**ULL PAPER** 

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

Esther Delgado,\*.ª Elisa Hernández,ª Noelia Mansilla,ª M. Teresa Moreno<sup>b</sup> and Michal Sabat<sup>c</sup>

<sup>a</sup> Departamento de Química Inorgánica, Facultad de Ciencias, Universidad Autónoma de

<sup>b</sup> Departamento de Química, Universidad de la Rioja, 26001 Logroño, Spain

<sup>c</sup> Department of Chemistry, University of Virginia, VA 22901, Charlottesville, USA

Received 12th October 1998, Accepted 23rd December 1998

New mononuclear bis(alkyne) derivatives of functionalised titanocene [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub>(C=CBu<sup>t</sup>)<sub>2</sub>] (R = PPh<sub>2</sub> 1, Ph<sub>2</sub>P=O 7 or Ph<sub>2</sub>P=S 8) have been isolated by reaction of [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub>Cl<sub>2</sub>] (R = PPh<sub>2</sub>, Ph<sub>2</sub>P=O or Ph<sub>2</sub>P=S) and LiC=CBu<sup>t</sup> in diethyl ether. The reactions of the former species with (CuCl)<sub>n</sub> and [Mo(CO)<sub>4</sub>(nbd)] have been investigated. Novel heterobi- [L<sub>n</sub>M( $\mu$ - $\eta^5$ :  $\kappa$ P-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti( $\mu$ - $\eta^2$ -C=CBu<sup>t</sup>)<sub>2</sub>] [ML<sub>n</sub> = CuCl 4 or Mo(CO)<sub>4</sub> 5], [{ $\eta^5$ -C<sub>5</sub>H<sub>4</sub>P(E)Ph<sub>2</sub>}<sub>2</sub>Ti( $\mu$ - $\eta^2$ -C=CBu<sup>t</sup>)<sub>2</sub>CuCl] (E = O 9 or S 10) and heterotri-nuclear complexes [L<sub>n</sub>M( $\mu$ - $\eta^5$ :  $\kappa$ P-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti( $\mu$ - $\eta^2$ -C=CBu<sup>t</sup>)<sub>2</sub>Ti( $\mu$ - $\eta^2$ -C=CBu<sup>t</sup>)<sub>2</sub>CuCl] [ML<sub>n</sub> = CuCl 2 or Mo(CO)<sub>4</sub> 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  $[(\eta^{5}-C_{5}H_{4}R')_{2}Ti(\mu-SR)_{2}M(C_{6}F_{5})_{2}]$  (R' = H or SiMe<sub>3</sub>; R = Ph or C<sub>6</sub>F<sub>5</sub>),<sup>1</sup> [(OC)<sub>4</sub>Mo( $\mu$ - $\eta^5$ :  $\kappa P$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>- $\begin{array}{c} \text{Ti}(\mu\text{-SPh})_2 M(C_6F_5)_2] & (M = \text{Pd} \quad \text{or} \quad \text{Pt}),^2 \quad [(C_6F_5)_2 \text{Pt}(\mu\text{-}\eta^5:\kappa P\text{-}C_5H_4 \text{PPh}_2)_2 \text{Ti}(\text{SPh}_2]^3 \quad \text{and} \quad [(\eta^5\text{-}C_5H_4 \text{SiMe}_3)(\text{SC=CBu}^t)\text{Ti}\text{-}\text{I}) \\ \end{array}$  $(\mu-\eta^5:\kappa P-C_5H_4PPh_2)(\mu-SC\equiv CBu^t)M(C_6F_5)_2]$  (M = Pd or Pt).<sup>4</sup> 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.<sup>5</sup> In particular for titanocene acetylides, whereas complexes [(n<sup>5</sup>- $C_5H_5_2Ti(C=CPh_2Pt(PR_3)]$  (R = Ph or  $C_6H_{11})^6$  and  $[(\eta^5-C_5H_5)_2-$ Ti(C=CBu<sup>t</sup>)<sub>2</sub>Pt(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>]<sup>7</sup> show a symmetrical double bridge  $\mu$ - $\eta^2$  or  $\mu$ - $\eta^1$  alkyne, the compound  $[(\eta^5-C_5H_5)_2Ti(C\equiv CBu^t)_2-$ Pt(PPh<sub>3</sub>)]<sup>8</sup> exhibits asymmetric  $\mu$ - $\eta^2$  and  $\mu$ - $\eta^1$  bridges.

Although chelating bis(alkynyl) systems  $(\mu - \eta^2)$  can be inplane (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,  $[(\eta^5-C_5H_4SiMe_3)_2Ti(C=CSiMe_3)_2-$ MR] (M = Cu or Ag; R = alkyl or aryl),<sup>9</sup>  $[(\eta^5-C_5H_4 SiMe_3)_2Ti(C=CSiMe_3)_2MCl_2]$  (M = Fe, Co or Ni)<sup>10</sup> and  $[(\eta^5-C_5H_4SiMe_3)_2Ti(C=CSiMe_3)_2MX]$  (M = Cu or Ag; X = halide or pseudohalide).<sup>11</sup> In addition, extended Hückel calculations carried out by these authors on some of the above mentioned complexes justify this type of interaction.<sup>9,11</sup>

On the other hand, the co-ordination chemistry of phosphine oxides and sulfides has been a subject of study,<sup>12</sup> however data reported on related phosphoryl- and thiophosphoryl-cyclopentadienyl ligands are scarce.<sup>13</sup> We report here the synthesis of new mononuclear complexes [Ti( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>R)<sub>2</sub>(C=CBu<sup>t</sup>)<sub>2</sub>] (R =

PPh<sub>2</sub>, Ph<sub>2</sub>P=O or Ph<sub>2</sub>P=S) and their reactions as precursors of heterodi- and heterotri-nuclear species. The crystal structure of  $[ClCu(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2Ti(\mu-\eta^2-C\equiv CBu^t)_2CuCl]$  has been determined by a X-ray diffraction study.

# **Results and discussion**

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

The chemistry of Cu<sup>I</sup> with phosphines is quite well known, particularly that related to monophosphines.<sup>15</sup> 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.<sup>16</sup> Taking into account these precedents and due to the possibility for  $[Ti(\eta^5-C_5H_4PPh_2)_2(C=CBu^t)_2]$  **1** to act as a Lewis base through the PPh<sub>2</sub> and C=CBu<sup>t</sup> 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  $[ClCu(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2Ti(\mu-\eta^2-C=$  $CBu<sup>t</sup>)_2CuCl]$  **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

Madrid, 28249 Madrid, Spain. E-mail: esther.delgado@uam.es

solid state shows a v(C=C) at 1984 cm<sup>-1</sup>, shifted to lower frequency after co-ordination to the copper(I) fragment, and two resonances are observed in the <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum for the acetylide carbon atoms at lower field ( $\delta$  149.8 and 134.1) in comparison to those of the mononuclear titanium precursor. A broad signal corresponding to the PPh<sub>2</sub> groups of complex [ClCu( $\mu$ - $\eta^5$ :  $\kappa P$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti( $\mu$ - $\eta^2$ -C=CBu<sup>t</sup>)<sub>2</sub>CuCl] **2**, only slightly shifted ( $\delta$  -17.0) to higher field, is recorded in the <sup>31</sup>P-{<sup>1</sup>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<sub>2</sub> group, but it is in agreement with data found for other copper phosphine complexes.<sup>17</sup> The <sup>1</sup>H NMR spectrum exhibits two multiplets at  $\delta$  6.08 and 5.98 and a singlet at  $\delta$  1.35 attributable to the protons of Cp and Bu<sup>t</sup> 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  $(\eta^2-C=C)_2$ , although a recent report<sup>18</sup> on reactions of copper(I) halides and X(C=CBu<sup>1</sup>)<sub>2</sub> (X = PPh, S, SO or SO<sub>2</sub>) 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 PPh2 or C=CBut groups, we studied the reaction between [Ti(n<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] and CuCl in CH<sub>2</sub>Cl<sub>2</sub>. Stirring this mixture at room temperature afforded the complex  $[ClCu(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2TiCl_2]$  3. Further reaction of 3 with the stoichiometric amount of LiC=CBut in diethyl ether-dichloromethane (1:3) at -20 °C gave [ClCu( $\mu$ - $\eta^5$ : $\kappa P$ - $C_5H_4PPh_2_2Ti(C=CBu^t)_2$ ] 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( $\mu$ - $\eta^5$ :  $\kappa P$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti( $\mu$ - $\eta^2$ -C=CBu<sup>t</sup>)<sub>2</sub>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  $[(OC)_4Mo(\mu-\eta^5):\kappa P C_5H_4PPh_2_2Ti(C \equiv CBu^t)_2$  as starting material. Molybdenum(0) carbonyl complexes are known to have a great tendency to bind phosphines,<sup>19</sup> in fact  $[(OC)_4Mo(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2TiCl_2]$  was reported several years ago.<sup>20</sup> That is the reason why we initially attempted the reaction between  $[Ti(\eta^5-C_5H_4PPh_2)_2(C\equiv CBu^t)_2]$ 1 and [Mo(CO)<sub>4</sub>(nbd)] under different conditions, obtaining in all cases unsatisfactory results. Then a mixture of [(OC)<sub>4</sub>- $Mo(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2TiCl_2$  and  $LiC \equiv CBu^t$  was allowed to react in diethyl ether at -20 °C to afford the new compound  $[(OC)_4Mo(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2Ti(C\equiv CBu^t)_2]$  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)<sub>4</sub>Mo- $(\mu - \eta^5 : \kappa P - C_5 H_4 PPh_2)_2 Ti(\mu - \eta^2 - C \equiv CBu^t)_2 CuCl] 6$  (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 ( $\delta$  32.8) and 6 ( $\delta$  33.8) a very slight one is exhibited by 3 ( $\delta$  -10.00) and 4 ( $\delta$  -9.4). Owing to the instability in solution of compound 4 it was not possible to run its <sup>13</sup>C-{<sup>1</sup>H} NMR spectrum. For the rest of the compounds the spectra show the resonances corresponding to the  $\alpha$ - and  $\beta$ -carbon atoms of the C=CBu<sup>t</sup> 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.<sup>16</sup> 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 <sup>1</sup>H NMR spectra two signals shifted downfield indicative of the linking of a metal fragment to the titanium atom through the PPh<sub>2</sub> groups. We have recently established<sup>21</sup> how the oxidation of the Cp

We have recently established<sup>21</sup> how the oxidation of the Cp substituents in  $[Ti(\eta^5-C_5H_4PPh_2)_2X_2]$  (X = Cl or SR) provokes a significant enhancement of stability in the resulting species  $[Ti\{\eta^5-C_5H_4P(E)Ph_2\}_2X_2]$  (X = Cl or SR; E = O or S). The reactions of compound 1 and  $H_2O_2$  or S<sub>8</sub> as oxidisers led to complexes  $[Ti\{\eta^5-C_5H_4P(E)Ph_2\}_2(C\equiv CBu^t)_2]$  (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



The soft base character of a sulfur donor ligand, as well as the existence of some examples on complexes of Cu<sup>I</sup> with phosphine oxides,<sup>22</sup> 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  $[Fe{\eta^5-C_5H_4P(E)Ph_2}_2]$  [E = O (dpopf) or S (dptpf)],<sup>13</sup> 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  $[{\eta^5-C_5H_4P(E)Ph_2}_2Ti(\mu-\eta^2-C=CBu^t)_2CuCl]$  (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 <sup>1</sup>H NMR spectra ( $\delta$  7.01 and 6.51 7 and 6.95 and 6.50 8) compared to those of the starting material 1 ( $\delta$  6.24 and 6.12). The same tendency is observed in the <sup>31</sup>P-{<sup>1</sup>H} NMR spectra ( $\delta$  23.9 7 and 34.7 8) consistent with the oxidation of P<sup>III</sup> to P<sup>v</sup>, 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 <sup>13</sup>C-{<sup>1</sup>H} 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  $\nu$  (P=E) (E = O or S) remains almost unchanged.

#### Crystal structure of complex 2

An ORTEP<sup>23</sup> 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  $\eta^2$ -bonded C=CBu<sup>t</sup> groups and the chloride ligand. Although crystal data for the precursor [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(C=CBu<sup>t</sup>)<sub>2</sub>] **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( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>SiMe<sub>3</sub>)<sub>2</sub>(C=CSiMe<sub>3</sub>)<sub>2</sub>]<sup>16*a*</sup> 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  $\eta^2$ 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



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)

analogous complexes  $[(\eta^5-C_5H_4SiMe_3)_2Ti(C=CPh)_2CuCl]^{24}$  and  $[(\eta^5-C_5H_4SiMe_3)_2Ti(C=CSiMe_3)_2CuX]$  (X = C=CSiMe\_3 or Cl)<sup>9</sup> 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  $\pi$  interaction along the  $\sigma$  bond between the titanium and the C=CBu<sup>t</sup> group, as has been indicated for the compound  $[(\eta^5-C_5H_5)_2Ti(\mu-\sigma:\eta^2-C=CPh)(\mu-PPh_2)Ni(PPh_3)]^{25}$  where a Ti–C distance of 2.065(8) Å has been reported. The least squares plane defined by TiC<sub>4</sub>CuCl shows a deviation of 0.0229 Å, indicating a tweezer interaction between the copper atom and the [Ti](C=CBu<sup>t</sup>)<sub>2</sub> entity.<sup>9,11</sup> 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.<sup>16</sup>

The Ti–Cu distance of 2.899(4) Å is the shortest found, as far as we know, in acetylide derivatives of this type  $[(\eta^5-C_5H_4SiMe_3)_2Ti(C=CSiMe_3)_2CuR]$  {R = Cl [2.9645(5) Å];<sup>9</sup> C=CSiMe\_3 [2.9665(8) Å];<sup>26</sup> or C<sub>6</sub>H<sub>2</sub>Me<sub>3</sub>-2,4,6 [2.9418(5) Å] <sup>16b</sup>} but it is quite close to that reported for the compound  $[(\eta^5-C_5H_4SiMe_3)_2Ti(C=CPh)_2CuCl]$  [2.909(3) Å].<sup>24</sup> 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<sub>2</sub> 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<sub>2</sub>CuX [P = PPh<sub>3</sub> (126.9°);<sup>27</sup> PPh<sub>2</sub>(C<sub>6</sub>H<sub>4</sub>Me-*o*) (126°);<sup>28</sup> or PCy<sub>3</sub> (134.06°)<sup>29</sup>], 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

# Conclusion

The complex  $[Ti(\eta^5-C_5H_4PPh_2)_2(C\equiv CBu^t)_2]$  behaves as a metalloligand through both  $C\equiv CBu^t$  and  $PPh_2$  groups. A different behaviour of  $[Ti(\eta^5-C_5H_4PPh_2)_2Cl_2]$  and  $[Ti(\eta^5-C_5H_4PPh_2)_2(C\equiv CBu^t)_2]$  has been observed, thus it has been reported that  $[(OC)_4Mo(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2TiCl_2]$  is obtained by reaction of  $[Ti(\eta^5-C_5H_4PPh_2)_2Cl_2]$  and  $[Mo(CO)_4(nbd)]$ , however we have found that the same molybdenum reagent does not react when  $[Ti(\eta^5-C_5H_4PPh_2)_2(C\equiv CBu^t)_2]$  is used as starting material.

On the other hand, CuCl acts as a Lewis acid towards the PPh<sub>2</sub> groups to afford the complex [ClCu( $\mu$ - $\eta^5$ : $\kappa$ *P*-C<sub>5</sub>H<sub>4</sub>-PPh<sub>2</sub>)<sub>2</sub>TiCl<sub>2</sub>], but we have not been able to isolate the heterodinuclear species [ClCu( $\mu$ - $\eta^5$ : $\kappa$ *P*-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti(C=CBu<sup>t</sup>)<sub>2</sub>] or [( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti( $\mu$ - $\eta^2$ -C=CBu<sup>t</sup>)<sub>2</sub>CuCl] by reaction of [Ti( $\eta^5$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>(C=CBu<sup>t</sup>)<sub>2</sub>] and CuCl. No selective co-ordination has been found in the last reaction and [ClCu( $\mu$ - $\eta^5$ : $\kappa$ *P*-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti( $\mu$ - $\eta^2$ -C=CBu<sup>t</sup>)<sub>2</sub>CuCl] was the sole compound obtained under all conditions we have studied.

Finally, the stability of the complex  $[Ti(\eta^5-C_5H_4PPh_2)_2-(C\equiv CBu^t)_2]$  does not increase by oxidation of the PPh<sub>2</sub> groups, in contrast to the enhancement observed for the analogous thiolate derivatives  $[Ti\{\eta^5-C_5H_4P(E)Ph_2\}_2(SR)_2]$  (E = O or S).

### Experimental

Reactions were carried out under an atmosphere of argon by means of conventional Schlenk techniques.<sup>30</sup> Solvents were purified according to standard procedures.<sup>31</sup> The complexes  $[Ti(\eta^5-C_5H_4PPh_2)_2Cl_2]$ ,<sup>3</sup> $[(OC)_4Mo(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2TiCl_2]^{20}$ and  $[Mo(CO)_4(nbd)]^{32}$  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 (SiMe<sub>4</sub> for <sup>1</sup>H and <sup>13</sup>C and H<sub>3</sub>PO<sub>4</sub> for <sup>31</sup>P) and mass spectra (FAB+) on a VG Autospec spectrometer.

### Syntheses

 $[Ti(\eta^5-C_5H_4PPh_2)_2(C \equiv CBu^t)_2]$  1. To a diethyl ether solution (20 cm<sup>3</sup>) of HC=CBu<sup>t</sup> (0.10 cm<sup>3</sup>, 0.84 mmol) cooled at -20 °C was added dropwise LiBu<sup>n</sup> (0.52 cm<sup>3</sup>, 0.84 mmol). After 10 min of stirring  $[Ti(\eta^5-C_5H_4PPh_2)_2Cl_2]$  (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.  $C_{46}H_{46}P_2$ Ti requires C, 77.96 ; H, 6.54%).  $v_{max}/cm^{-1}$  2069 (C=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.40–7.27 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.24 (m, 4 H,  $C_5H_4$ ), 6.12 (m, 4 H,  $C_5H_4$ ) and 1.14 (s, 18 H, Bu<sup>t</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -15.1 (s, PPh<sub>2</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  138.3–128.0 (m, C<sub>6</sub>H<sub>5</sub>), 138.2 (s, C=C), 122.1 (t, J<sub>PC</sub> = 12.8 Hz o-C of C<sub>5</sub>H<sub>4</sub>), 118.4 (t,  $J_{PC} = 10.3$ , m-C of C<sub>5</sub>H<sub>4</sub>), i-C of C<sub>5</sub>H<sub>4</sub> not observed, 115.8 (s, C≡C), 31.0 (CH<sub>3</sub>) and 30.6 [s, C(CH<sub>3</sub>)]. FAB-MS: m/z 708,  $M^+$ ; 627,  $[M - C \equiv CBu^t]^+$ ; and 546,  $[M - C \equiv CBu^t]^+$ ; and 546, a  $2C \equiv CBu^t$ ]<sup>+</sup>.

[ClCu(μ-η<sup>5</sup>: κP-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti(μ-η<sup>2</sup>-C≡CBu<sup>†</sup>)<sub>2</sub>CuCl] 2. To a solution of complex 1 (0.40 g, 0.56 mmol) in thf (25 cm<sup>3</sup>) was added (CuCl)<sub>n</sub> (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.  $C_{46}H_{46}Cl_2Cu_2P_2$ -Ti·CH<sub>3</sub>OH requires C, 60.21; H, 5.33%).  $v_{max}/cm^{-1}$  1984 (C=C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.86–7.34 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.08 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 5.98 (m, 4 H, C<sub>5</sub>H<sub>4</sub>) and 1.35 (s, 18 H, Bu<sup>1</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –17.0 (s, br, PPh<sub>2</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  149.8 (s, C=C), 134.1 (s, C=C), 133.0-128.3 (m, C<sub>6</sub>H<sub>5</sub>), 127.6 (d,  $J_{PC}$  = 9.9, *i*-C of C<sub>5</sub>H<sub>4</sub>), 114.7, 113.2 (m,  $J_{PC}$  = 12.8 Hz, *o*-, *m*-C of C<sub>5</sub>H<sub>4</sub>), 30.7 [s, C(CH<sub>3</sub>)] and 30.0 (CH<sub>3</sub>). FAB-MS: *m*/*z* 906, *M*<sup>+</sup>; 871, [*M* – Cl]<sup>+</sup>; 807, [*M* – CuCl]<sup>+</sup>; and 708, [*M* – 2CuCl]<sup>+</sup>.

[ClCu(μ-η<sup>5</sup>:  $\kappa P$ -C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>TiCl<sub>2</sub>] **3.** To a dichloromethane solution (30 cm<sup>3</sup>) of [Ti(η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Cl<sub>2</sub>] (0.40 g, 0.64 mmol) was added (CuCl)<sub>n</sub> (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 cm<sup>3</sup>). Addition of *n*-hexane (15 cm<sup>3</sup>) afforded a brown solid that was washed with several portions of *n*-hexane (3 × 5 cm<sup>3</sup>) and dried under vacuum (0.38 g, 80%) (Found: C, 56.35; H, 3.51. C<sub>34</sub>H<sub>28</sub>Cl<sub>3</sub>CuP<sub>2</sub>Ti requires C, 57.01; H, 3.94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.75–7.40 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.74 (m, 4 H, C<sub>5</sub>H<sub>4</sub>) and 6.65 (m, 4 H, C<sub>5</sub>H<sub>4</sub>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  – 10.0 (s, PPh<sub>2</sub>).

[ClCu(μ-η<sup>5</sup>: κ*P*-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti(C≡CBu<sup>t</sup>)<sub>2</sub>] **4.** To a solution of LiBu<sup>n</sup> (0.40 cm<sup>3</sup>, 0.65 mmol) in ether (25 cm<sup>3</sup>) at -20 °C was added HC≡CBu<sup>t</sup> (0.08 cm<sup>3</sup>, 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 cm<sup>3</sup>) 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 [ClCu( $\mu$ -η<sup>5</sup>: κ*P*-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti(C≡CBu<sup>t</sup>)<sub>2</sub>] **4** (70%).  $\nu_{max}$ /cm<sup>-1</sup> 2072 (C≡C). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.57–7.15 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.19 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 6.05 (m, 4 H, C<sub>5</sub>H<sub>4</sub>) and 1.16 (s, 18 H, Bu<sup>t</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -9.4 (s, PPh<sub>2</sub>). Complex **4** could not be characterised by elemental analyses and mass spectroscopy due to its instability in solution.

**[(OC)<sub>4</sub>Mo(μ-η<sup>5</sup>: κP-C<sub>5</sub>H<sub>4</sub>PPh<sub>2</sub>)<sub>2</sub>Ti(C≡CBu<sup>1</sup>)<sub>2</sub>] 5.** This compound was obtained following the procedure described for 1 by reaction of  $[(OC)_4Mo(\mu-\eta^5: \kappa P-C_5H_4PPh_2)_2TiCl_2]$  and LiC= ≡CBu<sup>t</sup> (70%) (Found: C, 64.98; H, 5.02. C<sub>50</sub>H<sub>46</sub>MoO<sub>4</sub>P<sub>2</sub>Ti requires C, 65.51; H, 5.06%).  $v_{max}$ /cm<sup>-1</sup> 2069 (C≡C); (thf solution) 2019m, 1920s and 1896vs (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.57–7.15 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.87 (q, 4 H, C<sub>5</sub>H<sub>4</sub>), 6.34 (q, 4 H, C<sub>5</sub>H<sub>4</sub>) and 1.11 (s, 18 H, Bu<sup>t</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  32.8 (s, PPh<sub>2</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  214.2 (m, CO<sub>eq</sub>), 209.6 (t, CO<sub>ax</sub>), 139.7 (s, C≡C), 135.1–127.7 (m, C<sub>6</sub>H<sub>5</sub>), 127.3 (d, J<sub>PC</sub> = 9.5, *i*-C of C<sub>5</sub>H<sub>4</sub>), 123.5 (s, C≡C), 121.3 (m, *m*-C of C<sub>5</sub>H<sub>4</sub>), 117.7 (t, J<sub>PC</sub> = 5.8 Hz, *o*-C of C<sub>5</sub>H<sub>4</sub>), 31.1 (CH<sub>3</sub>) and 28.7 [s, C(CH<sub>3</sub>)]. FAB-MS: *m*/z 916, *M*<sup>+</sup>; 888, [*M* − CO]<sup>+</sup>; 804, [*M* − 4CO]<sup>+</sup>; 754, [*M* − 2C≡CBu<sup>t</sup>]<sup>+</sup>; and 708, [*M* − Mo-(CO)<sub>4</sub>]<sup>+</sup>.

 $[(OC)_{4}Mo(\mu-\eta^{5}:\kappa P-C_{5}H_{4}PPh_{2}),Ti(\mu-\eta^{2}-C\equiv CBu^{t}),CuCl]$ 6. To a thf solution (30 cm<sup>3</sup>) of complex 5 (0.25 g, 0.27 mmol) was added (CuCl)<sub>n</sub> (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. C<sub>50</sub>H<sub>46</sub>ClCuMoO<sub>4</sub>P<sub>2</sub>Ti requires C, 59.13; H, 4.56%);  $v_{max}/cm^{-1}$  1995 (C=C); (thf solution): 2017m, 1922m and 1896vs (CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.48–7.39 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.25 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 6.05 (m, 4 H, C<sub>5</sub>H<sub>4</sub>) and 1.40 (s, 18 H, Bu<sup>t</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>): δ 33.8 (s, PPh<sub>2</sub>). <sup>13</sup>C-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  213.8 (m, CO<sub>eq</sub>), 209.5 (t, J = 8.6, CO<sub>ax</sub>), 152.6 (s, C=C), 135.5 (s, C=C), 133.4 (d,  $J_{PC}$  = 15.2, *i*-C of C<sub>5</sub>H<sub>4</sub>), 132.5–128.3 (m, C<sub>6</sub>H<sub>5</sub>), 117.8 (s, *m*-C of C<sub>5</sub>H<sub>4</sub>), 114.6 (t,  $J_{PC}$  = 6.0 Hz, *o*-C of

 $C_5H_4$ ), 31.8 [s,  $C(CH_3)$ ] and 30.7 (CH<sub>3</sub>). 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<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>P(O)Ph<sub>2</sub>}<sub>2</sub>(C=CBu<sup>4</sup>)<sub>2</sub>] 7. To a solution of complex 1 (0.25 g, 0.32 mmol) in thf (30 cm<sup>3</sup>) was added a 30% solution of H<sub>2</sub>O<sub>2</sub> (0.02 cm<sup>3</sup>, 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%).  $v_{max}$ /cm<sup>-1</sup> 2064 (C=C) and 1178 (P=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.65–7.26 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 7.01 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 6.51 (m, 4 H, C<sub>5</sub>H<sub>4</sub>) and 0.95 (s, 18 H, Bu<sup>4</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  23.9 [s, P(O)Ph<sub>2</sub>]. Complex 7 could not be characterised by elemental analyses and mass spectroscopy due to its instability in solution.

**[Ti**{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>P(S)Ph<sub>2</sub>}<sub>2</sub>(C≡CBu<sup>†</sup>)<sub>2</sub>] 8. To a solution of complex 1 (0.25 g, 0.32 mmol) in thf (30 cm<sup>3</sup>) at 0 °C was added S<sub>8</sub> (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<sub>46</sub>H<sub>46</sub>P<sub>2</sub>S<sub>2</sub>Ti requires C, 71.49; H, 6.00%).  $v_{max}$ /cm<sup>-1</sup>: 2067 (C≡C) and 653 (P=S). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.65–7.42 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.95 (m, 4 H, C<sub>5</sub>H<sub>4</sub>), 6.50 (m, 4 H, C<sub>5</sub>H<sub>4</sub>) and 1.00 (s, 18 H, Bu<sup>†</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  34.7 [s, P(S)Ph<sub>2</sub>]. <sup>13</sup>C-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  140.7 (s, C≡C), 135.7 (d, J<sub>PC</sub> = 10.2, *i*-C of C<sub>5</sub>H<sub>4</sub>), 134.4–128.2 (m, C<sub>6</sub>H<sub>5</sub>), 121.6, 119.5 (d, J<sub>PC</sub> = 10.5 Hz, overlapping doublets, *o*-C of C<sub>5</sub>H<sub>4</sub>), 118.8 (s, C≡C), 113.4, 112.7 (s, *m*-C of C<sub>5</sub>H<sub>4</sub>), 31.4 (CH<sub>3</sub>) and 28.9 [s, C(CH<sub>3</sub>)]. FAB-MS: *m*/z 772, *M*<sup>+</sup>; 691, [*M* – C≡CBu<sup>t</sup>]<sup>+</sup>; 659, [*M* – S – C≡CBu<sup>t</sup>]<sup>+</sup>; and 610, [*M* – 2C≡CBu<sup>t</sup>]<sup>+</sup>.

 $[\{\eta^5 - C_5 H_4 P(O) Ph_2\}_2 Ti(\mu - \eta^2 - C \equiv CBu^t)_2 CuCl]$  9. To a thf solution (30 cm<sup>3</sup>) 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<sub>46</sub>H<sub>46</sub>ClCuO<sub>2</sub>P<sub>2</sub>Ti·CH<sub>3</sub>OH requires C, 64.76; H, 5.78%).  $v_{\text{max}}/\text{cm}^{-1}$  1986 (C=C) and 1176 (P=O). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 7.62-7.46 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.63 (q, 4 H, C<sub>5</sub>H<sub>4</sub>), 6.10 (q, 4 H,  $C_5H_4$ ) and 1.25 (s, 18 H, Bu<sup>t</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  20.7 [s, P(O)Ph<sub>2</sub>]. <sup>13</sup>C-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  150.8 (s, C=C), 134.7 (s, C=C), 134.0-128.4 (m, C<sub>6</sub>H<sub>5</sub>), 132.9 (t,  $J_{PC} = 17.0$ Hz, i-C of C5H4), 115.5, 113.8 (s, o-, m-C of C5H4), 31.6 [s, C(CH<sub>3</sub>)] and 30.8 (CH<sub>3</sub>). FAB-MS: m/z 839, M<sup>+</sup>; 803,  $[M - Cl]^+$ ; and 659,  $[M - CuCl - C \equiv CBu^t]^+$ .

[{η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>P(S)Ph<sub>3</sub>}<sub>2</sub>Ti(μ-η<sup>2</sup>-C≡CBu<sup>1</sup>)<sub>2</sub>CuCl] 10. This complex was synthesized following the above procedure by reaction between 8 and (CuCl)<sub>n</sub> (67%) (Found: C, 63.45; H, 5.18. C<sub>46</sub>H<sub>46</sub>ClCuP<sub>2</sub>S<sub>2</sub>Ti requires C, 63.37; H, 5.32%);  $v_{max}$ /cm<sup>-1</sup> 1986 (C≡C) and 654 (P=S). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  7.63–7.45 (m, 20 H, C<sub>6</sub>H<sub>5</sub>), 6.40 (q, 4 H, C<sub>5</sub>H<sub>4</sub>), 6.00 (q, 4 H, C<sub>5</sub>H<sub>4</sub>) and 1.35 (s, 18 H, Bu<sup>1</sup>). <sup>31</sup>P-{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  34.1 [s, P(S)Ph<sub>2</sub>]. <sup>13</sup>C-{<sup>1</sup>H} NMR (50 MHz, CDCl<sub>3</sub>):  $\delta$  149.6 (s, C≡C), 134.7 (s, C≡C), 133.6–128.8 (m, C<sub>6</sub>H<sub>5</sub>), 127.5 (d, *J*<sub>PC</sub> = 9.5, *i*-C of C<sub>5</sub>H<sub>4</sub>), 118.6, 115.6 (d, *J*<sub>PC</sub> = 10.2 Hz, *o*-, *m*-C of C<sub>5</sub>H<sub>4</sub>), 32.0 [s, *C*(CH<sub>3</sub>)] and 30.8 (s, CH<sub>3</sub>). FAB-MS: *m*/z 871, *M*<sup>+</sup>; 835, [M – Cl]<sup>+</sup>; 691, [*M* – CuCl – C≡CBu<sup>1</sup>]<sup>+</sup>; and 610, [*M* – CuCl – 2C≡CBu<sup>1</sup>]<sup>+</sup>.

## 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  $0.08 \times 0.08 \times 0.36$  mm was selected for the data collection. All X-ray measurements were carried out on a Rigaku AFC6S diffractometer at 173 K using Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å). The diffraction peaks were generally weak.

Table 2Crystal data and structure refinement for  $[ClCu(\mu-\eta^5:\kappa P-C_5H_4PPh_2)_2Ti(\mu-\eta^2-C=CBu^1)_2CuCl]$ 

Empirical Formula	C47H50Cl2Cu2OP2T
M	938.76
Crystal system	Orthorhombic
Space group	<i>Pna</i> 2 <sub>1</sub> (no. 33)
aĺÅ	28.989(8)
b/Å	14.109(4)
c/Å	10.606(2)
$U/Å^3$	4337(1)
Ζ	4
$D_{\rm c}/{\rm Mg}~{\rm m}^{-3}$	1.44
R <sub>int</sub>	0.042
F(000)	1936
$\mu$ (Mo-K $\alpha$ )mm <sup>-1</sup>	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<sup>33</sup> and in the later stages on a Silicon Graphics Indigo 2 Extreme computer with the TEXSAN 1.7 package.<sup>34</sup>

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  $\Psi$  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.<sup>35</sup> 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  $0 \le h \le 16$ ,  $0 \le k \le 32$  and  $0 \le l \le 12$ . The final electron density map was essentially featureless with the highest peak of 0.75 e Å<sup>-3</sup>.

CCDC reference number 186/1295.

### Acknowledgements

We thank the Dirección General de Investigación Científica y Técnica (Spain) (Projects PB93-0250 and PB95-0003-CO2-01-02) and the University of La Rioja (Project API-98/B16) for financial support. We thank Dr Esther García (University of Oviedo) for NMR help.

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Paper 8/07905F