [(OC)$_4$Mo(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$Ti(C≡CBu^t)$_2$] as starting material. Molybdenum(0) carbonyl complexes are known to have a great tendency to bind phosphines,[19] in fact [(OC)$_4$Mo(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$TiCl$_2$] was reported several years ago.[20] That is the reason why we initially attempted the reaction between [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(C≡CBu^t)$_2$] **1** and [Mo(CO)$_4$(nbd)] under different conditions, obtaining in all cases unsatisfactory results. Then a mixture of [(OC)$_4$-Mo(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$TiCl$_2$] and LiC≡CBu^t was allowed to react in diethyl ether at −20 °C to afford the new compound [(OC)$_4$Mo(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$Ti(C≡CBu^t)$_2$] **5** as a brown solid. Further reaction of complex **5** and CuCl in 1:1 stoichiometry using thf as solvent gave the heteronuclear species [(OC)$_4$Mo-(μ-η^5:κ*P*-C$_5$H$_4$PPh$_2$)$_2$Ti(μ-η^2-C≡CBu^t)$_2$CuCl] **6** (Scheme 1).

It has been previously noted that different shifts are observed for the signal corresponding to the PPh$_2$ groups in the ^{31}P-{^{1}H} NMR of all these compounds. While a strong downfield shift was recorded for complexes **5** (δ 32.8) and **6** (δ 33.8) a very slight one is exhibited by **3** (δ −10.00) and **4** (δ −9.4). Owing to the instability in solution of compound **4** it was not possible to run its ^{13}C-{^{1}H} NMR spectrum. For the rest of the compounds the spectra show the resonances corresponding to the α- and β-carbon atoms of the C≡CBu^t groups that experience a downfield shift in relation to that of **1**, more pronounced for **6** but in both cases similar to the ones founded for analogous acetylides.[16] A stretching band appears in the IR spectra of compounds **4**–**6** in the C≡C region, moved for compound **6** to lower frequency as a consequence of the co-ordination of the CuCl fragment to the acetylenic ligands. All these species show in the Cp region of the ^{1}H NMR spectra two signals shifted downfield indicative of the linking of a metal fragment to the titanium atom through the PPh$_2$ groups.

We have recently established[21] how the oxidation of the Cp substituents in [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$X$_2$] (X = Cl or SR) provokes a significant enhancement of stability in the resulting species [Ti{η^5-C$_5$H$_4$P(E)Ph$_2$}$_2$X$_2$] (X = Cl or SR; E = O or S). The reactions of compound **1** and H$_2$O$_2$ or S$_8$ as oxidisers led to complexes [Ti{η^5-C$_5$H$_4$P(E)Ph$_2$}$_2$(C≡CBu^t)$_2$] (E = O **7** or S **8** Scheme 2), nevertheless in this case only **8** seems to be more stable than the starting material **1**.



Scheme 1



Scheme 2

The soft base character of a sulfur donor ligand, as well as the existence of some examples on complexes of Cu^I with phosphine oxides,[22] prompted us to study the co-ordination chemistry of phosphoryl- and thiophosphoryl-cyclopentadienyl derivatives **7** and **8** with CuCl. Although there have been reported several complexes where CuCl co-ordinates to oxygen and sulfur atoms of $[Fe\{\eta^5\text{-}C_5H_4P(E)Ph_2\}_2]$ [E = O (dpopf) or S (dptpf)],[13] in our case no evidence has been observed of co-ordination through these atoms, the copper fragment showing a preference for the alkyne ligands to give heterodinuclear compounds $[\{\eta^5\text{-}C_5H_4P(E)Ph_2\}_2Ti(\mu\text{-}\eta^2\text{-}C{\equiv}CBu^t)_2CuCl]$ (E = O **9** or S **10** Scheme 2).

Compounds **7**–**10** have been characterised by spectroscopic and analytical techniques. The presence of phosphoryl and thiophosphoryl groups in the Cp rings of complexes **7** and **8** provokes a downfield shift of these proton signals in the ^1H NMR spectra (δ 7.01 and 6.51 **7** and 6.95 and 6.50 **8**) compared to those of the starting material **1** (δ 6.24 and 6.12). The same tendency is observed in the $^{31}P\text{-}\{^1H\}$ NMR spectra (δ 23.9 **7** and 34.7 **8**) consistent with the oxidation of P^{III} to P^V, however the signals are only slightly shifted for complexes **9** and **10** suggesting the non-co-ordination of the CuCl fragment to these groups.

The instability in solution of complex **7** does not allow the acquisition of satisfactory analytical data or a $^{13}C\text{-}\{^1H\}$ NMR spectrum. For **8** two resonances for the acetylenic carbons are obtained in the range expected, while for **9** and **10** the same signals are shifted downfield by co-ordination of the CuCl fragments to these groups. In addition for **9** and **10** the IR spectra show a modification of the C≡C stretching frequency, while the ν (P=E) (E = O or S) remains almost unchanged.

Crystal structure of complex 2

An ORTEP[23] drawing of the molecular structure showing the atom numbering scheme is presented in Fig. 1. Selected bond distances and angles are collected in Table 1.

The titanium atom lies in a pseudo-tetrahedral environment involving the two cyclopentadienyl rings and the two acetylide ligands and both copper atoms show a distorted trigonal planar geometry. Atom Cu(1) is surrounded by the two η^2-bonded $C{\equiv}CBu^t$ groups and the chloride ligand. Although crystal data for the precursor $[Ti(\eta^5\text{-}C_5H_4PPh_2)_2(C{\equiv}CBu^t)_2]$ **1** are not available, the Ti–C≡C and C≡C–C angles [165(2), 169(2) and 162(2), 163(2)°] in complex **2** are shifted from the linearity observed in the analogous acetylide titanocene $[Ti(\eta^5\text{-}C_5H_4SiMe_3)_2(C{\equiv}CSiMe_3)_2]$[16a] as a result of the co-ordination to the Group 11 metal.

It is noteworthy that the different Ti–C and C≡C distances for each alkyne group suggest that although both of them are η^2 bonded to the copper atom, the strength of the interaction is not the same. Thus, whereas the Ti–C(3) [2.15(2) Å] and C(3)-C(4) [1.18(3) Å] distances are in the range observed for other analogous complexes $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2CuCl]$[24] and $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2CuX]$ (X = $C{\equiv}CSiMe_3$ or Cl)[9] the Ti–C(1) [2.02(2) Å] and C(1)–C(2) [1.28(2) Å] distances are slightly different. The smaller Ti–C(1) bond value is probably due to a π interaction along the σ bond between the titanium and the $C{\equiv}CBu^t$ group, as has been indicated for the compound $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}\sigma:\eta^2\text{-}C{\equiv}CPh)(\mu\text{-}PPh_2)Ni(PPh_3)]$[25] where a Ti–C distance of 2.065(8) Å has been reported. The least squares plane defined by TiC_4CuCl shows a deviation of 0.0229 Å, indicating a tweezer interaction between the copper atom and the $[Ti](C{\equiv}CBu^t)_2$ entity.[9,11] In addition a C(1)–Ti–C(3) angle of 92.2(8)° is similar to that found in the above mentioned complex and other related compounds.[16]

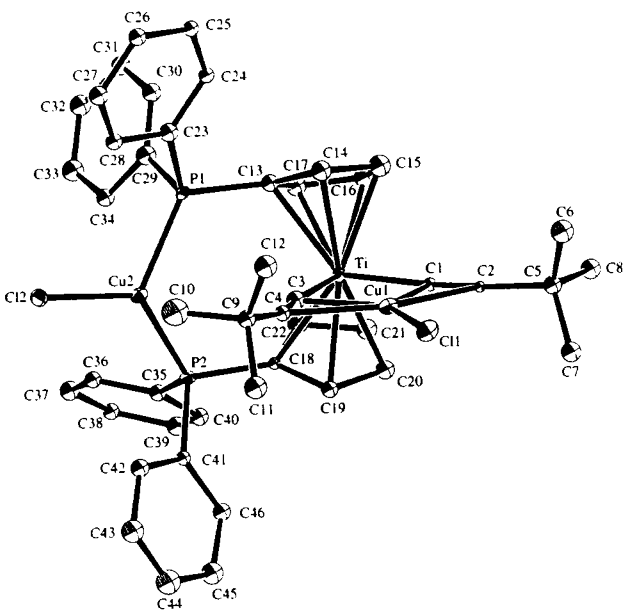


Fig. 1 An ORTEP drawing and atom numbering scheme of the complex **2**.

Table 1 Selected bond lengths (Å) and angles (°) of complex **2**

Cu(1)–Ti(1)	2.899(4)	Ti(1)–C(3)	2.15(2)
Cu(1)–Cl(1)	2.180(6)	C(3)–C(4)	1.18(3)
Cu(1)–C(1)	2.12(2)	Ti(1)–Cp(1)	2.0491
Cu(1)–C(2)	2.23(2)	Ti(1)–Cp(2)	2.0671
Cu(1)–C(3)	2.06(2)		
Cu(1)–C(4)	2.22(2)	Cp(1)–Ti(1)–Cp(2)	135.5
Cu(2)-Cl(2)	2.219(6)	C(1)–Ti(1)–C(3)	92.2(8)
Cu(2)–P(1)	2.279(6)	Ti(1)–C(1)–C(2)	165(2)
Cu(2)–P(2)	2.259(5)	C(1)–C(2)–C(5)	162(2)
C(1)–C(2)	1.28(2)	Ti(1)–C(3)–C(4)	169(2)
Ti(1)–C(1)	2.02(2)	C(3)–C(4)–C(9)	163(2)

The Ti–Cu distance of 2.899(4) Å is the shortest found, as far as we know, in acetylide derivatives of this type $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CSiMe_3)_2CuR]$ {R = Cl [2.9645(5) Å];[9] $C{\equiv}CSiMe_3$ [2.9665(8) Å];[26] or $C_6H_2Me_3$-2,4,6 [2.9418(5) Å][16b]} but it is quite close to that reported for the compound $[(\eta^5\text{-}C_5H_4SiMe_3)_2Ti(C{\equiv}CPh)_2CuCl]$ [2.909(3) Å].[24] Although this bond distance is slightly greater than the sum of covalent radii it could suggest a weak interaction between the two metal centres.

The Cu(2) centre is co-ordinated to the PPh_2 groups of the phosphinocyclopentadienyl ligands and a chlorine atom. The two Cu–P bond distances [2.279(6) and 2.259(5) Å] are slightly different and the P(1)-Cu(2)-P(2) angle of 119.1(2)° is smaller than those found in complexes P_2CuX [P = PPh_3 (126.9°);[27] $PPh_2(C_6H_4Me\text{-}o)$ (126°);[28] or PCy_3 (134.06°)[29]], due to the fact that the titanium precursor is acting as a chelate ligand.

The Cu–Cl distances [2.180(6) and 2.219(6) Å] found for this complex are in agreement with normal Cu–Cl bond distances and in the range observed for other heterodinuclear Ti–Cu derivatives.[16]

Conclusion

The complex $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2(\mathrm{C{\equiv}CBu^t})_2]$ behaves as a metalloligand through both $\mathrm{C{\equiv}CBu^t}$ and $\mathrm{PPh_2}$ groups. A different behaviour of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Cl_2}]$ and $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2(\mathrm{C{\equiv}CBu^t})_2]$ has been observed, thus it has been reported that $[(\mathrm{OC})_4\mathrm{Mo}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{TiCl_2}]$ is obtained by reaction of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Cl_2}]$ and $[\mathrm{Mo(CO)_4(nbd)}]$, however we have found that the same molybdenum reagent does not react when $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2(\mathrm{C{\equiv}CBu^t})_2]$ is used as starting material.

On the other hand, CuCl acts as a Lewis acid towards the $\mathrm{PPh_2}$ groups to afford the complex $[\mathrm{ClCu}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{TiCl_2}]$, but we have not been able to isolate the heterodinuclear species $[\mathrm{ClCu}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Ti}(\mathrm{C{\equiv}CBu^t})_2]$ or $[(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Ti}(\mu\text{-}\eta^2\text{-}\mathrm{C{\equiv}CBu^t})_2\mathrm{CuCl}]$ by reaction of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2(\mathrm{C{\equiv}CBu^t})_2]$ and CuCl. No selective co-ordination has been found in the last reaction and $[\mathrm{ClCu}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Ti}(\mu\text{-}\eta^2\text{-}\mathrm{C{\equiv}CBu^t})_2\mathrm{CuCl}]$ was the sole compound obtained under all conditions we have studied.

Finally, the stability of the complex $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2(\mathrm{C{\equiv}CBu^t})_2]$ does not increase by oxidation of the $\mathrm{PPh_2}$ groups, in contrast to the enhancement observed for the analogous thiolate derivatives $[\mathrm{Ti}\{\eta^5\text{-}\mathrm{C_5H_4P(E)Ph_2}\}_2(\mathrm{SR})_2]$ (E = O or S).

Experimental

Reactions were carried out under an atmosphere of argon by means of conventional Schlenk techniques.[30] Solvents were purified according to standard procedures.[31] The complexes $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Cl_2}]$,[3] $[(\mathrm{OC})_4\mathrm{Mo}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{TiCl_2}]$[20] and $[\mathrm{Mo(CO)_4(nbd)}]$[32] were prepared as previously published. All other reagents were used as obtained commercially. Microanalyses were determined with a Perkin-Elmer 2400 microanalyser. Infrared spectra (thf solution or KBr) were recorded on a Perkin-Elmer 1600 FT spectrophotometer, NMR spectra on Bruker AMX-300 or -400 spectrometers with chemical shifts reported in ppm relative to external standards ($\mathrm{SiMe_4}$ for ^{1}H and ^{13}C and $\mathrm{H_3PO_4}$ for ^{31}P) and mass spectra (FAB+) on a VG Autospec spectrometer.

Syntheses

$[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2(\mathrm{C{\equiv}CBu^t})_2]$ 1. To a diethyl ether solution (20 $\mathrm{cm^3}$) of $\mathrm{HC{\equiv}CBu^t}$ (0.10 $\mathrm{cm^3}$, 0.84 mmol) cooled at −20 °C was added dropwise $\mathrm{LiBu^n}$ (0.52 $\mathrm{cm^3}$, 0.84 mmol). After 10 min of stirring $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Cl_2}]$ (0.25 g, 0.40 mmol) was added and subsequently the cooling bath removed. Stirring at room temperature was maintained for 1 h. Concentration and filtration of the solution through Celite afforded complex **1** as an orange-brown crystalline solid after evaporation of the solvent to dryness (0.23 g, 83%) (Found: C, 77.80; H, 6.38. $\mathrm{C_{46}H_{46}P_2Ti}$ requires C, 77.96 ; H, 6.54%). $\nu_\mathrm{max}/\mathrm{cm^{-1}}$ 2069 (C≡C). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.40–7.27 (m, 20 H, $\mathrm{C_6H_5}$), 6.24 (m, 4 H, $\mathrm{C_5H_4}$), 6.12 (m, 4 H, $\mathrm{C_5H_4}$) and 1.14 (s, 18 H, $\mathrm{Bu^t}$). ^{31}P-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −15.1 (s, $\mathrm{PPh_2}$). ^{13}C-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 138.3–128.0 (m, $\mathrm{C_6H_5}$), 138.2 (s, C≡C), 122.1 (t, J_PC = 12.8 Hz *o*-C of $\mathrm{C_5H_4}$), 118.4 (t, J_PC = 10.3, *m*-C of $\mathrm{C_5H_4}$), *i*-C of $\mathrm{C_5H_4}$ not observed, 115.8 (s, C≡C), 31.0 ($\mathrm{CH_3}$) and 30.6 [s, *C*($\mathrm{CH_3}$)]. FAB-MS: *m*/*z* 708, M^+; 627, $[M - \mathrm{C{\equiv}CBu^t}]^+$; and 546, $[M - 2\mathrm{C{\equiv}CBu^t}]^+$.

$[\mathrm{ClCu}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Ti}(\mu\text{-}\eta^2\text{-}\mathrm{C{\equiv}CBu^t})_2\mathrm{CuCl}]$ 2. To a solution of complex **1** (0.40 g, 0.56 mmol) in thf (25 $\mathrm{cm^3}$) was added $(\mathrm{CuCl})_n$ (0.05 g, 0.56 mmol). The mixture was stirred in the darkness for 2 h and then the solvent removed *in vacuo*. The solid residue was purified by chromatography on silica gel 100. A red band was eluted from hexane–thf (1 : 1). Recrystallisation from dichloromethane–methanol (1 : 1) afforded red needles of **2** (0.24 g, 47%) (Found: C, 60.14; H, 5.22. $\mathrm{C_{46}H_{46}Cl_2Cu_2P_2Ti{\cdot}CH_3OH}$ requires C, 60.21 ; H, 5.33%). $\nu_\mathrm{max}/\mathrm{cm^{-1}}$ 1984 (C≡C). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.86–7.34 (m, 20 H, $\mathrm{C_6H_5}$), 6.08 (m, 4 H, $\mathrm{C_5H_4}$), 5.98 (m, 4 H, $\mathrm{C_5H_4}$) and 1.35 (s, 18 H, $\mathrm{Bu^t}$). ^{31}P-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −17.0 (s, br, $\mathrm{PPh_2}$). ^{13}C-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 149.8 (s, C≡C), 134.1 (s, C≡C), 133.0-128.3 (m, $\mathrm{C_6H_5}$), 127.6 (d, J_PC = 9.9, *i*-C of $\mathrm{C_5H_4}$), 114.7, 113.2 (m, J_PC = 12.8 Hz, *o*-, *m*-C of $\mathrm{C_5H_4}$), 30.7 [s, *C*($\mathrm{CH_3}$)] and 30.0 ($\mathrm{CH_3}$). FAB-MS: *m*/*z* 906, M^+; 871, $[M - \mathrm{Cl}]^+$; 807, $[M - \mathrm{CuCl}]^+$; and 708, $[M - 2\mathrm{CuCl}]^+$.

$[\mathrm{ClCu}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{TiCl_2}]$ 3. To a dichloromethane solution (30 $\mathrm{cm^3}$) of $[\mathrm{Ti}(\eta^5\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Cl_2}]$ (0.40 g, 0.64 mmol) was added $(\mathrm{CuCl})_n$ (0.06 g, 0.64 mmol) and the mixture stirred for 1 h in the darkness. The resulting brown solution was filtered through Celite and then concentrated (*ca.* 10 $\mathrm{cm^3}$). Addition of *n*-hexane (15 $\mathrm{cm^3}$) afforded a brown solid that was washed with several portions of *n*-hexane (3 × 5 $\mathrm{cm^3}$) and dried under vacuum (0.38 g, 80%) (Found: C, 56.35; H, 3.51. $\mathrm{C_{34}H_{28}Cl_3CuP_2Ti}$ requires C, 57.01; H, 3.94%). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.75–7.40 (m, 20 H, $\mathrm{C_6H_5}$), 6.74 (m, 4 H, $\mathrm{C_5H_4}$) and 6.65 (m, 4 H, $\mathrm{C_5H_4}$). ^{31}P-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −10.0 (s, $\mathrm{PPh_2}$).

$[\mathrm{ClCu}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Ti}(\mathrm{C{\equiv}CBu^t})_2]$ 4. To a solution of $\mathrm{LiBu^n}$ (0.40 $\mathrm{cm^3}$, 0.65 mmol) in ether (25 $\mathrm{cm^3}$) at −20 °C was added $\mathrm{HC{\equiv}CBu^t}$ (0.08 $\mathrm{cm^3}$, 0.65 mmol). The mixture was stirred for 5 min, then a solution of complex **3** (0.21 g, 0.30 mmol) in dichloromethane (15 $\mathrm{cm^3}$) was added. After stirring for 45 min the resulting solution was filtered over Celite and the solvent removed *in vacuo* to give the brown compound $[\mathrm{ClCu}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Ti}(\mathrm{C{\equiv}CBu^t})_2]$ **4** (70%). $\nu_\mathrm{max}/\mathrm{cm^{-1}}$ 2072 (C≡C). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.57–7.15 (m, 20 H, $\mathrm{C_6H_5}$), 6.19 (m, 4 H, $\mathrm{C_5H_4}$), 6.05 (m, 4 H, $\mathrm{C_5H_4}$) and 1.16 (s, 18 H, $\mathrm{Bu^t}$). ^{31}P-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ −9.4 (s, $\mathrm{PPh_2}$). Complex **4** could not be characterised by elemental analyses and mass spectroscopy due to its instability in solution.

$[(\mathrm{OC})_4\mathrm{Mo}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Ti}(\mathrm{C{\equiv}CBu^t})_2]$ 5. This compound was obtained following the procedure described for **1** by reaction of $[(\mathrm{OC})_4\mathrm{Mo}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{TiCl_2}]$ and $\mathrm{LiC{\equiv}CBu^t}$ (70%) (Found: C, 64.98; H, 5.02. $\mathrm{C_{50}H_{46}MoO_4P_2Ti}$ requires C, 65.51; H, 5.06%). $\nu_\mathrm{max}/\mathrm{cm^{-1}}$ 2069 (C≡C); (thf solution) 2019m, 1920s and 1896vs (CO). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.57–7.15 (m, 20 H, $\mathrm{C_6H_5}$), 6.87 (q, 4 H, $\mathrm{C_5H_4}$), 6.34 (q, 4 H, $\mathrm{C_5H_4}$) and 1.11 (s, 18 H, $\mathrm{Bu^t}$). ^{31}P-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 32.8 (s, $\mathrm{PPh_2}$). ^{13}C-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 214.2 (m, $\mathrm{CO_{eq}}$), 209.6 (t, $\mathrm{CO_{ax}}$), 139.7 (s, C≡C), 135.1–127.7 (m, $\mathrm{C_6H_5}$), 127.3 (d, J_PC = 9.5, *i*-C of $\mathrm{C_5H_4}$), 123.5 (s, C≡C), 121.3 (m, *m*-C of $\mathrm{C_5H_4}$), 117.7 (t, J_PC = 5.8 Hz, *o*-C of $\mathrm{C_5H_4}$), 31.1 ($\mathrm{CH_3}$) and 28.7 [s, *C*($\mathrm{CH_3}$)]. FAB-MS: *m*/*z* 916, M^+; 888, $[M - \mathrm{CO}]^+$; 860, $[M - 2\mathrm{CO}]^+$; 835, $[M - \mathrm{C{\equiv}CBu^t}]^+$; 832, $[M - 3\mathrm{CO}]^+$; 804, $[M - 4\mathrm{CO}]^+$; 754, $[M - 2\mathrm{C{\equiv}CBu^t}]^+$; and 708, $[M - \mathrm{Mo(CO)_4}]^+$.

$[(\mathrm{OC})_4\mathrm{Mo}(\mu\text{-}\eta^5{:}\kappa P\text{-}\mathrm{C_5H_4PPh_2})_2\mathrm{Ti}(\mu\text{-}\eta^2\text{-}\mathrm{C{\equiv}CBu^t})_2\mathrm{CuCl}]$ 6. To a thf solution (30 $\mathrm{cm^3}$) of complex **5** (0.25 g, 0.27 mmol) was added $(\mathrm{CuCl})_n$ (0.03 g, 0.27 mmol). After 1.5 h of stirring in the darkness the resulting solution was filtered through Celite and the solvent removed under vacuum. The residue was recrystallised from thf–pentane (1 : 1) at −20 °C to yield an orange solid corresponding to **6** (0.17 g, 55%) (Found: C, 59.22; H, 4.51. $\mathrm{C_{50}H_{46}ClCuMoO_4P_2Ti}$ requires C, 59.13; H, 4.56%); $\nu_\mathrm{max}/\mathrm{cm^{-1}}$ 1995 (C≡C); (thf solution): 2017m, 1922m and 1896vs (CO). ^{1}H NMR ($\mathrm{CDCl_3}$): δ 7.48–7.39 (m, 20 H, $\mathrm{C_6H_5}$), 6.25 (m, 4 H, $\mathrm{C_5H_4}$), 6.05 (m, 4 H, $\mathrm{C_5H_4}$) and 1.40 (s, 18 H, $\mathrm{Bu^t}$). ^{31}P-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 33.8 (s, $\mathrm{PPh_2}$). ^{13}C-{^{1}H} NMR ($\mathrm{CDCl_3}$): δ 213.8 (m, $\mathrm{CO_{eq}}$), 209.5 (t, *J* = 8.6, $\mathrm{CO_{ax}}$), 152.6 (s, C≡C), 135.5 (s, C≡C), 133.4 (d, J_PC = 15.2, *i*-C of $\mathrm{C_5H_4}$), 132.5–128.3 (m, $\mathrm{C_6H_5}$), 117.8 (s, *m*-C of $\mathrm{C_5H_4}$), 114.6 (t, J_PC = 6.0 Hz, *o*-C of

C_5H_4), 31.8 [s, *C*(CH_3)] and 30.7 (CH_3). FAB-MS: *m*/*z* 1015, *M*$^+$; 987, [*M* − CO]$^+$; 980, [*M* − Cl]$^+$; 959, [*M* − 2CO]$^+$; 932, [*M* − 3CO]$^+$; 916, [*M* − CuCl]$^+$; 904, [*M* − 4CO]$^+$ and 808, [*M*-Mo(CO)$_4$]$^+$.

[Ti{η^5-C_5H_4P(O)Ph_2}$_2$(C≡CBu^t)$_2$] 7. To a solution of complex **1** (0.25 g, 0.32 mmol) in thf (30 cm^3) was added a 30% solution of H_2O_2 (0.02 cm^3, 0.32 mmol), and the mixture stirred for 30 min. Then the solution was filtered through Celite and the solvent removed to dryness (0.16 g, 70%). ν_{max}/cm^{-1} 2064 (C≡C) and 1178 (P=O). ^{1}H NMR ($CDCl_3$): δ 7.65–7.26 (m, 20 H, C_6H_5), 7.01 (m, 4 H, C_5H_4), 6.51 (m, 4 H, C_5H_4) and 0.95 (s, 18 H, Bu^t). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 23.9 [s, P(O)Ph_2]. Complex **7** could not be characterised by elemental analyses and mass spectroscopy due to its instability in solution.

[Ti{η^5-C_5H_4P(S)Ph_2}$_2$(C≡CBu^t)$_2$] 8. To a solution of complex **1** (0.25 g, 0.32 mmol) in thf (30 cm^3) at 0 °C was added S_8 (0.0262 g, 0.08 mmol). After stirring for 30 min the solution was filtered through Celite and the solvent removed (0.21 g, 85%) (Found: C, 71.52; H, 5.88. $C_{46}H_{46}P_2S_2Ti$ requires C, 71.49; H, 6.00%). ν_{max}/cm^{-1}: 2067 (C≡C) and 653 (P=S). ^{1}H NMR ($CDCl_3$): δ 7.65–7.42 (m, 20 H, C_6H_5), 6.95 (m, 4 H, C_5H_4), 6.50 (m, 4 H, C_5H_4) and 1.00 (s, 18 H, Bu^t). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 34.7 [s, P(S)Ph_2]. ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 140.7 (s, C≡C), 135.7 (d, J_{PC} = 10.2, *i*-C of C_5H_4), 134.4–128.2 (m, C_6H_5), 121.6, 119.5 (d, J_{PC} = 10.5 Hz, overlapping doublets, *o*-C of C_5H_4), 118.8 (s, C≡C), 113.4, 112.7 (s, *m*-C of C_5H_4), 31.4 (CH_3) and 28.9 [s, *C*(CH_3)]. FAB-MS: *m*/*z* 772, *M*$^+$; 691, [*M* − C≡CBu^t]$^+$; 659, [*M* − S − C≡CBu^t]$^+$; and 610, [*M* − 2C≡CBu^t]$^+$.

[{η^5-C_5H_4P(O)Ph_2}$_2$Ti(μ-η^2-C≡CBu^t)$_2$CuCl] 9. To a thf solution (30 cm^3) of complex **7** (0.35 g, 0.47 mmol) was added (CuCl)$_n$ (0.0465 g, 0.47 mmol) and the mixture stirred for 1 h in the darkness. Subsequently the solvent was removed and the residue chromatographed on silica gel 100. A red band was eluted by thf–hexane (2:1) to yield a solid that afforded red needles of complex **9** after recrystallisation from dichloromethane–methanol (1:1) (0.25 g, 65%) (Found: C, 64.56; H, 5.77. $C_{46}H_{46}ClCuO_2P_2Ti\cdot CH_3OH$ requires C, 64.76; H, 5.78%). ν_{max}/cm^{-1} 1986 (C≡C) and 1176 (P=O). ^{1}H NMR ($CDCl_3$): δ 7.62–7.46 (m, 20 H, C_6H_5), 6.63 (q, 4 H, C_5H_4), 6.10 (q, 4 H, C_5H_4) and 1.25 (s, 18 H, Bu^t). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 20.7 [s, P(O)Ph_2]. ^{13}C-{^{1}H} NMR ($CDCl_3$): δ 150.8 (s, C≡C), 134.7 (s, C≡C), 134.0-128.4 (m, C_6H_5), 132.9 (t, J_{PC} = 17.0 Hz, *i*-C of C_5H_4), 115.5, 113.8 (s, *o*-, *m*-C of C_5H_4), 31.6 [s, *C*(CH_3)] and 30.8 (CH_3). FAB-MS: *m*/*z* 839, *M*$^+$; 803, [*M* − Cl]$^+$; and 659, [*M* − CuCl − C≡CBu^t]$^+$.

[{η^5-C_5H_4P(S)Ph_2}$_2$Ti(μ-η^2-C≡CBu^t)$_2$CuCl] 10. This complex was synthesized following the above procedure by reaction between **8** and (CuCl)$_n$ (67%) (Found: C, 63.45; H, 5.18. $C_{46}H_{46}ClCuP_2S_2Ti$ requires C, 63.37; H, 5.32%); ν_{max}/cm^{-1} 1986 (C≡C) and 654 (P=S). ^{1}H NMR ($CDCl_3$): δ 7.63–7.45 (m, 20 H, C_6H_5), 6.40 (q, 4 H, C_5H_4), 6.00 (q, 4 H, C_5H_4) and 1.35 (s, 18 H, Bu^t). ^{31}P-{^{1}H} NMR ($CDCl_3$): δ 34.1 [s, P(S)Ph_2]. ^{13}C-{^{1}H} NMR (50 MHz, $CDCl_3$): δ 149.6 (s, C≡C), 134.7 (s, C≡C), 133.6–128.8 (m, C_6H_5), 127.5 (d, J_{PC} = 9.5, *i*-C of C_5H_4), 118.6, 115.6 (d, J_{PC}= 10.2 Hz, *o*-, *m*-C of C_5H_4), 32.0 [s, *C*(CH_3)] and 30.8 (s, CH_3). FAB-MS: *m*/*z* 871, *M*$^+$; 835, [M − Cl]$^+$; 691, [*M* − CuCl − C≡CBu^t]$^+$; and 610, [*M* − CuCl − 2C≡CBu^t]$^+$.

Crystal structure of complex 2

Crystals of complex **2** suitable for X-ray analysis were grown as very thin red needles by slow diffusion of methanol into a dichloromethane solution of the compound. A crystal of dimensions 0.08 × 0.08 × 0.36 mm was selected for the data collection. All X-ray measurements were carried out on a Rigaku AFC6S diffractometer at 173 K using Mo-Kα radiation (λ = 0.71069 Å). The diffraction peaks were generally weak.

Table 2 Crystal data and structure refinement for [ClCu(μ-η^5:κ*P*-$C_5H_4PPh_2$)$_2$Ti(μ-η^2-C≡CBu^t)$_2$CuCl] **2**

Empirical Formula	$C_{47}H_{50}Cl_2Cu_2OP_2T$
M	938.76
Crystal system	Orthorhombic
Space group	$Pna2_1$ (no. 33)
a/Å	28.989(8)
b/Å	14.109(4)
c/Å	10.606(2)
U/Å^3	4337(1)
Z	4
D_c/Mg m^{-3}	1.44
R_{int}	0.042
F(000)	1936
μ(Mo-Kα)mm^{-1}	1.383
Reflections collected	3424
Unique reflections	3424
No. reflections [$I > 3.5\sigma(I)$]	1904
Data/restraints/parameters	1904/0/255
Residuals R, *R*′	0.064, 0.083

Calculations were performed on a VAXstation 3520 computer applying the TEXSAN 5.0 software[33] and in the later stages on a Silicon Graphics Indigo 2 Extreme computer with the TEXSAN 1.7 package.[34]

Relevant crystallographic data are listed in Table 2. Unit cell dimensions were determined by applying the setting angles of 25 high-angle reflections. Three standard reflections were monitored during the data collection, showing no significant variance. The intensities were corrected for absorption by applying Ψ scans of several reflections with the transmission factors within the range 0.92–1.00.

The structures were solved by direct methods in SIR 92.[35] Full-matrix least-squares refinement with anisotropic thermal displacement parameters for the Cu, Ti, Cl and P atoms yielded the final *R* of 0.064. The hydrogen atoms were found in the Fourier-difference maps and included in the calculations without further refinement . The goodness of fit has a value of S = 1.95. A total of 3424 reflections were collected, covering indices $0 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 32$ and $0 \leqslant l \leqslant 12$. The final electron density map was essentially featureless with the highest peak of 0.75 e Å^{-3}.

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