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Synthesis of heteronuclear compounds by use of [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SR)$_2$] (R = Et or Ph) as metalloligands. Crystal structures of [{Mo(CO)$_4$}$_2${μ-(Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$}] and [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(μ-SPh)$_2$Pt(C$_6$F$_5$)$_2$]

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The complexes [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(SR)$_2$] (R = Et 1 or Ph 2), [{Mo(CO)$_4$}$_2${μ-(Ph$_2$PC$_5$H$_4$)$_2$Ti(SR)$_2$}] (R = Et 3 or Ph 4) and [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(μ-SPh)$_2$M(C$_6$F$_5$)$_2$] (M = Pt 5 or Pd 6) have been prepared and characterized. Complexes 1 and 2 were obtained by reaction of [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SR)$_2$] and [Mo(CO)$_4$(nbd)] (nbd = norbornadiene) in 1:1 molar ratio by replacement of the nbd by two cyclopentadienyldiphenylphosphines co-ordinated by the P atoms. The ability of the S atoms in the thiolate ligands to act as Lewis bases leads to a further increase in nuclearity. Thus, when the reaction was carried out in a 1:3 molar ratio, heterotrinuclear complexes 3 and 4 were obtained. The crystal structure of 4 showed that the titanium mononuclear compound acts as a symmetric S,P-bridging tetradentate ligand towards two Mo(CO)$_4$ fragments. Compound 2 reacted with cis-[M(C$_6$F$_5$)$_2$(thf)$_2$] (M = Pt or Pd, thf = tetrahydrofuran) to give 5 and 6, respectively. The crystal structure of 5 showed that 2 acts as an S,S-bidentate metalloligand towards the M(C$_6$F$_5$)$_2$ fragment. It is remarkable that both structures reveal a different co-ordination mode of the tetradentate [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SR)$_2$] ligand.

In the last few years the synthesis of heterobimetallic compounds has been of interest in the field of organometallic chemistry.[1,2] The presence of two different metals in such compounds seems to provide an important co-operative reactivity, particularly between early (electron-deficient) and late (electron-rich) metals.[3–5] Many of these bimetallic compounds contain cyclopentadienyl derivatives of Group 4 metals as fragments.[6–8] The oxophilic character of these 'early metals', in combination with the ability of the 'late metals' to act as catalysts, seems to favour reactions where CO is involved. In such systems both metals are joined by phosphide, thiolate, etc., bridging ligands. Stephan and co-workers[9,10] have made an important contribution to this field by using thiolate derivatives of titanocene as metalloligands.

On the other hand, the use of cyclopentadienylphosphines in the synthesis of mononuclear transition-metal complexes has recently increased because of the ability of these compounds to bridge another metal through the phosphorus atom.[11–14] In contrast to the number of papers published on heteronuclear Ti–M derivatives with thiolate bridging ligands, the literature on the analogous complexes with cyclopentadienylphosphine bridging ligands is scarce.[15–18] Schenk and Neuland-Labude[16] have reported the reaction between [(OC)$_3$Mo(η^5-C$_5$H$_4$PPh$_2$)$_2$TiCl$_2$] and NaSMe to give [(OC)$_3$Mo(η^5-C$_5$H$_4$PPh$_2$)$_2$Ti(SMe)$_2$], and Rausch et al.[17] have obtained new Ti–Mn compounds containing a cyclopentadienyldiphenylphosphine bridging ligand.

As part of our current research project on thiolate derivatives of Ti[IV] as precursors to heteropolynuclear compounds, we have recently described[19] the synthesis of a series of mononuclear compounds [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SR)$_2$]. The combination of thiolate and cyclopentadienylphosphine ligands allowed us to observe the competition between the phosphorus and sulfur atoms to co-ordinate other ML$_n$ fragments, in order to obtain

hetero-di- and -tri-nuclear compounds. We report here the synthesis of Mo–Ti and Mo–Ti–Mo derivatives by reaction of [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SR)$_2$] (R = Ph or Et) with [Mo-(CO)$_4$(nbd)] (nbd = norbornadiene = bicyclo[2.2.1]hepta-2,5-diene), as well as the synthesis of heterotrimetallic compounds [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(μ-SPh)$_2$M(C$_6$F$_5$)$_2$] (M = Pt or Pd). The crystal structures of the trinuclear complexes Mo–Ti–Mo (R = Ph) and Mo–Ti–Pt (R = Ph) have been established by X-ray diffraction methods, showing a different co-ordination mode of the central tetradentate (η^5-C$_5$H$_4$PPh$_2$)$_2$Ti(SR)$_2$ ligand.

Experimental

All reactions were carried out under a nitrogen atmosphere using Schlenk techniques.[20] Solvents were dried by standard methods.[21] The starting materials [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$-(SR)$_2$],[19] [Mo(CO)$_4$(nbd)][22] and cis-[M(C$_6$F$_5$)$_2$(thf)$_2$] (M = Pt or Pd, thf = tetrahydrofuran)[23] were prepared as previously described. Microanalyses were determined with Perkin-Elmer 2400 and 240-B microanalysers. Infrared spectra were recorded on Perkin-Elmer 1600-FT and 883 (Nujol mulls) spectrophotometers, NMR spectra on Bruker AMX-300 or ARX-300 and Varian Unity 500 Plus (^{13}C) instruments with chemical shifts reported in ppm relative to external standards (SiMe$_4$ for ^{1}H and ^{13}C, CFCl$_3$ for ^{19}F and H$_3$PO$_4$ for ^{31}P) and mass spectra on a VG Autospec spectrometer.

Syntheses

[(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(SEt)$_2$] 1. To a solution of [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SEt)$_2$] (0.40 g, 0.60 mmol) in toluene (60 cm^3) was added [Mo(CO)$_4$(nbd)] (0.18 g, 0.60 mmol) and the resulting mixture stirred at room temperature for 2 h. Then the solvent

was removed under vacuum to dryness and the purple solid obtained chromatographed on silica gel 100. Elution with hexane–toluene (2:1) afforded a green fraction of compound **3** (traces). Elution with hexane–toluene (1:2) gave a purple band, which afforded [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(SEt)$_2$] (0.24 g, 46%) (Found: C, 58.45; H, 4.45. C$_{42}$H$_{38}$MoO$_4$P$_2$S$_2$Ti·C$_4$H$_8$O requires C, 58.25; H, 4.90%). $\tilde{v}_{max}$/cm^{-1} (toluene solution) 2019m, 1921s and 1903vs (CO).

[(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$] 2. This compound was obtained following the above procedure and 6 h as reaction time (52% yield) (Found: C, 62.2; H, 4.25. C$_{50}$H$_{38}$MoO$_4$P$_2$S$_2$Ti·C$_4$H$_8$O requires C, 62.1; H, 4.45%). $\tilde{v}_{max}$/cm^{-1} (toluene solution) 2023m, 1928s, 1911vs and 1900s (CO).

[{Mo(CO)$_4$}$_2${μ-(Ph$_2$PC$_5$H$_4$)$_2$Ti(SEt)$_2$}] 3. To a hexane (40 cm^3) solution of [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SEt)$_2$] (0.24 g, 0.36 mmol) was added [Mo(CO)$_4$(nbd)] (0.33 g, 1.08 mmol). After 14 h of stirring at 50 °C the green solid was filtered off, washed with hexane and dried *in vacuo*. Further purification by chromatography on a silica column, using hexane–toluene (2:1) as eluent, gave a purple-brown band of compound **1** (traces) and pure toluene gave a green band of **3** (0.16 g, 40%) (Found: C, 49.15; H, 3.40. C$_{46}$H$_{38}$Mo$_2$O$_8$P$_2$S$_2$Ti requires C, 50.95; H, 3.55%). The poor analysis was due to the low stability of the compound. $\tilde{v}_{max}$/cm^{-1} (toluene solution) 2013s, 1917vs, 1901s and 1865s (CO).

[{Mo(CO)$_4$}$_2${μ-(Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$}] 4. This compound was prepared similarly, keeping the mixture stirring at 50 °C for 24 h (48% yield) (Found: C, 54.7; H, 3.15. C$_{54}$H$_{38}$Mo$_2$O$_8$P$_2$S$_2$Ti requires C, 54.95; H, 3.25%). $\tilde{v}_{max}$/cm^{-1} (toluene solution) 2017 (sh), 2010s, 1923s, 1903vs and 1870s (CO).

[(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(μ-SPh)$_2$Pt(C$_6$F$_5$)$_2$] 5. A solid mixture of [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$] (0.11 g, 0.12 mmol) and *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$] (0.08 g, 0.12 mmol) was stirred in toluene (15 cm^3) for 5 min. The resulting turbid brown-red solution was filtered through a plug of Celite contained on a frit and the solution evaporated at *ca.* 2 cm^3. Addition of hexane produced complex **5** as a brown solid. Recrystallization from diethyl ether–hexane (1:3) gave a pure brown-red compound (0.09 g, 51%) (Found: C, 49.15; H, 2.30. C$_{62}$H$_{38}$F$_{10}$MoO$_4$P$_2$PtS$_2$Ti requires C, 49.6; H, 2.55%). $\tilde{v}_{max}$/cm^{-1} (Nujol mull) 2095m, 2025vs and 1899vs (br) (CO); 799s and 789 (sh) (C$_6$F$_5$); (toluene solution) 2026s, 1934m and 1911vs (CO). δ_F(CDCl$_3$, relative to CFCl$_3$) −117.8 [m, F$_o$, J(Pt–F$_o$) = 366], −118.3 [d, F$_o$, J(Pt–F$_o$) = 396 Hz], −161.5 (t, F$_p$), −163.1 (m, F$_m$) and −164.3 (m, F$_m$).

[(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(μ-SPh)$_2$Pd(C$_6$F$_5$)$_2$] 6. This complex was prepared from [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$] (0.11 g, 0.12 mmol) and *cis*-[Pd(C$_6$F$_5$)$_2$(thf)$_2$] (0.06 g, 0.11 mmol) in a similar fashion to that for **5**. Recrystallization from toluene–hexane (1:5) gave a pure brown solid (0.07 g, 47%) (Found: C, 52.3; H, 2.75. C$_{62}$H$_{38}$F$_{10}$MoO$_4$P$_2$PdS$_2$Ti requires C, 52.7; H, 2.70%). $\tilde{v}_{max}$/cm^{-1} (Nujol mull) 2028vs and 1903vs (br) (CO); 783m and 775m (C$_6$F$_5$); (toluene solution) 2027s, 1935m and 1912vs (CO). δ_F(CDCl$_3$, relative to CFCl$_3$) (at 20 °C) −114.7 (m, br, F$_o$), −115.5 (m, br, F$_o$), −160.8 (t, F$_p$), −162.6 (m, br, F$_m$) and −163.7 (m, br, F$_m$); (at −50 °C) −114.4 (m, br, F$_o$), −115.9 (s, br, F$_o$), −160.3 (t, F$_p$), −161.8 (m, F$_m$) and −163.2 (m, F$_m$).

Crystallography

[{Mo(CO)$_4$}$_2${μ-(Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$}]·3thf. Suitable crystals were obtained by slow diffusion of hexane into a thf solution of this complex at room temperature. A crystal was

selected and mounted on a Siemens P4 automated four-circle diffractometer. The main crystallographic parameters are shown in Table 2. Data were collected at 200 K by the ω–2θ scan technique. Three standard reflections, measured at regular intervals, showed no significant variation in intensity. An absorption correction based on ψ scans was applied (transmission factors = 0.889, 0.837). The structure was solved by the heavy-atom method and subjected to anisotropic full-matrix least-squares refinement on F^2. Hydrogen atoms were included at calculated positions (C–H 0.96 Å) and refined using a riding model with a common isotropic displacement parameter (0.058 Å^2). The molecule contains a crystallographic two-fold axis, so only half of it had to be solved. Residual electronic density was modelled as lattice thf. One of the solvent molecules was refined at full occupancy; the other was disordered over two positions, related by symmetry, at half occupancy. Final R factors were $R1 = 0.0499$, $wR2 = 0.1274$ [$I > 2\sigma(I)$] and $R1 = 0.0687$, $wR2 = 0.1465$ (all data). The largest difference peak was 1.125 e Å^{-3}, in the solvent area.

[(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(μ-SPh)$_2$Pt(C$_6$F$_5$)$_2$]·0.5C$_6$H$_5$Me·0.5C$_3$H$_7$Pr^i. Single crystals were grown by slow diffusion of light petroleum (b.p. 30–50 °C) into a toluene solution of the bulk solid at low temperature (−18 °C). Table 2 shows the main crystallographic parameters. A crystal was mounted on top of a glass fibre and transferred to the cold gas stream of the diffractometer (Siemens P4). Data were collected at 200 K by the ω–2θ method. Three standard reflections, measured at regular intervals, showed no significant variation in intensity. An absorption correction based on psi scans was applied (transmission factors = 0.993, 0.651). The stucture was solved by the heavy atom method. All non-hydrogen atoms were refined with anisotropic thermal parameters, by full-matrix least squares, on F^2. Hydrogen atoms were added at fixed positions (C–H 0.96 Å) and refined with isotropic displacement parameters being 1.2 times those of the corresponding C atoms. A molecule of lattice toluene was found and refined aniso-tropically at half occupancy. A molecule of 2-methylpentane is also present, and was refined at half occupancy with isotropic parameters. Final $R1 = 0.0315$, $wR2 = 0.0787$ [$I > 2\sigma(I)$] and $R1 = 0.0437$, $wR2 = 0.0993$ (all data). All residual peaks were below 1 e Å^{-3} (maximum = 0.723 e Å^{-3}).

All calculations were performed on a local area VAX cluster (VAX/VMS V5.5) with the Siemens SHELXTL PLUS and SHELXL 93 software packages.[24,25]

Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallo-graphic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/122.

Results and Discussion

The compounds [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SR)$_2$] may bond to other metal fragments, in different ways, through phosphorus, sulfur or both. As an example of co-ordination through the phosphorus, we have recently described[19] the synthesis of [(C$_6$F$_5$)$_2$Pt(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$] **7** by replacement of the thf ligands in *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$] by two cyclopenta-dienyldiphenylphosphines. On the other hand, Schenk and Neuland-Labude[16] reported that the Mo(CO)$_3$ fragment in [(OC)$_3$Mo(η^5-C$_5$H$_4$PPh$_2$)$_2$Ti(SMe)$_2$] is linked to the titanium atom through two cyclopentadienylphosphine and one methanethiolate ligands giving six-co-ordination around the molybdenum. As far as we know, the latter is the only example of a Mo–Ti heterometallic compound from a thiolate derivative of bis[(diphenylphosphino)cyclopentadienyl]-titanium(IV). Following our current research on the synthesis of heteronuclear compounds using thiolate derivatives of

titanocene as metalloligand we have carried out the preparation of new heterometallic species.

Heterodinuclear Mo–Ti compounds

Two new Mo–Ti compounds have been obtained by reaction of $[Ti(\eta^5-C_5H_4PPh_2)_2(SR)_2]$ (R = Et or Ph) and $[Mo(CO)_4(nbd)]$ in 1:1 stoichiometric ratio using toluene as solvent (Scheme 1). The reaction proceeds much more quickly with EtS^- than with PhS^-. The ethanethiolate derivative shows significant instability in different solvents. Microanalytical data indicate that these complexes are dinuclear species. As we will see in the following discussion on the spectroscopic data (Table 1), they seem to correspond to $[(OC)_4Mo(\mu-Ph_2P-C_5H_4)_2Ti(SR)_2]$ species (R = Et 1 or Ph 2), with the $Mo(CO)_4$ fragment co-ordinated by two phosphorus atoms. Moreover, we will show later that the proposed formulation is preserved in the mixed heterotrimetallic complexes Mo–Ti–M (M = Pt 5 or Pd 6), in which complex 2 is acting as a chelate towards cis-$[M(C_6F_5)_2(thf)_2]$. The IR spectra in solution of the new complexes 1 and 2 show the expected bands for a cis-disubstituted octahedral metal carbonyl, and are similar to those shown by other analogous compounds such as $[(\eta^5-C_5H_5)_2Ti(\mu-SPh)_2Mo(CO)_4]$[8] or $[(OC)_4Mo(\mu-Ph_2PC_5H_4)_2-ZrCl_2]$.[12] Their ^{13}C NMR spectra reveal the presence of both the organic and carbonyl groups. The spectrum of complex 1 shows resonances due to ethyl and phenyl groups, as well as three triplet signals in the cyclopentadienyl region, as a consequence of the P–C coupling. Additionally, in the CO region, two signals at δ 209.7 (t) and 214.1 (m) corresponding to two axial and two equatorial CO groups, respectively, are observed. A similar ^{13}C pattern is found for compound 2.

The ^{31}P NMR spectra in $CDCl_3$ at room temperature of both complexes show a single peak [δ 33.6 (1) and 34.0 (2)] at much lower field than those observed for the starting materials (δ = −14.7 and −12.6, respectively), and similar to those found for analogous species.[12] This result indicates that the metallophosphine $[Ti(\eta^5-C_5H_4PPh_2)_2(SR)_2]$ is acting as a ligand through the two phosphorus atoms, leading to substitution of the nbd from $[Mo(CO)_4(nbd)]$ and giving the heterodinuclear compounds 1 and 2. Also, a ^{31}P NMR spectrum was run at variable temperature (+25 to −70 °C) for 2, showing again a single peak, indicative of the magnetic equivalence of the two phosphorus atoms. The ^1H NMR spectra at room temperature show slight downfield shifts of the cyclopentadienyl ring proton resonances compared to those observed for the starting materials $[Ti(\eta^5-C_5H_4PPh_2)_2(SR)_2]$ (δ at 5.88 and 5.92 for R = Et and 6.01 and 6.20 for R = Ph).[19] The orientation of

the R groups in the thiolate ligands might lead to a mixture of two isomeric forms in solution (syn and anti), however two unique signals for the protons of the ring were observed, not only when the spectrum was recorded at room temperature for 1 and 2, but also at variable temperature (+25 to −70 °C) for 2. This indicates the presence of only one isomer.

Positive-ion FAB mass spectra have been recorded for compounds 1 and 2. The assignment of the fragmentation peaks is easier for organometallic compounds with metals, like molybdenum, that show isotopic distribution. The molecular peaks of 1 and 2 are not observed, however peaks attributable to the loss of SR, R and CO groups are present.

Heterotrinuclear Mo–Ti–M (M = Mo, Pt or Pd) compounds

Since $Mo(CO)_4$ can be bonded to $[Ti(\eta^5-C_5H_4PPh_2)_2(SR)_2]$ through the two phosphorus atoms giving the heterodinuclear compound $[(OC)_4Mo(\mu-Ph_2PC_5H_4)_2Ti(SR)_2]$, a further increase in the nuclearity of the molecule is possible, due to the ability of sulfur atoms in the thiolate ligands to act as Lewis bases, especially by reaction with other ML_n fragments having substitution labile ligands.

Initially, we considered the synthesis of heterotrinuclear species Mo–Ti–Mo, but any attempts to obtain these by reaction of heterodinuclear derivatives $[(OC)_4Mo(\mu-Ph_2P-C_5H_4)_2Ti(SR)_2]$ (R = Et 1 or Ph 2) with $[Mo(CO)_4(nbd)]$ under different reaction conditions (solvent, temperature, etc.) failed. The ^1H NMR spectra of the reaction mixture showed the presence of the starting material as the main component along with a small amount of the heterotrimetallic compound. However, by reaction of the mononuclear compounds $[Ti(\eta^5-C_5H_4PPh_2)_2(SR)_2]$ (R = Et or Ph) and $[Mo(CO)_4(nbd)]$ in 1:3 molar ratio (Scheme 1) the trinuclear compounds 3 and 4 were obtained more readily and in higher yield. The IR spectra in the carbonyl region for 3 and 4 show a similar pattern to those of the dinuclear compounds, in agreement with a cis-disubstituted molybdenum tetracarbonyl derivative.

The ^1H NMR spectrum of compound 3 is consistent with the presence of ethyl and cyclopentadienyl groups. Two different resonances were observed for the methylene protons of the ethyl group, indicating their inequivalence due to the co-ordination of sulfur to the molybdenum atom. In the cyclopentadienyl region two resonances at δ 5.14 and 5.38 (Table 1), shifted to higher field compared with those for the dinuclear species, are present. Other analogous thiolate derivatives, such as $[(\eta^5-C_5H_5)_2Ti(\mu-SPh)_2Mo(CO)_4]$,[8] where the sulfur atoms have also replaced a nbd ligand, exhibit similar behaviour. In contrast, we observed four resonances for compound 4 in this region, indicating the magnetic inequivalence of these protons.


R = Et 1 or Ph 2

R = Et 3 or Ph 4
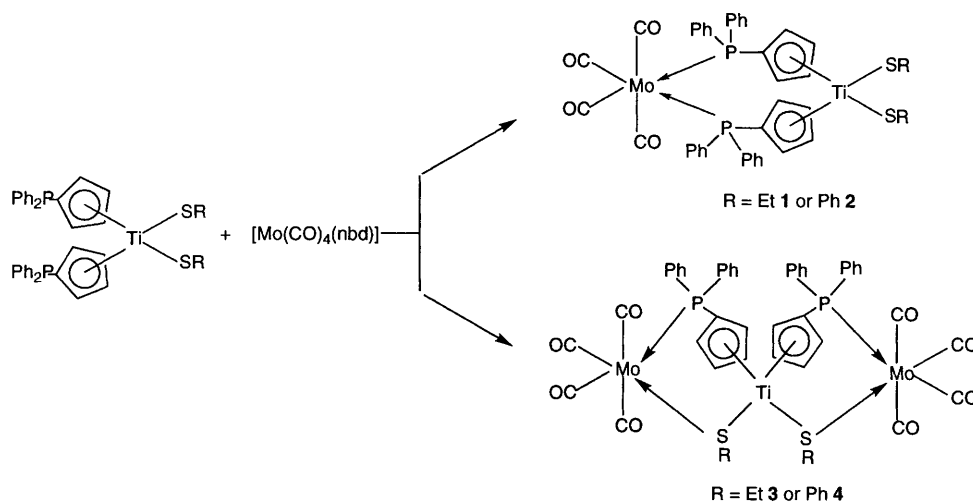
Scheme 1

Table 1 The NMR data for complexes **1–6**

Complex	$\delta_H{}^a$	$\delta_C{}^a$	$\delta_P{}^b$
1	1.11 (6 H, t, CH$_3$), 3.00 (4 H, q, CH$_2$), 6.20 (4 H, m, C$_5$H$_4$), 6.64 (4 H, m, C$_5$H$_4$), 7.35–7.47 (20 H, m, C$_6$H$_5$)	18.1 (s, CH$_3$), 40.4 (s, CH$_2$), 117.0 (t, J_{PC} = 5.2, C$_o$ of C$_5$H$_4$), 117.5 (t, J_{PC} = 3.2, C$_m$ of C$_5$H$_4$), 128.2–137.4 (C$_6$H$_5$), 133.2 (t, J_{PC} = 6.4, C$_{ipso}$ of C$_5$H$_4$), 209.7 (t, J_{PC} = 9.1, axial CO), 214.1 (m, equatorial CO)	33.6 (s)
2	6.23 (4 H, m, C$_5$H$_4$), 6.52 (4 H, m, C$_5$H$_4$), 7.29–7.54 (30 H, m, C$_6$H$_5$)	119.0 (t, J_{PC} = 6.6, C$_o$ of C$_5$H$_4$), 122.0 (t, J_{PC} = 3.2, C$_m$ of C$_5$H$_4$), 128.6–138.6 (C$_6$H$_5$), 133.2 (t, J_{PC} = 6.0, C$_{ipso}$ of C$_5$H$_4$), 210.2 (t, J_{PC} = 8.6, axial CO), 214.9 (m, equatorial CO)	34.0 (s)
3	1.28 (6 H, t, J = 7.3, CH$_3$), 3.34 (m), 3.45 (m) (4 H, J = 7.3, CH$_2$), 5.14 (4 H, m, C$_5$H$_4$), 5.38 (4 H, m, C$_5$H$_4$), 7.40–7.51 (20 H, m, C$_6$H$_5$)	21.5 (s, CH$_3$), 45.2 (d, J_{PC} = 4.4, CH$_2$), 122.0 (d, J_{PC} = 5.6, C$_m$ of C$_5$H$_4$), 122.4 (d, J_{PC} = 13.4, C$_o$ of C$_5$H$_4$), 128.7–137.0 (C$_6$H$_5$), 134.1 (d, J_{PC} = 14.5, C$_{ipso}$ of C$_5$H$_4$), 206.0 (d, J_{PC} = 7.6, axial CO), 211.9 (d, J_{PC} = 9.3, axial CO), 215.4 (d, J_{PC} = 31.8, *trans* CO), 219.7 (d, J_{PC} = 8.9, *cis* CO)	35.8 (s)
4	4.96 (2 H, m, C$_5$H$_4$), 5.29 (2 H, m, C$_5$H$_4$), 6.74 (2 H, m, C$_5$H$_4$), 6.80 (2 H, m, C$_5$H$_4$), 7.35–7.47 (20 H, m, C$_6$H$_5$)	118.2 (d, J_{PC} = 16.9, C$_o$ of C$_5$H$_4$), 127.3 (d, J_{PC} = 6.4, C$_m$ of C$_5$H$_4$), 127.8–144.9 (C$_6$H$_5$), 133.2 (d, J_{PC} = 12.9, C$_{ipso}$ of C$_5$H$_4$), 207.3 (d, J_{PC} = 8.1, axial CO), 211.1 (d, J_{PC} = 10.5, axial CO), 213.7 (d, J_{PC} = 33.4, *trans* CO), 221 (s, *cis* CO)	40.2 (s)
5	4.92 (2 H, s, C$_5$H$_4$), 5.94 (2 H, s, C$_5$H$_4$), 6.38 (2 H, s, C$_5$H$_4$), 6.59 (2 H, s, C$_5$H$_4$), 7.26–7.46 (20 H, m, C$_6$H$_5$)		35.7 (s)
6^c	5.08 (4 H, s, C$_5$H$_4$), 6.45 (4 H, s, C$_5$H$_4$), 7.27–7.45 (30 H, m, C$_6$H$_5$)		35.9 (s)

^{a} Relative to SiMe$_4$, CDCl$_3$ solvent; J in Hz. ^{b} Relative to H$_3$PO$_4$, CDCl$_3$ solvent. ^{c} At −50 °C.
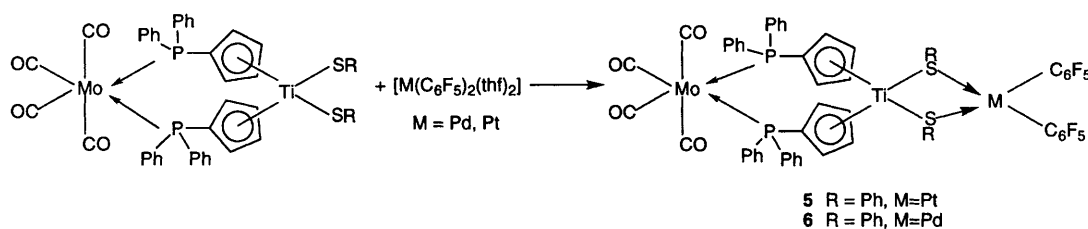
Scheme 2

The ^{1}H NMR spectrum at variable temperature (+25 to −70 °C) was recorded for **4**, displaying again four resonances at δ 4.96, 5.29, 6.74 and 6.80, therefore no geometrical isomers were detected in solution for these trinuclear species. The ^{31}P NMR spectra, recorded at room temperature for compounds **3** and **4** and at variable temperature for **4**, show a single resonance, indicating that the two phosphorus atoms are equivalent on the NMR time-scale. No significant differences are observed on comparing with the dinuclear Ti–Mo compounds. The ^{13}C NMR spectral data for **3** and **4** show the typical resonances of the ethyl and phenyl groups. In addition, four split resonances due to coupling between phosphorus and carbon atoms were observed in the region of the terminal CO groups.

The FAB mass spectra of heterotrinuclear compounds **3** and **4** show the molecular peak, in addition to other peaks which reveal sequential loss of CO groups and also loss of SR and R fragments. There was good agreement between the observed and calculated parent-ion (M^+) peak for **4**.

An X-ray study carried out for compound **4** revealed that each Mo(CO)$_4$ fragment is linked to the titanium atom through one sulfur and one phosphorus atom, in contrast to the initially expected *cis*-P,P and *cis*-S,S disubstituted Mo(CO)$_4$. In order to clarify whether this type of co-ordination occurred only because the two ML$_n$ fragments co-ordinated to the Ti atom were identical, we carried out the synthesis of new trinuclear compounds with three different metals in the molecule. Our initial attempts to use the dinuclear derivative [(C$_6$F$_5$)$_2$Pt(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$][19] as a sulfur chelating ligand towards the Mo(CO)$_4$ fragment were unsuccessful. The reaction with [Mo(CO)$_4$(nbd)] (toluene, 1:1 molar ratio) afforded a complex mixture of products, the ^{31}P NMR spectrum of which revealed

that the Mo–Ti–Mo derivative **4** was the main component. Although it has been previously shown that bis(thiolato)-titanocene complexes may transfer the thiolate ligand to d^8 transition-metal complexes, to give thiolate complexes of the late transition metals,[26] we have recently observed facile formation of heterobimetallics containing titanocene and d^8 (Pd^{II} and Pt^{II}) transition metals bridged by thiolate ligands using *cis*-[M(C$_6$F$_5$)$_2$(thf)$_2$] (M = Pd or Pt) as starting material.[27] Therefore, we turned our interest to the dinuclear derivative **2** as a building block for trimetallic species. As expected, **2** reacts with *cis*-[M(C$_6$F$_5$)$_2$(thf)$_2$] (M = Pt or Pd) in toluene (molar ratio 1:1) under mild conditions [room temperature (r.t.), 5 min of stirring] to give, after work-up, new heterotrimetallic derivatives [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(μ-SPh)$_2$M(C$_6$F$_5$)$_2$] (M = Pt **5** or Pd **6**) in moderate yield (51% for **5**, 47% for **6**) (Scheme 2).

The formulation in Scheme 2 is consistent with the ^{31}P NMR spectra, which showed only a singlet resonance [δ 35.7 (**5**) and 35.9 (**6**)] very close to that observed for the starting material **2** (δ 34.0). The fact that a unique signal is observed for these Mo–Ti–M (M = Pt **5** or Pd **6**) compounds suggests that the link between Ti and M takes place through two sulfur atoms, leaving unmodified the co-ordination around the molybdenum. In addition, the signal due to **5** does not show platinum satellites. This formulation was further confirmed by a crystallographic study on **5**. The ^{1}H NMR spectra at room temperature show four resonances in the cyclopentadienyl region (δ 4.92, 5.94, 6.38 and 6.59) for **5**, while only a very broad signal at δ 4.90–6.70 is observed for **6**. When the spectrum of **6** is recorded at −50 °C the broad signal is resolved into two singlets at δ 5.08 and 6.45. The ^{19}F NMR spectra of both

complexes **5** and **6** (see Experimental section) display the characteristic pattern for this type of compound: five resonances are observed, which suggest that both C_6F_5 groups are equivalent, but the five fluorine atoms on each C_6F_5 group are inequivalent. In addition, the v(CO) IR pattern of compounds **5** and **6** in toluene solution is similar to that recorded for the Mo–Ti and Mo–Ti–Mo complexes. Finally, a positive-ion FAB mass study of **5** and **6** gave the molecular-ion peak only for **5**. Nevertheless, fragments corresponding to the loss of C_6F_5, SPh and CO groups were observed for both derivatives.

Crystal structure of [{Mo(CO)$_4$}$_2${μ-(Ph$_2$PC$_5$H$_4$)$_2$Ti(SPh)$_2$}]·3thf

Selected bond distances and angles are listed in Table 3. The molecular structure is presented in Fig. 1, showing a pseudo-tetrahedral co-ordination geometry for the titanium atom. The asymmetric unit contains 1.5 thf solvent and only one half molecule, with the titanium atom lying on a crystallographic two-fold axis (symmetry-generated atoms are indicated by 'a' appended to atom names). Although no crystal data are known for [Ti(η^5-C$_5$H$_4$PPh$_2$)$_2$(SPh)$_2$], the titanium centroid and Ti–S distances [2.065(6), 2.452(2) Å] and the centroid(1)–titanium–centroid(1a) and S(1)–Ti–S(1a) angles in **4** [131.6(2), 94.43(8)°] are similar to those found for compounds [Ti(η^5-C$_5$H$_4$Si-Me$_3$)$_2$(SC$_6$F$_5$)$_2$],[28] [(η^5-C$_5$H$_5$)$_2$Ti(μ-SMe)$_2$Mo(CO)$_4$],[29] [(η^5-C$_5$H$_5$)$_2$Ti(μ-SC$_6$H$_4$Cl-*p*)$_2$Mo(CO)$_4$][6] and [Ti(η^5-C$_5$H$_5$)$_2$-(SPh)$_2$].[30]

The two cyclopentadienyl rings adopt a staggered disposition. Two identical Mo(CO)$_4$ moieties are linked to the Ti through both a sulfur and a phosphorus atom giving a distorted-octahedral co-ordination environment to the Mo atom. As far as we know this is the first example of a heteronuclear compound with a *cis*-P,S-disubstituted Mo(CO)$_4$ species. Although the Mo(CO)$_4$ fragment in [Mo(CO)$_4$(Ph$_2$PCH$_2$-CH$_2$SMe)][31] shows a *cis*-P,S co-ordination, most of the known mono- or di-nuclear molybdenum complexes have a *cis*-P,P or *cis*-S,S disubstituted Mo(CO)$_4$ species: [Mo-(CO)$_4$(Me$_2$PPMePMePMe$_2$)],[32] [(OC)$_4$Mo(η^5-C$_5$H$_4$PPh$_2$)$_2$-TiCl$_2$],[16] [Mo(CO)$_4$(RSCH$_2$CH$_2$SR)],[33] [Mo$_2$(MeCN)$_2$-(CO)$_6$(μ-SPh)$_2$],[34] [(η^5-C$_5$H$_5$)$_2$Ti(μ-SC$_6$H$_4$Cl-*p*)$_2$Mo(CO)$_4$],[6] *etc.*

The Mo–P distance in [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$ZrCl$_2$][12] and Mo–S distance in [(η^5-C$_5$H$_5$)$_2$Ti(μ-SMe)$_2$Mo(CO)$_4$][29] are in agreement with those [2.514(2) and 2.579(1) Å] observed in our compound. The axial carbonyl ligands form a C(2)–Mo–C(4) angle of 167.4(2)° similar to those in [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$ZrCl$_2$][12] (169.2°) and [Mo(CO)$_4$-(dppm)] (dppm = Ph$_2$PCH$_2$PPh$_2$) (168°).[35] The equatorial plane is formed by atoms P,S,C(1) and C(3). The S–Mo–P angle of 79.57(5)° shows the greatest deviation in the octahedral co-ordination environment. The two phenyl groups of the thiolate ligands in this compound are orientated to different sides of the quasi-planar four-membered ring system (Ti–S–Mo–P), indicating the presence of the transoid or *anti* isomer. Analogous behaviour was observed for the C$_6$H$_4$Cl groups in [(η^5-C$_5$H$_5$)$_2$Ti(μ-SC$_6$H$_4$Cl-*p*)$_2$Mo(CO)$_4$],[6] but, in contrast, the orientation of the Me groups in [(η^5-C$_5$H$_5$)$_2$Ti(μ-SMe)$_2$-Mo(CO)$_4$][29] led to the cisoid isomer. An X-ray study of the last compound shows a Mo–Ti distance of 3.321 Å indicative of a metal–metal interaction, but, in our complex, a distance of 4.562(1) Å between Mo and Ti atoms suggests no such interaction.

Crystal structure of [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$Ti(μ-SPh)$_2$Pt-(C$_6$F$_5$)$_2$]·0.5C$_6$H$_5$Me·0.5C$_3$H$_7$Pr^i

The molecular structure showing the atom numbering scheme is presented in Fig. 2 and selected bond distances and angles are in Table 4. The trinuclear complex displays a Mo–Ti–Pt bent
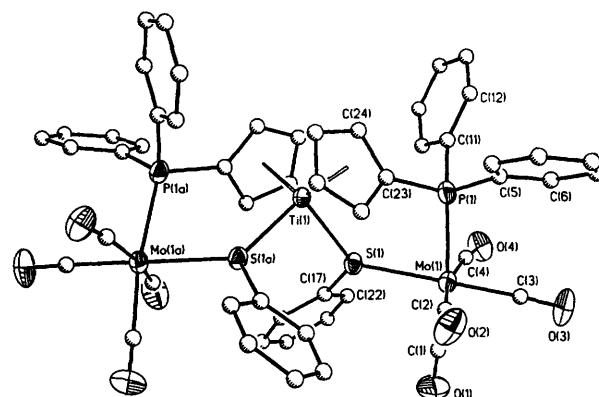

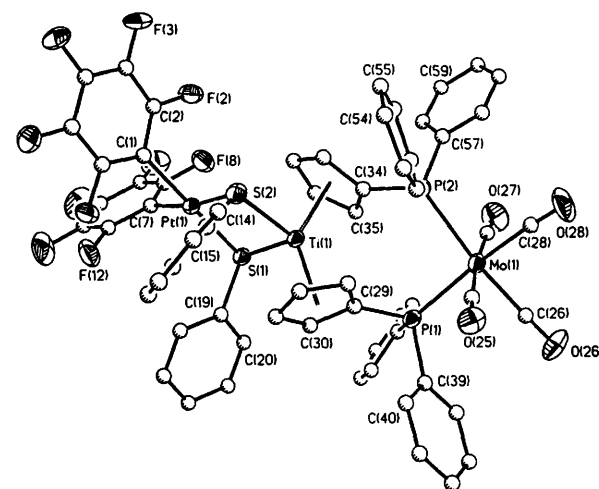**Fig. 1** Structure of complex **4** showing the atom labelling scheme

Fig. 2 Molecular structure and numbering scheme for complex **5**

chain (angle 169.1°) in which the Mo–Ti and Ti–Pt pairs are connected by a double cyclopentadienyldiphenylphosphine and benzenethiolate bridging system. The metal co-ordination environments are clearly different. The central Ti atom lies in a pseudo-tetrahedral environment involving the two π-cyclo-pentadienyl rings from the two cyclopentadienyldiphenyl-phosphine ligands and the two sulfur atoms of the thiolate groups. The sulfur atoms are bonded to the platinum centre, which completes its distorted square-planar co-ordination with the C$_{ipso}$ atoms of the two C$_6$F$_5$ groups mutually *cis*. Finally, the Mo atom is octahedrally co-ordinated, being bound to four CO ligands and to two P atoms from the two C$_5$H$_4$PPh$_2$ groups. This geometry is consistent with the formulation of **5** as a Mo^0–Ti^{IV}–Pt^{II} species. Each of the organometallic units shows the expected structural features. Thus, the Mo–P distances [2.354(1) and 2.511(1) Å] and P(1)–Mo–P(2) angle [95.27(4)°] are comparable to those in [(OC)$_4$Mo(μ-Ph$_2$PC$_5$H$_4$)$_2$ZrCl$_2$][12] and, as expected, the Mo–CO distances *trans* to phosphorus are shorter than those for the CO groups *trans* to each other. The Ti–C, Pt–C and C–P bond lengths are typical. The centroid(1)–titanium–centroid(2) angle in **5** is 137.8(2)°, substantially greater than the corresponding one in **4** [131.6(2)°]. The structural parameters of the TiS$_2$Pt core can be compared with those of the dinuclear complex [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(μ-SPh)$_2$-Pd(C$_6$F$_5$)$_2$].[27] The angles at the metal centres [S(1)–Pd–S(2) 99.7(2) and S(1)–Ti–S(2) 95.7(2)°] are comparable to those of **5** [S(1)–Pt–S(2) 101.74(4) and S(1)–Ti–S(2) 97.14(5)°] as are the angles at the bridging sulfur atoms [80.8(2) and 80.9(1) *versus* 80.77(4) and 79.40(4)° in **5**]. As in [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(μ-SPh)$_2$Pd(C$_6$F$_5$)$_2$], the TiS$_2$Pt core of **5** is puckered, with an angle of 5.13(4)° between the S(1)–Ti–S(2) and the S(1)–Pt–S(2) planes and the double benzenethiolate bridging system adopts an *endo* (*syn*) conformation. The most remarkable difference is

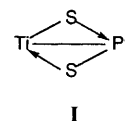**Table 2** Crystallographic data and structure refinement parameters for complexes 4·3thf and 5·0.5C$_6$H$_5$Me·0.5C$_3$H$_7$Pr^i *

	4·3thf	5·0.5C$_6$H$_5$Me·0.5C$_3$H$_7$Pr^i
Empirical formula	C$_{66}$H$_{52}$Mo$_2$O$_{11}$P$_2$S$_2$Ti	C$_{68.5}$H$_{49}$F$_{10}$MoO$_4$P$_2$PtS$_2$Ti
M	1386.92	1593.08
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$	$P\bar{1}$
a/Å	21.729(3)	13.706(3)
b/Å	12.675(2)	14.141(3)
c/Å	23.077(3)	19.670(4)
α/°		86.63(1)
β/°	95.64(1)	82.50(1)
γ/°		65.11(1)
U/Å^3	6325(2)	3428.7(13)
Z	4	2
D_c/Mg m^{-3}	1.456	1.543
μ/mm^{-1}	0.689	2.509
$F(000)$	2816	1576
Crystal size/mm	0.36 × 0.20 × 0.18	0.50 × 0.48 × 0.28
2θ range for data collection/°	4–47	4–52
hkl Ranges	−24 to 24, −14 to 0, −25 to 0	−1 to 15, −14 to 15, −22 to 22
Reflections collected	4820	12 153
Independent reflections (R_{int})	4679 (0.0201)	10 676 (0.0429)
Data, restraints, parameters	4377, 0, 349	10 267, 9, 835
Goodness of fit on F^2	1.051	1.089
Weighting parameters g_1, g_2	0.0775, 25.47	0.0463, 2.32
$R1$, $wR2$ [$I > 2\sigma(I)$]	0.0499, 0.1274	0.0315, 0.0787
(all data)	0.0687, 0.1465	0.0437, 0.0993
Mean, maximum |shift/e.s.d.|	0.000, 0.004	0.000, 0.001
Largest difference peak and hole/e Å^{-3}	1.125, −0.755	0.723, −0.972

* Details in common: dark red prism; graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,73$ Å; $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\ddagger}$; goodness of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{obs} - N_{param})]^{\ddagger}$; $w = [\sigma^2(F_o) + (g_1 P)^2 + g_2 P]^{-1}$; $P = [\max(F_o^2, 0) + 2\,F_c^2]/3$.

Table 3 Selected bond distances (Å) and angles (°) for complex 4·3thf

Mo(1)–C(3)	1.964(6)	Mo(1)–C(1)	2.011(7)
Mo(1)–C(4)	2.036(6)	Mo(1)–C(2)	2.039(6)
Mo(1)–P(1)	2.514(2)	Mo(1)–S(1)	2.579(1)
Ti(1)–cent(1)	2.065(6)	Ti(1)–S(1)	2.452(2)
C(3)–Mo(1)–C(1)	89.6(3)	C(4)–Mo(1)–C(2)	167.4(2)
C(3)–Mo(1)–P(1)	98.7(2)	C(3)–Mo(1)–S(1)	174.5(2)
cent(1)–Ti(1)–cent(1a)	131.6(2)	P(1)–Mo(1)–S(1)	79.57(5)
S(1)–Ti(1)–S(1a)	94.43(8)	Ti(1)–S(1)–Mo(1)	130.12(6)

Symmetry transformation used to generate equivalent atoms: a $-x + \frac{1}{2}$, y, $-z$. cent(1) refers to the centroid of the ring formed by atoms C(23)–C(27).

Table 4 Selected bond distances (Å) and angles (°) for complex 5·0.5C$_6$H$_5$Me·0.5C$_3$H$_7$Pr^i

Pt(1)–Ti(1)	3.014(1)	Pt(1)–C(7)	1.967(5)
Pt(1)–C(1)	2.027(5)	Pt(1)–S(2)	2.256(1)
Pt(1)–S(1)	2.347(1)	Mo(1)–C(28)	1.830(5)
Mo(1)–C(26)	1.967(5)	Mo(1)–C(25)	2.157(6)
Mo(1)–C(27)	2.206(6)	Mo(1)–P(1)	2.354(1)
Mo(1)–P(2)	2.511(1)	Ti(1)–S(1)	2.305(1)
Ti(1)–S(2)	2.456(2)	Ti(1)–cent(1)	2.120(5)
Ti(1)–cent(2)	2.139(4)		
C(7)–Pt(1)–C(1)	87.5(2)	C(7)–Pt(1)–S(2)	70.40(13)
C(7)–Pt(1)–S(1)	86.44(13)	S(2)–Pt(1)–S(1)	101.74(4)
C(28)–Mo(1)–C(26)	85.8(2)	C(25)–Mo(1)–C(27)	175.5(2)
C(28)–Mo(1)–P(1)	170.2(2)	C(26)–Mo(1)–P(1)	90.9(2)
C(28)–Mo(1)–P(2)	88.7(2)	C(26)–Mo(1)–P(2)	172.9(2)
P(1)–Mo(1)–P(2)	95.27(4)	cent(1)–Ti(1)–cent(2)	137.8(2)

cent(1) refers to the centroid of the ring formed by atoms C(29)–C(33), cent(2) to that formed by C(34)–C(38).

I

2.452(5) Å] and Pd–S [2.382(4) and 2.385(4) Å] distances in [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(μ-SPh)$_2$Pd(C$_6$F$_5$)$_2$],[27] it has been previously observed in the bimetallic cations [(η^5-C$_5$H$_5$)$_2$Ti{S(CH$_2$)$_n$PPh$_2$}$_2$M]$^+$ (M = Cu, n = 2,[36] M = Rh, n = 3[37]) and points to at least some degree of bonding character as illustrated in **I**.

Previous spectroscopic, structural and theoretical studies concerning early (d^0)–late (d^8, d^{10}) heterobimetallic complexes are consistent with the presence of a dative bonding interaction between the metal centres.[38] Although a similar metal–metal interaction could be suggested by the geometry of the TiS$_2$Pt core in **5**, the observed Ti · · · Pt distance [3.014(1) Å] is clearly longer than the sum of the covalent radii (2.62 Å) and than those seen in other Pt–Ti complexes for which Pt→Ti interactions have been postulated.[39] Notwithstanding, the Pt–Ti separation is shorter than that observed in [(η^5-C$_5$H$_4$SiMe$_3$)$_2$Ti(μ-SPh)$_2$-Pd(C$_6$F$_5$)$_2$] [3.140(3) Å] and in other related titanium–late metal thiolate-bridged heterobimetallics.[36–38,40]

Conclusion

Owing to the presence of thiolate and cyclopentadienylphosphine groups in [Ti(Ph$_2$PC$_5$H$_4$)$_2$(SR)$_2$], these species are able to act both as a bi- or tetra-dentate ligands. The synthesis of the binuclear Mo–Ti complexes **1** and **2** and the previously reported [(C$_6$F$_5$)$_2$Pt(μ-C$_5$H$_4$PPh$_2$)$_2$Ti(SPh)$_2$][19] **7** suggests a preference for a P,P chelation mode when the titanium mononuclear complex is acting only as a bidentate metalloligand. Treatment of compound **2** with *cis*-[M(C$_6$F$_5$)$_2$(thf)$_2$] (M = Pt or Pd) easily gives trinuclear Mo–Ti–M species (M = Pt **5** or Pd **6**) in which **2** chelates the *cis*-M(C$_6$F$_5$)$_2$ fragment through the sulfur atoms of the thiolate ligands in accord with the expected

that in **5** the μ-S bonds alternate in length about the TiS$_2$Pt core. The shorter Ti–S(1) and Pt–S(2) distances are 2.305(1) and 2.256(1) Å, respectively, while the longer Ti–S(2) and Pt–S(1) are 2.456(2) and 2.347(1) Å, respectively. Although this structural feature contrasts with the symmetrical Ti–S [2.462(5) and

preference of Mo^0 for π-acceptor ligands and M^{II} (M = Pt or Pd) for the soft S-donor ligands. On the other hand, in contrast with the facile formation of bis(thiolate) bridged complexes of the type $[(\eta^5\text{-}C_5H_5)_2Ti(\mu\text{-}SR)_2Mo(CO)_4]$[6,29] prepared from $[Ti(\eta^5\text{-}C_5H_5)_2(SR)_2]$, all attempts to obtain analogous cis-P,P, cis-S,S trinuclear Mo–Ti–Mo or Pt–Ti–Mo complexes starting from the corresponding dinuclear derivatives **1**, **2** or **7** and $[Mo(CO)_4(nbd)]$ have been unsuccessful. Surprisingly, trinuclear Mo–Ti–Mo derivatives (**3**, **4**) are easily obtained by treating the mononuclear titanium species $[Ti(Ph_2P\text{-}C_5H_4)_2(SR)_2]$ with an excess of $[Mo(CO)_4(nbd)]$ (1:3 molar ratio), but the X-ray structural analysis of **4** reveals that, in contrast with the unsymmetrical cis-P,P, cis-S,S chelation mode found in **5**, in this complex the more symmetrical bis (cis-P,S) chelation mode is preferred probably due to the identical steric and electronic requirements of the two ML$_n$ fragments.

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