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Reactivity of a di-Titanium Bis(pentalene) Complex towards Heteroallenes and Main Group Element–Element Bonds

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KEYWORDS: titanium; metal-metal bonds; pentalene; homobimetallic; heteroallene; chalcogenide; imido

INTRODUCTION

Interest in the chemistry of molecular compounds featuring bonds between transition metal atoms has rapidly increased over the past 50 years. There are a growing number of reports on compounds in which four metal atoms are directly bonded to late transition metals or p-block metals in heteronuclear di- and polynuclear complexes. Despite this, isolable compounds featuring a metal–metal bonding interaction between two group 4 metals are limited to a handful of examples.

We have recently reported the synthesis and isolation of the dititanium bis(pentalene) complex \( \left[ \mu:\eta^5,\eta^5\right]\text{Ti}_2 \) (1). \( \text{PN}^\text{N} = 1,4-\left[\text{SiPr_3}\right]_2\text{C}_8\text{H}_8 \), which density functional theory (DFT) studies revealed to have two metal–metal bonds and a low lying metal-based empty orbital. Complex 1 shows unprecedented reactivity amongst other known di-metal ‘double sandwich’ complexes, including multiple adduct formation with carbon monoxide and reductive activation of carbon dioxide. In the case of CO and CO, mechanistic studies have shown that an adduct is formed with 1 at low temperatures, which reacts further upon warming to RT. Furthermore, we have managed to model this thermally unstable CO adduct by the reaction of 1 with its sulfur congener, \( \text{CS}_2 \).

The reactivity of 1 towards CO and CO, encouraged us to examine its reactivity towards related organic substrates, in isocyanides, carbodiimides and isocyanates, and also toward organic substrates containing main group elements (E). Our aims were to form new adducts of the di-metal double-sandwich motif and explore the scope for multi-electron redox reactions across the Ti=Ti double bond.

RESULTS AND DISCUSSION

Isocyanides

Organic isocyanides (RN=CN) are isolobal with carbon monoxide, and have shown interesting reactivity with low-valent transition metals and M–M bonded complexes to complement that of CO. Treatment of a solution of 1 in toluene-\( \text{d}_8 \) with two equivalents of MeNC resulted in a purple reaction mixture, the \( \text{^1H NMR} \) spectrum of which showed two doublets in the aromatic region, similar to that of monocarbonyl adduct \( \left[\mu:\eta^5,\eta^5\right]\text{Ti}_2\left(\mu:\eta^5\right)\text{PN}^\text{N}\text{CO} \). \( \text{^1H NMR} \) resonance at 3.25 ppm was assigned to the methyl group of coordinated MeNC, in \( \text{ca.} \) equal ratio to the one at 1.18 ppm assignable to the free isocyanide. The \( \text{^13C}\left(\text{^1H} \right) \) spectrum displayed 16 aromatic signals, while a signal at \( \delta \text{C} = 289 \text{ ppm} \) (shifted downfield from \( \delta \text{C} = 158 \text{ ppm} \) for free MeNC) was also observed. Furthermore the \( \text{^29Si}\left(\text{^1H} \right) \) NMR spectrum consisted of 4 signals at \( \delta \text{Si} = 7.92, 7.26, 7.23 \text{ and } 6.25 \text{ ppm} \). These spectroscopic observations are consistent with a 1:1 adduct formation (2) where the \( \text{C}_8 \) molecular symmetry of 1 has been broken (Scheme 1).

Scheme 1. Synthesis of methylisocyanide adduct 2. \( R = \text{SiPr_3} \).
This is in contrast to the reactivity of 1 with CO, where ligation of more than one CO is observed under an overpressure of the gas, and is attributed to steric congestion.\textsuperscript{15} The solution structure of 2 was confirmed in the solid state by a single crystal X-ray diffraction (XRD) study, revealing a $\mu$-CNMe ligand asymmetrically bridging the Ti$_2$ core (Figure 1).

The IR spectrum of 2 shows a ν(CN) stretch at 1642 cm$^{-1}$, an unusually low value for bridging isocyanide ligands in bimetallic complexes, which typically range from 1700 to 1870 cm$^{-1}$.\textsuperscript{20} However, bridging isocyanide adducts of M–M bonded tungsten alkoxide dimers reported by Chisholm et al. also show very low ν(CN) values (ca. 1530 cm$^{-1}$),\textsuperscript{21} which has been attributed to increased back bonding from the metal d-orbitals to the vacant high-energy π*-orbitals of the isocyanide ligand. The calculated ν(CN) wavenumber for II is 1638 cm$^{-1}$, in good agreement with the experimental value. Inspection of the frontier MOs (Figure S5) indicates there is significant back donation from the HOMO of the Ti$_2$Pn$_2$ fragment which steers the MeNC ligand to a side-on position, as was found for the monocarbonyl adduct.\textsuperscript{14}

The formation of a 1:1 methylisocyanide adduct 2, which persists in the presence of excess MeNC, is in marked contrast to the higher adducts formed by reaction of 1 with 2 or 3 equivalents of CO. This encouraged us to investigate the chemistry of 1 with nitrogen containing heteroallenes, with the aim of forming adducts which are more thermally stable than that found with CO$_2$.

**Reactivity with Heteroallenes**

*Carbodiimides*

Heteroallenes, of general formula X=Y=Z where at least one of the functional atoms X, Y or Z is a heteroatom (in most cases N, O or S) are commonly used to model the reactivity of CO$_2$.\textsuperscript{22} However, reactivity of heteroallenes is strongly influenced by the electronic effects of the attached substituents.\textsuperscript{23}
and carbodiimides (X = Z = NR, Y = C) have shown particularly varied chemistry with low valent titanium complexes.\textsuperscript{24,25}

Addition of one equivalent of 1,3-N,N'-di-p-tolylcarbodiimide (p-TCD) to a solution of 1 in pentane resulted in a color change to brown-green. Subsequent work-up and recrystallization from SiMe\textsubscript{4} afforded bronze crystals in excellent yield (92\%), which were identified by analytical and spectroscopic methods as compound 3 (Scheme 2).

Scheme 2. Synthesis of carbodiimide adduct 3. \( R = \text{SiPr}_3 \).

In more detail the mass spectrum showed a complex mass envelope in the region 1144–1149 amu and an isotopic pattern consistent with the formulation of a 1:1 adduct depicted in Scheme 2. Furthermore, the \(^1\)H NMR spectrum of 3 displays four sharp doublets in the aromatic region assigned to the Ph ring protons (Figure S1), consistent with a \( C_2 \)-symmetric structure in solution. The \(^1\)C\{\( ^1\)H\} spectrum displayed 12 signals in the aromatic region assignable to the ligand scaffold (4 for the pentalene and 4 for the p-tolyl) while a signal at 182.3 ppm was assigned to the carbodiimide central carbon atom (Figure S2). NMR spectral assignments were verified by recourse to 2D \(^1\)H–\(^{13}\)C correlation experiments (Figures S3 and S4).

Single crystal X-ray diffraction studies unambiguously confirmed the molecular structure of 3 in the solid state, which agrees with solution NMR spectroscopic data. The molecular structure (Figure 2) shows a bent p-TCD ligand in a \( \mu:\eta^1:\eta^1 \)-binding mode between two Ti centers forming a dimetallocyclelopropane-like motif with a Ti–C–Ti angle of 68.2(2)\(^\circ\). In a similar fashion to the related mono(oxo) complex, \((\mu:\eta^1:\eta^1-\text{PN})_2\text{Ti}(\mu-\text{O})_2{\text{Ti(\mu-\text{O})}_2}}\), 3 possesses a \( S_2 \) axis passing through the carbodiimide carbon (C53) and the midpoint of the Ti–Ti bond, which results in one half of the dimer being generated by symmetry.

Figure 2. ORTEP (30\% probability) diagram of 3. H atoms and \(^{13}\)Pr groups omitted for clarity. Primed atoms are generated by symmetry (−x, y, −z+3/2). Selected distances (\( \AA \)), angles (\( \circ \)) and parameters: Ti1–Ti1' 2.4374(8), Ti1–C53 2.1762(2), Ti1–N1 2.1159(15), C53–N1 1.3004(15), Ti–Ct\( ^\alpha \) 2.1218, \( \delta^\alpha \) 0.0342, \( \text{PN} \) C–C\( ^\text{ring} \) 1.459(3), p-Tol C–C\( ^\text{ring} \) 1.390(3), Ti1–C53–Ti1' 68.13(7), C53–Ti1–Ti1' 55.94(4), Ti1–C53–N1 69.87(9), N1–C53–N1' 152.2(2), Ct1–Ti1–Ct2 137.83(4), TA 22.5(3). Ct denotes the \( \eta^1 \)-centroid of the Ph ring. \(^a\)Average values.

The distance of each Ti atom from the central carbon atom of the carbodiimide is 2.176(2) \( \AA \), in the range of a Ti–C single bond (\( \Sigma_{\text{cov}} = 2.11 \AA \)),\textsuperscript{26} and comparable to that found in Rosenthal's carbene-like dinuclear Ti(III) complex, [Cp\(_2\)Ti(\( \mu-\text{S}_2\)] (2.199(4) \( \AA \)).\textsuperscript{27} Indeed, the Ti–C distance in 3 is comparable with the shorter Ti–C carbene distances of titanium complexes with NHC ligands reported to date, which range from 2.160(3)\textsuperscript{28} to 2.212 \( \AA \),\textsuperscript{29} however, it is significantly longer than those for Schrock-type titanium carbene complexes (ca. 1.830 \( \AA \)).\textsuperscript{30} The Ti–N distance in 3 (2.1159(15) \( \AA \)), while in a range of a Ti–N single bond (\( \Sigma_{\text{cov}} = 2.07 \AA \)),\textsuperscript{30} is notably longer than those of titanocene(III) amides such as Cp\(_3\)Ti(NHRH) (1.9555(5) \( \AA \) R = Me,\textsuperscript{31} 1.944(2) \( \AA \) R = H,\textsuperscript{32} as these complexes have an additional \( \pi \)-bonding interaction from the N lone pair. However, this value is shorter than in Cp\(_3\)Ti(NMe\(_2\)) (2.157(5) \( \AA \)),\textsuperscript{33} where the Ti–amide bond lacks its \( \pi \)-constituent due to steric congestion. The metrics of the TiN unit in 3 are best compared with those found in monomeric titanocene(III) \( \eta^1 \)-aminoacyl complexes, for example Cp\(_3\)Ti(\( \eta^1 \)-[Ph]CN[Xyl])\textsuperscript{34} and [Cp\(_3\)Ti(\( \eta^1 \)-[Me]CN[Bu])\textsubscript{3}]\{[BPh\(_4\)] (Ti–C = 2.096(4) and 2.080(6) \( \AA \); Ti–N = 2.149(7) and 2.125(5) \( \AA \) respectively). Complex 3 features a more acute Ti–C–N angle (69.87(9)\( \circ \)) than in these \( \eta^1 \)-aminoacyl complexes presumably due to further conjugation at the carbodiimide central carbon atom to the second half of the dimer. The carbodiimide moiety in 3 is bent with a N–C–N angle of 152.2(2)\( \circ \) and the C–N bond lengths of 1.3004(15) \( \AA \) are consistent with the partial loss of the cumulene structure of the free substrate upon complexation. For comparison, in the free carbodiimide, the N=C=N angle is 170.4(4)\( \circ \) and the C–N bond lengths are 1.223(5) and 1.204(4) \( \AA \).\textsuperscript{35} This is further reflected in the IR spectrum which shows a \( \nu(NCN) \) asymmetric stretching vibration at 1659 cm\(^{-1}\), a value significantly lower than that of p-TCD (\( \nu(NCN) = 2139 \text{ cm}^{-1} \)).\textsuperscript{36} The molecular structure of 3 is reminiscent of carbodiimide adducts of M–M bonded di-tungsten complexes W\(_2\)(O\(_2\)Bu\(_6\))\(_2\) and W\(_2\)(OCMe\(_2\)CF\(_3\))\(_2\), which have been structurally characterized.\textsuperscript{37,38}

Compound 3 is thermally robust, with no change observed by \(^1\)H NMR spectroscopy after heating at 100 °C in methycyclohexane-\( d_{14} \) for 4 days. This may be attributed to the kinetic stability imparted on the carbenic carbon atom, which is a potential reactive site, but is somewhat buried in the ‘cleft’ provided by the Ti\(_2\) double-sandwich structure and the p-tolyl substituents of the carbodiimide.

Isocyanates

Organic isocyanates, RN=C=O, have also been studied as reagents for modeling the reactivity of CO\(_2\), since the introduction of an amido (RN) group results in polarization of the double bonds and thus increased reactivity.\textsuperscript{39} Slow addition of PhNCO to a pentane solution of 1 at −35 °C resulted in a green-brown solution upon warming to room temperature, which after concentration and cooling to −35 °C, deposited green single crystals suitable for X-ray diffraction analysis.
The molecular structure (Figure 3) revealed not the anticipated PhNCO adduct but complex 4 in which the double-sandwich structure has been cleaved and an unusual phenyl-carbonimidate ligand bridges two formally Ti(III) centers. Complex 4 was further characterized by mass spectrometry, elemental analysis and IR spectroscopy. The $^{1}H$ NMR spectrum of 4 in THF-$d_{8}$ displays only broad signals, and the effective magnetic moment determined by the Evans method was 1.3 $\mu$B per Ti, which is less than the spin-only value for a Ti$^{4+}$ ion (1.73 $\mu$B).

**Figure 3.** ORTEP (30% probability) diagram of 4. H atoms and $^{3}$Pr groups omitted. Selected distances ($\AA$) and angles (°): Ti1−Ti2 4.3011(11), Ti1−O1 2.145(2), Ti2−O1 2.146(2), Ti1−N1 2.124(3), Ti2−O2 2.081(3), C53−O1 1.350(4), C53−O2 1.275(4), C53−N1 1.314(4), Ti−Ct 1.9354(18); Ti1−O1−Ti2 176.44(12), O1−Ti1−N1 62.90(9), O1−Ti2−O2 63.10(9), O1−C53−N1 113.4(3), O1−C53−O2 114.8(3), O2−C53−N1 131.7(3), Ct−Ti−Ct a 57.32(9). Fold angle 35.1(3). Ct denotes the η$^{2}$-centroid of the Pn ring. a Average values.

The bond distances about the central carbon atom of the bridging ligand are between the range for a C(sp$^{3}$)−E single and double bond (C−O: 1.293−1.407; C=E: 1.187−1.255; C=N: 1.279−1.329; C=O: 1.321−1.416 Å). The ‘NCO$^{2-}$ core is planar and the sum of its angles is 360°. These data imply the delocalization of negative charge over the bidentate phenyl-carbonimidate ligand. Other examples of this ligand in the Cambridge Structural Database (CSD) are limited to a single report by Zhou and co-workers$^{42}$ which details a series of lanthanide(III) complexes, [CP$_{2}$Ln(THF)$_{2}$](μ-κ$^{2}$:κ$^{2}$-O$_{2}$CNPh) (Ln = Y, Er, Yb), showing similar metrics about the [PhNCO$^{2-}$]$^{2-}$ bridge. These complexes were prepared from the lanthanocene(III) hydroxides [CP$_{2}$Ln(μ-OH)(THF)$_{2}$] and PhNCO followed by reaction with the corresponding CpLn. In contrast a redox reaction has clearly taken place between the reactants.

The yield was 40% with respect to 1 and PhNCO, however, based on the formula of 4 with two oxygens atoms in the bimetallic product, the reaction stoichiometry requires two equivalents of PhNCO per dimer. Reaction of 1 in methylcyclohexane-$d_{14}$ with 1 equiv of PhNCO showed a mixture of products by $^{1}H$ NMR spectroscopy, including resonances assignable to mono(μ-oxo) complex (μ-$\eta^{3}$:$\eta^{2}$-PhN)$_{2}$Ti$_{2}$ (μ-O) and free PhNC. The analogous reaction using 2 equiv of PhNCO produced a complex $^{1}H$ NMR spectrum, indicating a mixture of diamagnetic and paramagnetic components that could not be assigned.

The mechanism for this unexpected transformation is as yet unclear, but it can be postulated to proceed via O-atom transfer from PhNCO to give (μ-$\eta^{3}$:$\eta^{2}$-PhN)$_{2}$Ti$_{2}$ (μ-O) (Scheme 3), which is known to be thermally unstable with respect to the more open triplet structure [(μ-PhN)$_{4}$Ti]$_{2}$ (μ-O). The third step involves nucleophilic attack of the μ-O ligand at the carbon atom of a second PhNCO molecule, a position which is generally nucleophilic.$^{43}$ It is noteworthy that the reaction 1 with PhNCO is kinetically stabilized at a carbonimide-bridged Ti(III)−Ti(III) complex, in contrast to the heteroallenes CO and COS which give oxo- and sulfido-bridged Ti(IV)−Ti(IV) products respectively.$^{44}$

**Scheme 3.** Synthetic route to 4 (R = SiPr$_{3}$), via postulated intermediates.

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**Reactivity with Main Group Element–Element Bonds**

**Diphenyl dichalcogenides**

Organic dichalcogenides, RE−ER (E = S, Se, Te; R = alkyl or aryl), are commonly employed as redox active substrates with low valent metal complexes including those of early transition metals.$^{44,45}$ With highly reducing metal complexes E−E bond cleavage of the dichalcogenide routinely occurs to yield a complex bearing the respective chalcogenoate (RE$^{2-}$) ligands.

When deep red solutions of 1 in toluene were treated with one equivalent of Ph$_{2}$E (E = S, Se and Te) an immediate color change from deep red to red-brown was observed. Subsequent work-up and recrystallization from pentane furnished the respective di-phenylchalcogenoate complexes (μ-$\eta^{3}$:$\eta^{2}$-PhN)$_{2}$[Ti(EPh)$_{2}$]$_{2}$, for E = S (5), Se (6) and Te (7) as analytically pure brown solids (Scheme 4).

**Scheme 4.** Synthesis of di-phenylchalcogenoate complexes 5−7. R = SiPr$_{3}$.
EI-MS showed a parent ion or a common fragment ([M − Ph]+ or [M − Pr]+) for each complex. Solid state IR for 6 and 7 showed essentially identical spectra with a sharp band at ca. 1570 cm⁻¹ assigned to the aromatic C=C stretch of the phenyl group. In contrast 5 shows a broad IR band at 1620 cm⁻¹. ¹H NMR spectroscopy showed very similar spectra for 5, 6 and 7, consisting of seven sharp signals in the aromatic region; three of which were assigned to the o, m, and p-H of the two equivalent Ph groups with integration and multiplicity as expected; four doublet signals of equal intensity were assigned to the Ph ring protons in a double-sandwich structure with C₂ symmetry on the NMR timescale. Multinuclear (¹³C, ²⁹Si) NMR spectra were consistent with this interpretation. The ⁷⁷Se(¹H) and ¹²⁵Te(¹H) NMR of 6 and 7 respectively showed one singlet signal at δse 511 and δte 418 respectively. These chemical shifts are relatively lower in frequency in comparison with those of known titanium selenolate and tellurolate complexes, for which ⁷⁷Se(¹H) and ¹²⁵Te(¹H) NMR spectroscopic data are shown in Table 2. This may be correlated with the formally Ti(III)–Ti(III) oxidation state in 6 and 7, which renders the chalcogenoate ligand more shielded with respect to monomeric d⁰ Ti(IV) complexes. However, the (RE)²⁻ ligands in these literature examples have very different electronic properties, so firm comparisons cannot be made. Known Ti(III) selenolate and tellurolate such as Cp₂Ti⁶[TeSi(SiMe₃)]PMes⁴₄ precluded NMR characterization due to their paramagnetic nature. The (Pr³)₂Ti₂ double-sandwich motif can incorporate both terminal and bridging ligands, and titanium thiolates complexes with terminal and bridging bonding modes are well known.⁴⁷ Spectroscopic and analytical data alone were not sufficient to distinguish between a terminal or bridging mode for the chalcogenolate ligands, so a single crystal XRD study was carried out.

Table 2. Solution ⁷⁷Se(¹H) and ¹²⁵Te(¹H) NMR data for 6, 7 and related Ti selenolate and telluroate complexes.

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<tr>
<th>Compound</th>
<th>δ</th>
<th>solvent</th>
<th>ref</th>
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<tr>
<td>6</td>
<td>511</td>
<td>cyclohexane</td>
<td>this work</td>
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<tr>
<td>Cp₂Ti(SePh)₂</td>
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<td>⁴⁹</td>
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<tr>
<td>Tl[SeSi(SiMe₃)]₄</td>
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<td>C₆D₆</td>
<td>⁵⁰</td>
</tr>
<tr>
<td>Tl[SeSi(SiMe₃)]₄</td>
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<td>828</td>
<td>C₆D₆</td>
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<tr>
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<td>CH₂(Ort)₂</td>
<td>416</td>
<td>C₆D₆</td>
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<td>C₆D₆</td>
<td>⁵²</td>
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Figure 4. ORTEP plots of (left to right) 5, 6 and 7. H atoms and Pr groups omitted for clarity. 30% ellipsoids.

Table 3. Selected distances (Å), angles (°) and parameters for 1, ⁵ 5, 6 and 7.

<table>
<thead>
<tr>
<th>Parameter</th>
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<th>⁵</th>
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<td>Ti–Ct</td>
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<td>Δ</td>
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<td>0.130(3)</td>
<td>0.120(6)</td>
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<tr>
<td>Pn C–C₁</td>
<td>1.449(5)</td>
<td>1.431(2)</td>
<td>1.437(9)</td>
<td>1.438(2)</td>
</tr>
</tbody>
</table>

The (Ph³)₂Ti₂ double-sandwich motif can incorporate both terminal and bridging ligands, and titanium thiolates complexes with terminal and bridging bonding modes are well known.⁴⁷ Spectroscopic and analytical data alone were not sufficient to distinguish between a terminal or bridging mode for the chalcogenolate ligands, so a single crystal XRD study was carried out.
Ph C−C_{ring} \; ^a & - & 1.381(4) & 1.384(14) & 1.384(4) \\
Ti−Ti−E \; ^a & - & 118.58(4) & 119.30(6) & 120.69(3) \\
Ti−E−C_{ipso} \; ^a & - & 118.27(15) & 115.0(2) & 112.65(13) \\
E−Ti−Ti−E & - & 120.5(2) & 127.6(3) & 140.73(18) \\
E−Ti−Ti−E & - & 15.26(7) & 13.19(8) & 7.01(5) \\
Ci−Ti−Ci \; ^a & 155.22(19) & 133.92(7) & 134.35(6) & 135.14(7) \\
TA & 20.1(8) & 21.6(3) & 19.1(5) & 17.4(3) \\

\( ^a \)Average values. Ci denotes the \( \eta^3 \)-centroid of a Ph ring.

Et₂O solutions of the respective thiolate and selenolate complexes 5 and 6, and a SiMe₃ solution of tellurolate complex 7, each produced single crystals which were of sufficient quality for structural determination by XRD. The general structural feature common to 5, 6 and 7 is the double-sandwich motif with terminal di-chalcogenolate ligands pointing out of one face, and the Ph groups pointing in opposite directions to minimize steric repulsions with the SiPr₃ substituents on this face. The molecular structures of 5, 6 and 7 are depicted in Figure 4 and selected structural parameters are compared in Table 3.

The most noteworthy structural feature is the longer Ti−Ti distance for 7 (2.653(9) Å) with respect to the starting compound 1 (2.399(2) Å), consistent with the loss of two electrons from the M−M bonding HOMO of 1 upon oxidative addition of Ph₅Te₂. Indeed, the intermetallic distance is significantly longer than in the mono(chalcogenide) complexes Ti₅(μ:η⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻⁻˓startrow
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\( ^a \)Average values

The tellurolate complex \( \text{Pn}_2\text{Ti}_2(\text{TePh})_2 \) was selected for fragment analysis as the Te orbitals were most separated from the π-orbitals of the Ph ring. The molecule was split into \( \text{Pn}_2\text{Ti}_2 \) and TePh fragments in the computed geometry of the molecule (see ref. 6 and Table S3 for the fragment orbitals of \( \text{Pn}_2\text{Ti}_2 \) and TePh respectively). Considering the \( \text{Pn}_2\text{Ti}_2 \) fragment, the HOMO (Figure 5) shows the Ti−Ti σ-bond remains intact and the other frontier MOs are all partially populated (see Supporting Information Table S2), presumably to maximize bonding to the EPh groups. The chalcogenolate ligands each use two π-orbitals to bind to titanium; the HOMO−3 (Figure 5) shows a Ti−Te σ-bond formed largely by the π-orbital perpendicular to the Ph ring (MO 23 in Figure S6), and the HOMO−4 and −5 show a π-type interaction between Ti and the π-orbital parallel to the Ph ring (MO 22 in Figure S6). The HOMO−1 (Figure 5) shows Te π-orbitals pointing towards each other and out of phase, which could explain the relatively large Te−Ti−Te torsion angle found for 7.

![Figure 5. Isosurfaces for the key Ti−Te bonding MOs of \( \text{Pn}_2\text{Ti}_2(\text{TePh})_2 \).](image)

Terminal chalcogenolate ligands act as one electron donors (X-function in the CBC method)\(^6\) meaning 5, 6 and 7 are formally 17 valence electron (VE) per Ti, with diamagnetic behavior which may be explained by a M−M single bond. This prompted us to investigate the potential for a 4e⁻ oxidation of...
Azobenzene and phenylazide

The redox chemistry of azobenzene, PhN=NPh, with low-valent metal complexes has been widely studied. Floriani et al. reported the synthesis of a cis-azidobenzene adduct of titanocene, Cp₂Ti(η²-N=Ph₂), by the reaction of Cp₂Ti(CO)₅ with Ph₃N₂. Subsequent ab initio MO calculations suggest this diamagnetic complex is best described as a 1,2-diphenylhydrazido(2−) ligand and a formally Ti(IV) center. Recent work by Beckhaus et al. has utilized this preference for cis-azo ligation to titanocene fragments to synthesize supra-molecular squares. There are also several examples of azobenzene reduction and cleavage leading to terminal phenylimido complexes in Ti chemistry, which constitutes a four-electron process per azobenzene.

Addition of one equivalent of azobenzene to a toluene solution of 1 resulted in a color change to dark red. Removal of the solvent and recrystallization from hexane furnished red crystals of [(η⁵-P₃N)Ti₂(μ-N-P₃H)₂ (8), isolated in 70% yield (Scheme 5). Elemental analysis and EI-MS data support the proposed formulation. Solution phase NMR spectroscopy data are consistent with a C₈ symmetric structure; the ¹H spectrum contains two signals assigned to the P₃N ring protons and three further signals in the aromatic region assigned to the two equivalent Ph groups.

X-ray diffraction analysis of single crystals of 8 revealed two phenylimido ligands bridging two formally Ti(IV) centers, forming a Ti₂N₂ heterocyclic ring (Figure 6). The coordination geometry of both titanium atoms is distorted tetrahedral, and the intermetallic distance (2.8935(5) Å) is not unusually short for a di-Ti(IV) complex, and similar distances have been observed in related species. The bridging region of the complex is asymmetric, such that the Ti–N bond lengths are different, ranging from 1.9830(17) Å to 1.9536(17) Å. Asymmetrically bridging imido ligands have previously been observed for several different transition-metal complexes, and Nugent et al. have ascribed this effect to an increase in π-donation to the metal center. However, these researchers suggested that a substantial distortion of the M–N bond lengths in four-coordinate group 4 [M₄(μ-PR₃)₂] containing complexes is not expected on electronic grounds. Hence, it is postulated that the difference in the Ti–N bond lengths in 8 is stericly induced by the asymmetric disposition of the P₃N ligands with respect to the [Ti₂(μ-N-P₃H)₂] unit. The reaction can be considered a 4e⁻ reduction per azobenzene molecule driven by the oxidative cleavage of the Ti=Ti double bond.

Organic azides (RN₃) are common reagents for the transfer of an imido (RN=) group to a metal complex, upon loss of N₂, and presented an alternative synthetic route to 8. Addition of 1 equivalent of azidobenzene (PhN₃) to a solution of 1 in C₆D₆ resulted in a rapid color change to red and the effervescence of dinitrogen. ¹H NMR spectroscopy showed two sets of characteristic P₃N ring signals corresponding to 8 and unreacted 1 in approximately equal ratio. Addition of a further 1 equivalent of PhN₃ showed complete conversion to 8 (Scheme 5).

**Scheme 5. Summary of synthetic routes to 8. R = SiPr₃.**

Metal-driven reductive transformations of organic azides to imido complexes are well known for titanium, and other early transition metals. However with Ti mononuclear terminal-imido complexes are typically formed. The reaction of 1 with PhN₃ can be considered a 2e⁻ redox process per organoazide. The imido [PhN]²⁻ fragment produced is isolobal with O²⁻, and hence this reaction parallels that of 1 with excess N₂O, which yields [η⁴-P₃N]₂[Ti]₂(μ-O)²⁻.

CONCLUSIONS

This study has expanded the chemistry of the di-titanium bis(pentalene) complex 1 towards isocyanides and het-
eroolenes, which provides useful insights into that with CO and CO₂.

Reaction of 1 with methylisocyanide yields a 1:1 adduct 2, in which is analogous to the monocarbonyl complex (μ₄-η²-Pn)₂Ti₂(μ-η²-CO), but in contrast to the CO chemistry previously reported, excess MeNC does not lead to the formation of higher adducts. The thermally stable carbodiimide adduct 3 shows symmetrical binding to the Ti₂ unit that can be seen as another model for the bonding situation in (μ₄-η²-Pn)₂Ti₂(μ-η²-CO). The reaction of 1 with PhNCO to give unusual phenyl-carbimidate bridged 4 shows that heteroallene reactions can be kinetically stabilized at the Ti(III)−Ti(III) stage, however further studies are required to fully rationalize this transformation. This would also help to clarify the proposed disproportionation step in the reductive activation of CO₂ by 1.

The reactivity with dichalcogenides and azobenzene shows 1 can act as a 2e⁻ and 4e⁻ reductant respectively. These reactions were clean and especially quantitative, giving diamagnetic products, which were straightforwardly identified by ¹H NMR spectroscopy. Hence, these studies provide a blueprint for more predictable redox transformations of the [Ti=Ti]₄⁺ core in 1, which are consistent with the irreversible oxidation potential measured at −1.06 vs FeCp²⁺.

The reactivity of 1 invites comparisons with that of the titanocene(II) fragment explored by Floriani and others, and also that of the electron rich di-tungsten hexaalkoxide complexes of Cotton, Chisholm and co-workers. However, the chemistry of titanium–titanium multiple bonds remains relatively unexplored and work is ongoing in our laboratory to provide further examples of their reactivity.

EXPERIMENTAL SECTION

General procedures

All manipulations were carried out using standard Schlenk techniques under Ar, or in an MBraun glovebox under N₂ or Ar. All glassware was dried at 160 °C overnight prior to use. Solvents were purified by pre-drying over sodium wire and then distilled over Na (toluene), K (THF, hexane) or Na-nitrate under vacuum. Dried solvents were collected, degassed three times and stored over argon in vacuo. MeNC was stored in ampoules containing acetic acid and were collected, degassed three times and stored over argon in vacuo.

Reagents 1,3-di-p-toly1carbodiimide (13 mg, 0.057 mmol) was added slowly to a solution of 1 (53 mg, 0.057 mmol) in pentane (2 mL) at room temperature, resulting in a color change from deep red to brown-green. The solvent was removed by slow evaporation at ambient pressure and the brown residue was redissolved in SiMe₅ (1 mL). Cooling this solution to −35 °C produced bronze crystals that were isolated by decantation and dried in vacuo. Total yield: 60 mg (92% with respect to 1). ¹H NMR (methylene-chloride-d₄, 400.20 MHz, 298 K): δ 7.23 (2H, H, 3JHH = 2.8 Hz, Pr H), 7.02 (4H, t, 3JHH = 8.0 Hz, Tol m-H), 6.66 (4H, t, 3JHH = 8.0 Hz, Tol o-H), 6.57 (2H, 3JHH = 3.3 Hz, Pr H), 6.39 (2H, 3JHH = 2.7 Hz, Pr H), 6.18 (2H, 3JHH = 3.4 Hz, Pr H), 2.36 (2H, s, Tol CH₂), 1.61 (6H, m, Tol CH₃), 1.23 (18H, d, 3JHH = 7.3 Hz, Pr CH₃), 1.14 (6H, m, Tol CH₃), 1.11 (18H, d, 3JHH = 7.4 Hz, Pr CH₃), 0.98 (18H, d, 3JHH = 7.3 Hz, Tol CH₂), 0.86 (18H, d, 3JHH = 7.3 Hz, Tol CH₃). ¹C NMR (methylene-chloride-d₄, 100.65 MHz, 298 K): δ 182.3 (C(N(Tol)₂)), 147.0 (Tol p-C), 134.0 (Pr bridgehead C), 132.6 (Tol i-C), 132.5 (Pr CH), 129.5 (Tol o-C), 129.1 (Pr bridgehead C), 126.6 (Tol m-C), 125.4 (Pr CH), 118.7 (Pr CH), 109.4 (Pr CH), 99.00 (Pr C-Si), 93.93 (Pr C-Si), 22.07 (Tol CH₃), 21.05 (Pr CH₃), 21.03 (Pr CH₂), 20.82 (Pr CH₃), 20.67
products were extracted with pentane (4 mL) and filtered. The solvent was removed under reduced pressure and the products were isolated by decantation and dried in vacuo. Total yield: 106 mg (86% with respect to 1). Subsequent recrystallization from EtO at −35 °C afforded X-ray quality crystals. 1H NMR (cyclohexane-d$_{12}$, 399.5 MHz, 303 K): $\delta$ 8.08 (2H, d, $^{1}J_{HH} = 3.2$ Hz, Ph $H_{7}$), 7.40 (4H, d, $^{1}J_{HH} = 7.0$ Hz, Ph o-$H_{7}$), 7.27 (2H, d, $^{1}J_{HH} = 3.5$ Hz, Ph $H_{7}$), 7.11 (4H, t, $^{1}J_{HH} = 7.3$ Hz, Ph $m-H_{7}$), 7.04 (2H, $^{1}J_{HH} = 7.3$ Hz, Ph p-$H_{7}$), 5.37 (2H, d, $^{1}J_{HH} = 3.1$ Hz, Ph $H_{7}$), 5.04 (2H, d, $^{1}J_{HH} = 3.2$ Hz, Ph $H_{7}$), 1.69–1.58 (12H, overlapping m, Pr $CH_{2}$), 1.26 (18H, $^{3}J_{HH} = 7.4$ Hz, Pr $CH_{3}$), 1.05 (18H, d, $^{3}J_{HH} = 7.4$ Hz, Pr $CH_{3}$), 0.97 (18H, d, $^{3}J_{HH} = 7.5$ Hz, Pr $CH_{3}$), 0.92 (18H, d, $^{3}J_{HH} = 7.5$ Hz, Pr $CH_{3}$). 13C[C] NMR (cyclohexane-d$_{12}$, 100.5 MHz, 303 K): $\delta$ 511. $^{25}$Si[C] NMR (cyclohexane-d$_{12}$, 100.5 MHz, 303 K): $\delta$ 4.88, 2.77. El-MS: $m/z = 1237$ (60%), [M]$.^\ddagger$ Anal. found (cald. for C$_{41}$H$_{60}$Si$_{3}$Te$_{2}$Si): C, 61.97 (61.22); H, 8.35 (8.31) %. IR (NaCl): 1575 (sh, v aromatic C=C) cm$^{-1}$.

(89 mg, 0.0956 mmol) in toluene (2 mL) was added a solution of PhSeTePh (39.1 mg, 0.0956 mmol) in toluene (2 mL), dropwise at room temperature. A color change from deep red to dark brown was observed and the mixture was allowed to stir for 30 min. The solvent was removed under reduced pressure and the products were extracted with pentane (4 mL) and filtered. The red-brown filtrate was concentrated to ca. 1 mL and after cooling to −35 °C, deposited dark brown crystals that were isolated by decantation and dried in vacuo. Total yield: 90 mg (71% with respect to 1). ^1H NMR (cyclohexane-d$_{12}$, 499.9 MHz, 303 K): $\delta$ 7.95 (2H, d, $^{1}J_{HH} = 3.0$ Hz, Ph $H_{7}$), 7.90 (2H, d, $^{1}J_{HH} = 3.1$ Hz, Ph $H_{7}$), 7.74 (4H, d, $^{1}J_{HH} = 6.2$ Hz, Ph o-$H_{7}$), 7.20–7.16 (6H, overlapping m, Ph m- and p-$H_{7}$), 5.44 (2H, d, $^{3}J_{HH} = 2.9$ Hz, Ph $H_{7}$), 5.31 (2H, d, $^{3}J_{HH} = 3.1$ Hz, Ph $H_{7}$), 1.69 (6H, m, Pr $CH_{3}$), 1.54 (6H, m, Pr $CH_{3}$), 1.23 (18H, d, $^{3}J_{HH} = 7.3$ Hz, Pr $CH_{3}$), 1.04–0.96 (32H, overlapping m, Pr $CH_{3}$), 0.90 (18H, d, $^{3}J_{HH} = 7.5$ Hz, Pr $CH_{3}$). 13C[C] NMR (cyclohexane-d$_{12}$, 125.7 MHz, 303 K): $\delta$ 141.5 (Ph o-$C$), 139.5 (Ph $C$), 133.9 (Ph $C$), 129.2 (Ph $C$), 129.0 (Ph $C$), 127.1 (Ph $C$), 126.7 (Ph $C$), 122.2 (Ph $C$), 112.4 (Ph $C$), 111.0 (Ph $C$), 92.80 (Ph $C$), 20.79 (Pr $CH_{2}$), 20.77 (Pr $CH_{2}$), 20.62 (Pr $CH_{2}$), 20.13 (Pr $CH_{2}$), 15.01–14.90 (overlapping m, Pr $CH_{2}$). $^{29}$Si[C] NMR (cyclohexane-d$_{12}$, 303 K): $\delta$ 5.20, 2.74. $^{125}$Te[C] NMR (cyclohexane-d$_{12}$, 126.04 MHz, 303 K): $\delta$ 418. El-MS: $m/z = 1303–1312$ (principal peak 1307, 50%), [M – CMe$_{4}$]$^{+}$; 1174–1183 (principal peak 1179, 80%), [M – Pr]$^{+}$. Anal. found (cald. for C$_{29}$H$_{90}$Si$_{3}$Te$_{2}$Si): C, 57.60 (57.59); H, 7.69 (7.70) %. IR (NaCl): 2193, 2092, 1572 (sh, v aromatic C=C) cm$^{-1}$.

$\{\eta^3$-Ph$_{3}$Te$\}$_{2}$[Ti(SePh)$_{2}$] (6). METHOD A: To a solution of 1 (87 mg, 0.094 mmol) in toluene (2 mL) was added a solution of azobenzene (17 mg, 0.094 mmol) in toluene (2 mL), dropwise at room temperature. A color change to dark red was observed and the mixture was allowed to stir for 30 min. The solvent was removed under reduced pressure and the products were extracted with hexane (2 mL) and filtered. The red filtrate was concentrated to ca. 1 mL and after cooling to −35 °C, deposited red crystals that were isolated by decantation and dried in vacuo. Total yield: 73 mg (70% with respect to 1). METHOD B: To a solution of 1 (15 mg, 0.016 mmol) in pen-
tane (3 mL) at −35 °C was added azidobenzene (32 μL, 0.016 mmol, 0.5 M solution in Me-THF), dropwise. Effervescence and a color change to red was observed, and the reaction mixture was allowed to warm to room temperature and stir for 10 mins. The solvent was removed in vacuo and 1H NMR spectroscopy showed ca. 50% conversion of 1 to 8. Addition of further azidobenzene (32 μL, 0.016 mmol, 0.5 M solution in Me-THF) to the reaction mixture furnished 8 in essentially quantitative yield. 1H NMR (CD3CN, 399.5 MHz, 303 K): δ 6.98 (4H, t, JHH = 7.8 Hz, Ph -H), 6.71 (4H, d, JHH = 3.2 Hz, Ph -H), 6.62 (2H, t, JHH = 7.3 Hz, Ph -H), 6.42 (4H, d, JHH = 7.3 Hz, Ph -H), 5.22 (4H, d, JHH = 3.2 Hz, Ph -H), 1.15 (36H, d, JHH = 7.5 Hz, Pr -H), 1.13 (36H, d, JHH = 7.6 Hz, Pr -H), 0.93 (12H, m, Pr -CH2), 1.3C(1H) NMR (CD3CN, 100.5 MHz, 303 K): δ 167.3 (Ph -C), 149.0 (Ph bridgehead C), 134.0 (Ph -CH), 127.3 (Ph -m-C), 120.6 (Ph -p-C), 119.8 (Ph -o-C), 114.4 (Ph -CH), 111.4 (Pr -C-Si), 20.01 (Pr -CH), 19.87 (Pr -CH3), 12.78 (Pr -CH). 29Si(1H) NMR (CD3CN, 100.5 MHz, 303 K): [M] 1T; 1030–1054 (principal peak 1032, 30%), [M - Ph]T. Anal. found (calcld. for C32H30N2Si3T2): C, 67.13 (67.12); H, 9.14 (8.99) %. IR (NaCl): 1581 (ν aromatic C=C) cm⁻¹.

X-ray crystallography

Single crystal XRD data for 2, 4, 5 and 6 were collected by the UK National Crystallography Service (NCS), 79 at the University of Southampton on a Rigaku FR-E+ Ultra High Flux diffractometer (λMo(Kα)) equipped with VariMax VHF optics and a Saturn 72+ CCD area detector. The data were collected at 100 or 150 K using an Oxford Cryosystems Cobra low temperature device. An empirical absorption correction was carried out using the MULTI-SCAN program. 80 Single crystal XRD data for 3 were collected by the NCS at the Diamond Light Source using synchrotron radiation (λMo(Kα)). An empirical absorption correction was carried out using the DTABSCOR program. Data collected by the NCS were processed using CrystalClear-SM Expert 3.1 b18. 82 and unit cell parameters were refined against all data. Single crystal XRD data for 5 and 7 were collected at the University of Sussex on a Enraf-Nonius CAD4 diffractometer with graphite-monochromated (λMo(Kα)) radiation or an Agilent Technologies Xcalibur Gemini ultra diffractometer (λMo(Kα) or λCu(Kα) source) equipped with a Eos CCD area detector. The data were collected at 173 K using an Oxford Cryosystems Cobra low temperature device. Data were processed using KappaCCD software or CrystAlisPro (version 1.171.36.32), 83 and unit cell parameters were refined against all data. An empirical absorption correction was carried out using the MULTI-SCAN program. 80,81 All structures were solved using SHELXL-2013. 84 DIFREROF-2008 85 or SUPERFLIP 86 and refined on F² by full-matrix least-squares refinements using SHELXL-2013. 84 Solutions and refinements were performed using the OLEX2 87 or WinGX 88 packages and software packages within. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using a riding model. Disordered solvent molecules in 5 and 7 could not be modelled properly; therefore, this disorder was treated by using the SQUEEZE routine in PLATON. 89 The solid state structures of 2 and 4 display positional disorder in the MeNC and SiPr groups respectively, and suffer relatively high wR2 values. This does not effect the key metrical parameters around the metal centers.

Computational details

Density functional calculations were carried using the Amsterdam Density Functional package (version ADF2012.01 and ADF2014.01). 90 The Slater-type orbital (STO) basis sets were of triple-ζ quality augmented with a one polarization function (ADF basis TZP). Core electrons were frozen (C 1s; Ti 2p) in the model of the electronic configuration for each atom. The local density approximation (LDA) by Vosko, Wilk and Nusair (VWN) 93 was used together with the exchange correlation corrections of Becke and Perdew (BP86). 94

SUPPORTING INFORMATION

Tables of crystallographic data, additional NMR spectroscopic and computational data, a text file of computed molecule Cartesian coordinates for all structures in .xyz format for convenient visualization; crystallographic data for 2–7 in CIF format. The Supporting Information is available free of charge on the ACS publications website at DOI:

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Author Contributions

The manuscript was written through contributions of all authors.

Notes

The authors declare no competing financial interest.

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