A quasi-covalent metal–metal bond in an early–late heterobimetallic Ti–Pt complex stabilized by phosphinoenolate ligands† ‡

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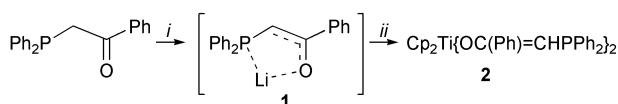
An unusual early–late bimetallic complex with direct metal–metal bonding is obtained from a phosphinoenolate ligand-assisted reaction between Ti(IV) and Pt(0) reagents which occurs by formal insertion of the Pt(0) centre into a Ti(IV)–O bond; X-ray data and EHMO calculations indicate the presence of a quasi-covalent Ti(III)–Pt(I) bond (2.721(2) Å).

Although the synthesis of heterometallic complexes which combine a soft, nucleophilic metal centre with a harder, electrophilic metal is often challenging, such complexes continue to attract much attention owing to their potential for the stoichiometric or catalytic cooperative activation of organic substrates, and as models for strong metal–support interactions of the type occurring in heterogeneous catalysis or for biological systems.[1] When considering electronically very different metals, such as those in Groups 4 and 10, formation of a metal–metal bond is rarely observed owing, in particular, to the too large difference in redox potentials between the metal centres which results in the formation of mononuclear redox products. The assistance of bridging ligands is thus a determining factor in early–late heterobimetallic synthesis and it is no surprise that heterofunctional ligands combining hard and soft donors have been widely used.[1a–c,2,3] Only few complexes have been shown by X-ray diffraction to contain a direct Ti–Pt bond and we report here on the formation of an unusual complex with a direct, quasi-covalent Ti–Pt bond resulting from the reaction between Ti(IV) and Pt(0) reagents.

The phosphinoenolate 1 was prepared from $Ph_2PCH_2C(O)Ph$ and lithium diisopropylamide (THF, −78 °C, 1 mol. equiv. LDA), and reacted *in situ* with $[Cp_2TiCl_2]$ (Cp = η-C_5H_5) (0.5 mol. equiv.) to afford the bis-enolate complex 2 (Scheme 1).[4a] Its $^{31}P\{^1H\}$ NMR (C_6D_6) spectrum contains a singlet at δ −29.3 ppm, indicative of non-coordinated PPh_2 groups. The presence of only one set of NMR signals suggested the formation of a symmetrical isomer, which most likely corresponds to a Z arrangement of the substituents about both C=C bonds. This assumption is based on the stereoselective synthesis of the enolphosphato-phosphines cis-$Ph_2PCH=C(Ph)OP(O)(OR)_2$ (R = Et, Ph), obtained from $Ph_2PCH_2C(O)Ph$ and $ClP(O)(OR)_2$ in the presence of KH,[4b] and on the cyclic structure of the enolate intermediate 1.[5] Attempts to prepare the monochlorotitanium

complex $[Cp_2TiCl\{OC(Ph)=CHPPh_2\}]$ led to unreacted $[Cp_2TiCl_2]$ and 2.

Reaction of the metalloligand 2 with $[Mo(CO)_4(nbd)]$ (nbd = norbornadiene) led to the Ti/Mo complex 3 (Scheme 2).† However, when 2 was reacted with $[MCl_2(cod)]$ (M = Pd, Pt; cod = cyclooctadiene), transmetallation reactions were observed and the known complexes 4 (a M = Pd, b M = Pt) were formed almost quantitatively.[6]

In contrast, the phosphinoacetate complex $[Cp_2Ti\{OC(O)CH_2PPh_2\}_2]$ afforded with $[PdCl_2(NCPh)_2]$ a hetero-dinuclear complex which, however, did not contain a Ti–Pd bond.[3b] With the hope to prevent complete transmetallation, 2 was reacted with the Pt(0) complex $[Pt(C_2H_4)(PPh_3)_2]$, which led to the unexpected formation of a metal–metal bonded Ti–Pt complex, 5, in which one phosphinoenolate acts as a bridging ligand, whereas the other chelates the Pt centre (Fig. 1).†§ Accordingly, there are two $^{31}P\{^1H\}$ NMR resonances at δ −5.1 ($^1J_{PtP}$ = 4805 Hz) and 56.1 ($^1J_{PtP}$ = 1053 Hz), assigned to

Scheme 2 Reagents and conditions: (i) $[Mo(nbd)(CO)_4]$; (ii) $[MCl_2(cod)]$ (M = Pd or Pt); (iii) $[Pt(CH_2=CH_2)(PPh_3)_2]$.

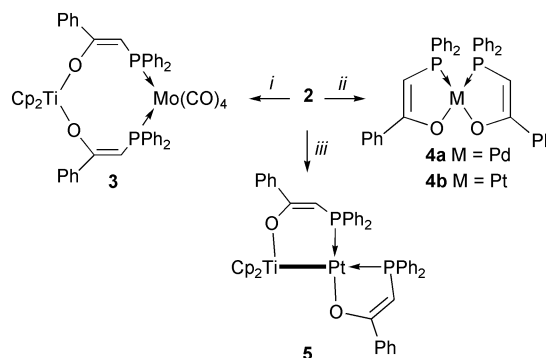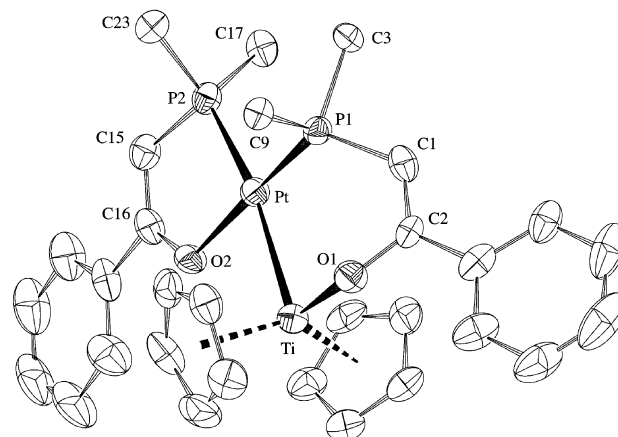**Scheme 1** Reagents and conditions: (i) LDA, THF, −78 °C to RT; (ii) Cp_2TiCl_2, THF, −50 °C to RT.

† Electronic supplementary information (ESI) available: syntheic details, crystallography for 5, and atomic parameters used in the EHMO calculations. See http://www.rsc.org/suppdata/cc/b2/b211289m/
‡ Dedicated to Prof. J. Harrod, for his major contributions to organometallic chemistry and homogeneous catalysis.

Fig. 1

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bridging and chelating phosphinoenolates, respectively. Although it was anticipated that P-coordination *trans* to a Pt–M bond would result in a marked ^{31}P NMR low-field shift and a reduced $^{1}J_{PtP}$ value compared to mononuclear platinum–phosphine complexes,[7] the magnitude of these two phenomena was unusually large. To the best of our knowledge, the $^{1}J_{PtP}$ value of 1053 Hz is one of the lowest reported to date and reflects a considerable influence of the Ti–Pt bond. The Ti–Pt distance of 2.721(2) Å is shorter than that found in the few other structurally characterized Ti–Pt heterobimetallic complexes,[8] and than the sum of the atomic radii (2.836 Å). The Pt centre displays a slightly distorted square-planar environment and the Pt–P(2) distance 2.341(3) Å is considerably longer than Pt–P(1) 2.211(2) Å, as a result of the *trans* influence of the Ti–Pt bond. Bond distances and angles involving the P,O chelate are similar to those in other transition metal complexes.[9] Whereas the atoms Pt, O(2), C(16), C(15) and P(2) form an almost planar five membered ring, the rare[10] bridging phosphinoenolate ligand adopts a pseudo sofa configuration, with a dihedral angle of 37.04° between the planes containing C(1), C(2), O(1) and P(1) and that containing O(1), Ti, Pt and P(1).

EHMO calculations on Cp$_2$TiPt[(PH$_2$)(CH)$_2$O]$_2$ as a model[11] yielded the interaction diagram of Fig. 2 between the frontier orbitals of the bent TiCp$_2$ and of the Pt(phosphinoenolate)$_2$ moieties. The highest metal orbital of the Pt fragment is a counterpart to the Pt–P σ bonding orbital oritented opposite to the Pt–P bond. Its antibonding character is attenuated by means of a strong hybridization with the s and p$_x$ valence orbitals of Pt. This fragment orbital is notably destabilized with respect to a pure d-type orbital of platinum (-10.6 *vs* -12.6 eV) and this makes it isoenergetic with the lowest, in-plane metal orbitals of the bent titanocene fragment, thus giving rise to a strong σ-type interaction between the two metal moieties. Contrary to the highly polar or dative metal–metal interactions found in most early–late bimetallic complexes,[12] **5** could be considered to contain a quasi-covalent Ti–Pt σ bond. It is completed by two stabilizing interactions: (i) a donation from the dangling oxygen of the 'open' phosphinoenolate ligand toward the titanium orbitals with appropriate orientation, and (ii) a π-bonding interaction between the d$_{xy}$ orbitals of both metals. At variance with the σ bond, this π interaction can be interpreted as a Pt to Ti donation, in view of the 2.0 eV difference in the fragment orbital energies. Although this interaction is weak it raises the d$_{xy}$ orbital of Ti by 0.6 eV, thus providing complex **5** with an enlarged HOMO–LUMO gap (1.77 eV).

The formation of this unusual complex **5** may be viewed as resulting from the formal insertion of a naked Pt(0) into a
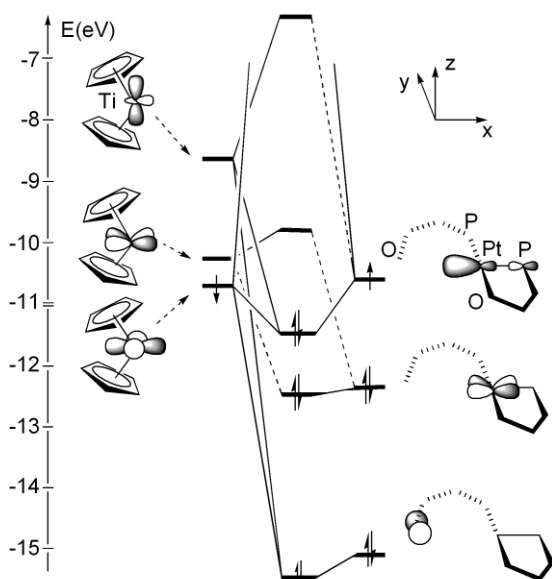
Ti(IV)–O covalent bond, accompanied by a redox reaction which does not lead, as often the case, to mononuclear fragments but to a P,O ligand-supported bimetallic structure. The structural parameters, coordination geometries and EHMO calculations are consistent with an unprecedented Ti(III)–Pt(I) bonding situation, which contrasts with that in non metal–metal bonded Ti(IV)/Pt(II) systems.[8c,13] We also considered an opposite synthetic approach consisting in the reaction of a Ti(II) fragment with a Pt(II) complex. However, no insertion of 'Cp$_2$Ti' (generated *in situ*) into a Pt–O bond of **4a** was observed. This emphasizes the importance of specific reagents and/or the sequence of reactions necessary for the successful assembling of such complexes.

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Fig. 2