Bonding in Complexes of Bis(pentalene)dititanium, Ti$_2$(C$_8$H$_6$)$_2$

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Supporting Information

ABSTRACT: Bonding in the bis(pentalene)dititanium “double-sandwich” species Ti$_3$Pn$_2$ (Pn = C$_8$H$_6$) and its interaction with other fragments have been investigated by density functional calculations and fragment analysis. Ti$_3$Pn$_2$ with C$_{2h}$ symmetry has two metal–metal bonds and a low-lying metal-based empty orbital, all three frontier orbitals having a$_1$ symmetry. The latter may be regarded as being derived by symmetric combinations of the classic three frontier orbitals of two bent bis(cyclopentadienyl) metal fragments. Electrochemical studies on Ti$_3$Pn$_2$ (Pn$^-$ = 1,4-[SiPr$_3$]$_2$C$_8$H$_4$) revealed a one-electron oxidation, and the formally mixed-valence Ti(II)–Ti(III) cationic complex [Ti$_3$Pn$_2$][B(C$_6$F$_5$)$_4$]$_2$ has been structurally characterized. Theory indicates an $S = 1/2$ ground-state electronic configuration for the latter, which was confirmed by EPR spectroscopy and SQUID magnetometry. Carbon dioxide binds symmetrically to Ti$_3$Pn$_2$, preserving the C$_{2h}$ symmetry, as does carbon disulfide. The dominant interaction in Ti$_3$Pn$_2$CO$_2$ is $\sigma$ donation into the LUMO of bent CO$_2$, and donation from the O atoms to Ti$_3$Pn$_2$ is minimal, whereas in Ti$_3$Pn$_2$CS$_2$ there is significant interaction with the S atoms. The bridging O atom in the mono(oxo) species Ti$_3$Pn$_2$O, however, employs all three O 2p orbitals in binding and competes strongly with Pn, leading to weaker binding of the carbocyclic ligand, and the sulfur analogue Ti$_3$Pn$_2$S behaves similarly. Ti$_3$Pn$_2$ is also capable of binding one, two, or three molecules of carbon monoxide. The bonding demands of a single CO molecule are incompatible with symmetric binding, and an asymmetric structure is found. The dicarbonyl adduct Ti$_3$Pn$_2$(CO)$_2$ has C$_1$ symmetry with the Ti$_3$Pn$_2$ unit acting as two MCP$_2$ fragments. Synthetic studies showed that in the presence of excess CO the tricarbonyl complex Ti$_3$Pn$_2$(CO)$_3$ is formed, which optimizes to an asymmetric structure with one semibridging and two terminal CO ligands. Low-temperature $^{13}$C NMR spectroscopy revealed a rapid dynamic exchange between the two bound CO sites and free CO.

INTRODUCTION

Pentalene (Pn, C$_8$H$_6$) and its derivatives show a variety of coordination modes to transition metals.$^5$ When acting as a ligand, pentalene is formally classified as a dianion, [C$_8$H$_6$]$^{2-}$, or as an L$_1$X$_1$ ligand in the Covalent Bond Classification (CBC) method.$^6$–$^8$ To a certain extent, its coordination chemistry resembles that of cyclooctatetraene, which is also a member of the L$_1$X$_1$ class, but when coordinated to a single metal in an $\eta^5$ fashion it is nonplanar, folding around the two bridgehead carbons.$^5$–$^7$ Much progress has been made in synthesizing compounds so-called “double-sandwich” complexes, where two metals are sandwiched between two pentalene ligands. Early work by Katz employed unsubstituted pentalene forming M$_2$Pn$_2$ complexes with Co and Ni,$^9,^{10}$ but substituted pentalenals that offer solubility and steric protection have extended the number of these double sandwiches across the whole transition series.$^{11–14}$ Computational studies using density functional theory (DFT) have established the metal–metal bond order in these bimetallic compounds.$^{11–14}$ If the bridgehead carbons are treated as donating their two $\pi$ electrons to both metals in a $\mu$-L fashion, use of the 18 electron rule enables the metal–metal bond order to be predicted correctly$^{15}$ (Figure 1) and establishes that all except the Ti derivative are electronically saturated.

We have recently extended the series of known bis(pentalene) double-sandwich compounds to titanium using the silylated pentalene ligand 1,4-[SiPr$_3$]$_2$C$_8$H$_4$ (Pn$^-$), and Ti$_2$Pn$^-$$_2$ shows unique reactivity among pentalene double-
sandwich complexes, leading to a number of novel derivatives.16,17 The mechanism of the reaction of its CO$_2$ complex is described in the companion paper;17 here we examine the bonding in a range of derivatives in more detail.

### RESULTS AND DISCUSSION

All of the calculations employed a model system with the pentalene substituents replaced by H atoms. Key structural parameters are given in Table 1. Optimized coordinates are given in the Supporting Information (SI). Numbers obtained by two different computational methods are given in normal text for ADF (BP/TZP) and in italics for Gaussian (B3LYP/TZP).

$\textbf{Ti}_2(\mu_5\eta^5\eta^5\text{Pn})_2$. $\textbf{Ti}_2(\mu_5\eta^5\eta^5\text{Pn})_2$ has a bent structure.14 Optimizations of the structure of $\textbf{Ti}_2(\mu_5\eta^5\eta^5\text{Pn})_2$ (abbreviated $\textbf{Ti}_2\text{Pn}_2$) were carried out with $D_{2h}$ symmetry (1) and no symmetry constraints (2).

Table 1. Selected Calculated Structural Parameters ($\text{Å}, \text{deg}$) for Optimized Structures$^a$

| compound | Ti–Ti | Ti–Ct | Ct–Ti–Ct | Ti–C | Ti–O/S | C–O/S | O–Ti–O |
|----------|-------|-------|----------|------|--------|-------|--------|
| $\textbf{Ti}_2\text{Pn}_2$ (1) | 2.33, 2.34 | 2.01, 2.01 | 180, 180 | | | | |
| $\textbf{Ti}_2\text{Pn}_2$ (2) | 2.37, 2.31 | 2.00, 2.03 | 153, 158 | | | | |
| $\textbf{Ti}_2\text{Pn}_2^*$ (2$^*$) | 2.47, 2.43 | 2.03, 2.04 | 145, 147 | | | | |
| $\textbf{Ti}_2\text{Pn}_2\text{CO}_2$ (3) | 2.41, 2.40 | 2.07, 2.10 | 141, 141 | 2.18, 2.14 | 2.27, 2.25 | 1.26, 1.29 | |
| $\textbf{Ti}_2\text{Pn}_2\text{CS}_2$ (4) | 2.43, 2.41 | 2.10, 2.11 | 138, 138 | 2.27, 2.24 | 2.54, 2.58 | 1.67, 1.72 | |
| $\textbf{Ti}_2\text{Pn}_2\text{COS}$ (5) | 2.41, 2.40 | 2.08, 2.09 | 140, 141 | 2.19, 2.17 | 2.19, 2.16 | 1.26, 1.29 | |
| $\textbf{Ti}_2\text{Pn}_2\text{CS}_2$ (6) | 2.38, 2.36 | 2.06, 2.08 | 143, 143 | 2.04, 2.02 | 2.35, 2.26 | 1.21, 1.25 | |
| $\textbf{Ti}_2\text{Pn}_2\text{CO}_2$ (7) | 2.42, 2.42 | 2.05, 2.05 | 144, 144 | 2.08, 2.08 | 1.17, 1.17 | | |
| $\textbf{Ti}_2\text{Pn}_2\text{CO}_2$ (8) | 2.63, 2.64 | 2.04, 2.07 | 143, 142 | 2.02, 1.99 | 1.17, 1.19 | | |
| $\textbf{Ti}_2\text{Pn}_2\text{O}$ (9) | 2.38, 2.36 | 2.13, 2.14 | 139, 140 | 1.87, 1.85 | | | 79, 79 |
| $\text{PnTiOTiPn}$ ($S = 1$) (10) | 3.40, 3.69 | 1.96, 1.99 | 57, 57 | 1.86, 1.85 | | | 133, 180 |
| $\text{PnTiOTiPn}$ ($S = 0$) (11) | 2.88, 2.80 | 1.96, 1.99 | 57, 57 | 1.85, 1.83 | | | 103, 100 |
| $\textbf{Ti}_2\text{Pn}_2\text{O(CO)}$ (12) | 2.46, 2.43 | 2.18, 2.17 | 135, 137 | 2.08, 2.07 | 1.76, 1.74 | 1.16, 1.17 | |
| $\textbf{Ti}_2\text{Pn}_2\text{S}$ (13) | 2.44, 2.42 | 2.11, 2.13 | 138, 138 | 2.10, 2.07 | | | |
| $\textbf{Ti}_2\text{Pn}_2\text{S(CO)}$ (14) | 2.48 | 2.12 | 135 | 2.08 | 2.30 | | 61 |
| $\text{PnTiOTiPn}$ (15) | 2.74, 2.75 | 2.00, 2.02 | 56, 56 | 1.87, 1.85 | | | 95, 96 |

$^a\text{Ct}$ denotes the $\eta^5$ centroid of the Pn ring.
becomes the 12b2 orbital in C2v symmetry, and its energy decreases. This situation is reminiscent of the effect of bending in parallel metallocenes.25

Electrochemical Studies. Cyclic voltammetry (CV) of Ti2Pn2† 2 was carried out to assess the stability of the mixed-valence form of the bimetallic complex and to choose an appropriate chemical redox agent for its preparation on a synthetic scale. CV of Ti2Pn2† 2 in THF/0.1 M [nBu4N][PF6] revealed two major redox processes within the electrochemical window, as shown in Figure 5; the data are summarized in Table 2. Process I, centered at $E_1/2 = −2.48$ V vs FeCp2+/0, is assigned to a reduction to the monoanion [Ti2Pn2†]−. Repetitive potential

Figure 2. Frontier MOs of Ti2Pn2 with D2h symmetry (1) and C2v symmetry (2).

Figure 3. Derivation of the frontier orbitals of Ti2Pn2 from those of two metallocenes.

Figure 4. MOs of 1 and 2 derived from π5 and π4 of pentalene.

Figure 5. Overlaid CV scans (three cycles) for Ti2Pn2† 2 in THF/0.1 M [nBu4N][PF6] at a scan rate of 100 mV s−1.
cycling over process I in isolation using variable scan rates from 100 to 1000 mV s\(^{-1}\) (see the SI), showed electrochemical behavior best described as quasi-reversible.\(^{26}\) The peak-to-peak separation (\(\Delta E_{pp}\)) is similar to that for ferrocene under the same conditions (ca. 200 mV), suggesting the transfer of one electron. For comparison, the permethylpentane double-sandwich complexes \(\text{M}_2\text{Pn}^\ast\) (\(\text{M} = \text{V}, \text{Cr}, \text{Mn}, \text{Co}, \text{Ni}; \text{Pn}^\ast = \text{C}_9\text{Me}_9\)) studied by O’Hare and co-workers show a single-electron reduction process with electrode potentials ranging from −2.75 to −1.85 V vs FeCp\(^2\)/FeCp\(^0\). Process II is assigned to a one-electron oxidation with a peak potential (\(E_{pp}\)) of −1.06 V vs FeCp\(^2\)/FeCp\(^0\) in the forward scan, and an associated cathodic wave was observed at \(E_{pc} = −1.95\) V vs FeCp\(^2\)/FeCp\(^0\) in the reverse scan. Irreversible behavior suggests that the product of this oxidation, \([\text{Ti}_2\text{Pn}\]^\text{2+}\) is not stable under the conditions and time scale of the CV experiment. The mononuclear bis-(cyclopentadienyl)titanium sandwich complexes studied by Chirik and co-workers also showed irreversible voltammetric responses in THF/[\(\text{Bu}_4\text{N}\)]PF\(_6\).\(^{27}\) The oxidation of the double-sandwich complex \(\text{Ti}_2\text{Pn}^\ast\) occurs at a relatively cathodic potential (−1.06 V vs FeCp\(^2\)/FeCp\(^0\)), consistent with an electron-rich complex that can act as a reducing agent for substrates such as CO\(_2\).

Employing \([\text{Bu}_4\text{N}][\text{B(C}_6\text{F}_5\text{)}_4]\) as the supporting electrolyte resulted in better-resolution CV data for \(\text{Ti}_2\text{Pn}^\ast\) in oxidative scans compared with \([\text{Bu}_4\text{N}][\text{PF}_6]\) (see Figure S3 in the SI), and a further quasi-reversible oxidation, process III, was observed at \(E_{pc} = −0.54\) V vs FeCp\(^2\)/FeCp\(^0\). The \([\text{B(C}_9\text{F}_{18}\text{)}_4]\) anion is well-known for its lower ion-pairing capability (spherical diameters: \([\text{B(C}_9\text{F}_{18}\text{)}_4]\) = 10 Å; \([\text{PF}_6]\) = 3.3 Å),\(^{28}\) which is beneficial for the study of multielectron processes with positively charged analytes,\(^{29}\) and it was therefore chosen for the large-scale synthesis of the cationic species.

\([\text{Ti}_2(\mu\eta^1\text{Pn}^\ast\eta^1\text{Pn}^\ast)]\text{[B(C}_9\text{F}_{18}\text{)}_4]\). Reaction of \(\text{Ti}_2\text{Pn}^\ast\) with the mild oxidizing agent \([\text{FeCp}^\ast\text{]}][\text{B(C}_9\text{F}_{18}\text{)}_4]\) at −35 °C resulted in a brown suspension. Following evaporation of the solvent and FeCp\(^\ast\) residues were recrystallized from a concentrated Et\(_2\)O/hexane solution at −35 °C to obtain \([\text{Ti}_2(\mu\eta^1\text{Pn}^\ast\eta^1\text{Pn}^\ast)]\text{[B(C}_9\text{F}_{18}\text{)}_4]\) in 55% yield, which was fully characterized by spectroscopic and analytical methods. The cation \([\text{Ti}_2\text{Pn}^\ast\text{]}\) is, to the best of our knowledge, the first example of a formally a Ti(II)−Ti(III) mixed-valence species. The molecular structure (Figure 6) reveals a “naked” double-sandwich cation with no close contacts between the anion and the metal−metal bonded core.

The most noteworthy structural feature is the longer Ti−Ti bond distance in \([\text{Ti}_2\text{Pn}^\ast\text{]}\text{[B(C}_9\text{F}_{18}\text{)}_4]\) (2.5091(9) Å) compared with \(\text{Ti}_2\text{Pn}^\ast\) (2.399(2) Å). This elongation is consistent with the removal of an electron from the M−M bonding HOMO (16a\(_1\)) in the molecular orbital scheme for \(\text{Ti}_2\text{Pn}^\ast\) (Figure 2). There is no significant change in the Ti−C and pentane C−C bond lengths in \(\text{Ti}_2\text{Pn}^\ast\) relative to \([\text{Ti}_2\text{Pn}^\ast\text{]}\), but the pentane ligands bend around the Ti\(_2\) core to a greater extent in the cationic complex; the centroid−metal−centroid angles around Ti1 and Ti2 are 142.28(6)° and 142.48(6)°, respectively, compared with the respective angles of 153.84(17)° and 156.6(2)° in the neutral complex. The decamethyltitanocene cation in \([\text{Cp}^\ast\text{Ti]}\text{[BPh}_4]\) also adopts a more bent structure than the neutral titanocenes.\(^{31,32}\)

As expected, \([\text{Ti}_2\text{Pn}^\ast\text{]}\text{[B(C}_9\text{F}_{18}\text{)}_4]\) is paramagnetic; the \(^1\text{H}, ^{13}\text{C}\), and \(^{29}\text{Si}\) NMR spectra in THF-\(d_4\) were broad and uninformative, but the \(^{19}\text{F}\) and \(^{11}\text{B}\) NMR spectra showed well-resolved signals at \(\delta_F = −132.7, −165.2,\) and −168.7 and \(\delta_B = −14.75\), respectively, attributable to the outer-sphere tetakis-(perfluorophenyl)borate anion. The solution-phase magnetic moment of \([\text{Ti}_2\text{Pn}^\ast\text{]}\text{[B(C}_9\text{F}_{18}\text{)}_4]\) determined by the Evans method was 1.96μ\(_B\) per dimer,\(^{33,34}\) which is slightly greater than the spin-only moment for one unpaired electron (1.73μ\(_B\)). Comparable data were observed in the solid state by SQUID magnetometry (μ\(_{eff}\) (260 K) = 1.92μ\(_B\) per dimer; see Figure S4 in the SI).

The electron paramagnetic resonance (EPR) spectra of \([\text{Ti}_2\text{Pn}^\ast\text{]}\text{[B(C}_9\text{F}_{18}\text{)}_4]\) were consistent with an \(S = \frac{1}{2}\) ground-state electronic configuration. The X-band spectrum of a polycrystalline sample at room temperature (Figure 7) showed an axial signal with two principal g values simulated (\(g_L = 2.003\) and \(g_S = 1.944\)), giving an average g value of 1.964. The large line widths (\(\Delta B_L = 24.5\) G and \(\Delta B_S = 23\) G) meant that any hyperfine structure and further g anisotropy were not resolved. \([\text{Ti}_2\text{Pn}^\ast\text{]}\text{[B(C}_9\text{F}_{18}\text{)}_4]\). Calculations on the cation \([\text{Ti}_2\text{Pn}^\ast\text{]}\) (\(2\)\(^{1}\)) show a lengthening of the Ti−Ti distance by ca. 0.1 Å and an increase in the bonding of the pentane ligands around the Ti\(_2\) core (Table 1), as found experimentally for the silylated analogues. The orbital manifold shows the expected hole in the 16a\(_1\) orbital (Figure 2), which is delocalized over the Ti atoms. The principal g values calculated for \(2\)\(^{1}\) are \(g_L = 1.956, g_S = 2.000\), \(g_S = 2.008\). Their relative magnitude and ordering (\(g_L < g_S < g_S\)) explain the apparent axial symmetry of the experimental EPR spectrum, with the \(C_3\) axis perpendicular to the \(x\) axis (in a coordinate system with the \(x\) axis passing through the pentane ligands).
bridgehead C–C bonds), and are consistent with a singly occupied MO (SOMO) 16a1 (Figure 2).

Ti2(μη5,η5-Pn)2CO2. The CO2 adduct Ti2(μη5,η5-Pn†)2CO2 has been spectroscopically characterized in solution at low temperature but is too unstable to be isolated.17 Optimizing the geometry of Ti2Pn2CO2 from various starting geometries led to a minimum-energy structure with C2v symmetry (3). Selected geometric parameters are given in Table 1.

Further insight into the binding of CO2 is given by a fragment analysis. Upon bending of CO2, the LUMO of Ti2Pn2 is the predominant bonding interaction. The occupancies of the LUMO, HOMO, and HOMO−1 of the Ti2Pn2 fragment in 3 are given in Table 4. Some remixing between the HOMO and LUMO does occur, but on the whole the HOMO−1 of Ti2Pn2 retains its integrity to form the HOMO of the CO2 derivative, 19a1 (Figure 8). Thus, CO2 may be regarded as acting as a μ-Z ligand.

Table 3. Energies (in eV) of Orbital Interactions Divided According to Their Symmetries; The Various Molecules with C2v Symmetry Are Divided into Ti2Pn2 and Ligand Fragments

| 3  | 4  | 7  | 9  | 13 |
|----|----|----|----|----|
| A1 | −116 | −192 | −81 | −186 | −80 |
| A2 | −2 | −4 | −15 | 0 | −1 |
| B1 | −7 | −8 | −8 | −136 | −100 |
| B2 | −15 | −21 | −24 | −165 | −125 |

Table 4. Occupancies of the Fragment Orbitals of Ti2Pn2 in the Molecular Calculations for 2, 3, 4, 5, 6, 7, 8, 9, and 13

| 14b2 | 13b2 | 17a1 | 16a1 | 15a1 |
|------|------|------|------|------|
| 2 | 0 | 0 | 0 | 2.00 | 2.00 |
| 3 | 0.07 | 0.09 | 0.18 | 0.98 | 1.99 |
| 4 | 0.22 | 0.14 | 0.29 | 0.77 | 1.97 |
| 5 | 0.13 | 0.12 | 0.23 | 0.89 | 1.98 |
| 6 | 0.02 | 0.07 | 0.57 | 1.02 | 2.00 |
| 7 | 0 | 0 | 0.39 | 1.31 | 1.97 |
| 8 | 0.33 | 0.83 | 0.56 | 0.70 | 1.43 |
| 9 | 0.03 | 0.10 | 0.12 | 0.42 | 1.46 |
| 13 | 0.11 | 0.25 | 0.06 | 0.67 | 1.97 |

Some remixing between the HOMO and LUMO does occur, but on the whole the HOMO−1 of Ti2Pn2 retains its integrity to form the HOMO of the CO2 derivative, 19a1 (Figure 8). Thus, CO2 may be regarded as acting as a μ-Z ligand. Ti2(μη5,η5-Pn†)2CS2. The adduct of CO2 to Ti2Pn† has not been structurally characterized, but the product of CS2 addition has.17 Geometry optimization of Ti2Pn1CS led to structure 4, analogous to 3. Key structural parameters are given in Table 1,
and selected MOs are shown in Figure 9. The Ti−Ti distance is again consistent with significant Ti−Ti bonding. The Ti−C distance is 0.09 Å longer than in the CO2 analogue. The Ti−S distance is 0.27 Å longer than the Ti−O distance, whereas the covalent radii differ by 0.39 Å, indicating a more significant interaction with Ti for S than for O. The angles at C are very similar (137° in 3, 138° in 4).

Upon coordination of CS2, one Ti−Ti bonding orbital, 19a1, remains intact, as is the case for the CO2 complex. The orbital 18a1 that is responsible for CS2 binding is more delocalized and multicentered than the analogue in 3, consistent with the differences in distance discussed above. Sulfur, with its higher-energy orbitals, has a stronger interaction with the Ti atoms. The fragment analysis reinforces this view. Not only is the a1 interaction energy greater than for 3 (Table 3), but there is also greater Ti2Pn2 HOMO−LUMO mixing, indicating both donor and acceptor quality in the bonding interaction (Table 4). The higher-lying orbitals of b1 symmetry have greater fragment occupancy in 4 than in 3 (Table 4), denoting donation from the b1 HOMO of bent CS2. Examination of the overlap population matrices for the two molecules gives a value of 0.19 for 4, which is significantly greater than the value of 0.05 for 3. Comparison of the calculated charges on O and S in the two molecules also reinforces the view that S is a better donor having a less negative charge (O −0.60, S −0.09 Mulliken; O −0.21, S −0.05 Hirshfeld; O −0.20, S −0.08 Voronoi).

Ti2Pn2COS. The COS adduct, 5, has been identified in solution but not isolated, as it undergoes rapid decomposition below room temperature. The Ti−Ti bonding orbital (19a1) and Ti2−CS2 bonding orbital (18a1) of Ti2Pn2CS2 (4).

Figure 9. Top three occupied orbitals of Ti2Pn2COS (5).

Ti2Pn2CO. On the basis of the nature of CO as a π-acceptor ligand, symmetric bridging of the two Ti centers by CO is not favored because the high-lying occupied frontier orbitals of Ti2Pn2 are of the wrong symmetry. The structure of Ti2Pn2CO (6) has C2 symmetry with the CO bound sideways-on to the Ti2 core, in agreement with the experimentally determined structure of the monocarboxyl complex Ti2(μ-Pn)[η5-Pn′]CO. Inspection of the orbitals of 6 (Figure 11) indicates that the positioning of CO is steered by back-donation from the HOMO of the Ti2Pn2 fragment. Once again a Ti−Ti bond is retained, forming the HOMO of 6, 5a. The composition of
the top two occupied orbitals in terms of their fragment orbitals is given in Table 4. The HOMO−1, 54a, is composed of one of the 5π orbitals of CO and orbital 16a1 of 2. The calculated wavenumber for the CO stretch is rather lower than the range for symmetric bridging carbonyls but in good agreement with the experimental value (Table 6).

Ti2Pn2(CO)2. Geometry optimization of the dicarbonyl adduct Ti2Pn2(CO)2 by both computational methods gave a structure of Cs symmetry only slightly displaced from C2v symmetry, 7. The ADF-calculated structure had an imaginary frequency of a’ symmetry with a wavenumber of −i15 cm−1. The calculated geometry agrees well with that found experimentally.16

The Ti−Ti bonding orbital, 36a (Figure 12) remains intact, consistent with the short Ti−Ti distance of 2.42 Å, but it is straighter than those found for the other derivatives. Back-bonding to both CO groups occurs in orbital 35a, which has clear origins in the 6b3u orbital of 1.

The agreement between the experimental and calculated stretching wavenumbers (Table 6) follows the same pattern as for the monocarbonyl, 6. Although binding of CO to 6 is energetically favorable, the ligand redistribution of 6 to afford 7 and 2 in the absence of CO is not predicted to be spontaneous (Table 5).

Ti2Pn2(CO)3. It was previously observed that reaction of Ti2Pn2 with excess CO at −78 °C produced an orange-brown solution, which following removal of the reaction headspace in vacuo and warming to room temperature resulted in a color

| compound   | ligand(s) | ΔE  | ΔG° |
|------------|-----------|-----|-----|
| 3          | CO2       | −53 | −37 |
| 4          | CS2       | −70 | −52 |
| 5          | COS       | −61 | −44 |
| 6          | CO        | −48 | −31 |
| 7          | (CO)2     | −74 | −43 |
| 8          | (CO)3,    | −94 | −50 |
| 12         | CO        | −19 | −5  |
| 14         | CO        | −25 | −3  |

Table 5. Calculated SCF Energies (ΔE) and Standard Free Energies (ΔG°) (in kcal mol−1) for Binding of Ligands to the Ti2Pn2 Unit

| compound   | mode  | experimental | calculated |
|------------|-------|--------------|------------|
| Ti2Pn2CO2  | ν(CO) | solution: 1678, 1236 | 1669 (w), 1214 (w) |
| Ti2Pn2CO   | ν(CO) | solid: 1655 | 1644 (w) |
| Ti2Pn2(CO)2 | ν(CO) | solution: not observed | 1532 (w) |
| Ti2Pn2(CO)3 | ν(CO) | solid: 1987 (s), 1910 (m) | 1947 (s), 1878 (m) |
| Ti2Pn2O(CO) | ν(CO) | not observed | 1918 (s), 1868 (s), 1835 (w) |
| Ti2Pn2CS2  | ν(CS) | solid: 1101 | 1487 (w) |
| Ti2Pn2COS  | ν(CO) | solution: 1498 | 1428 (w) |
| Ti2Pn2S(CO) | ν(CO) | solution: 2011 | 1937 (m) |

Table 6. Experimental and Calculated (ADF and Gaussian) Wavenumbers (cm−1) for Selected Stretching Vibrations
change to green-brown, characteristic of the dicarbonyl complex Ti₂Pn²⁺(CO)₂.† These observations hinted that an additional product is formed in the presence of excess CO at low temperatures, which was investigated by variable-temperature (VT) NMR spectroscopy. A solution of Ti₂Pn²⁺(¹³CO)₂ in methylcyclohexane-d₁₄ was sealed under ¹³CO, and the ¹³C{¹H} NMR spectrum at 30 °C (Figure 13) showed a very broad resonance centered at 232 ppm (Δν₁/₂ = 190 Hz). The spectrum was resolved by cooling to −70 °C (Figure 13), with two peaks in a ca. 2:1 ratio at 268 and 257 ppm, assigned to two chemically inequivalent carbonyl environments in Ti₂Pn²⁺(¹³CO)₃, and a peak at 186 ppm, corresponding to free ¹³CO in solution. These three ¹³C peaks broaden upon warming and coalesce at 0 °C, consistent with a dynamic intermolecular exchange process with free ¹³CO. A ¹³C–¹³C EXSY experiment at −40 °C (mixing time = 500 ms) showed cross-peaks between the bridging and terminal carbonyl signals, which implies that an exchange process between these CO sites also occurs in Ti₂Pn²⁺(CO)₃ (Scheme 1).

The carbonylation of Ti₂Pn²⁺ in methylcyclohexane solution at −55 °C was studied by in situ IR spectroscopy, which showed initial growth of an IR band at 1992 cm⁻¹ that then decreased in intensity and leveled off as a ν(CO) stretch at 1910 cm⁻¹ grew in (Figure 14). This lower-energy ν(CO) stretch became the major IR band at −55 °C once gas addition was complete. At 26 °C under CO, the intensities of the two bands reversed, with 1992 cm⁻¹ as the major ν(CO) stretching band. Removal of the CO headspace in vacuo led to near complete removal in the lower-energy ν(CO) stretch at 1910 cm⁻¹ (see Figure S9 in the SI). These results suggest that the band centered at 1992 cm⁻¹ is due to Ti₂Pn²⁺(CO)₂, which is the major product in the initial stages of reaction and upon warming to 26 °C when CO becomes less soluble. The IR band at 1910 cm⁻¹ is assigned to the terminal ν(CO) stretch in Ti₂Pn²⁺(CO)₃, which is the major product in solution under excess CO at −55 °C but diminishes upon exposure to vacuum and warming to room temperature. An analogous experiment performed using ¹³CO gave similar qualitative results, with IR bands at 1948 and 1867 cm⁻¹ assigned to the terminal ν(CO) in Ti₂Pn²⁺(¹³CO)₂ and Ti₂Pn²⁺(¹³CO)₃, respectively. IR bands for the bridging CO ligands, expected in the region 1850–1600 cm⁻¹, were not observed in the solution spectra for Ti₂Pn²⁺(CO) and Ti₂Pn²⁺(CO)₃, possibly because of extensive broadening.

Orange crystals of Ti₂Pn²⁺(CO)₃ were grown under an atmosphere of CO from a saturated toluene solution stored at −80 °C. Unfortunately, analysis by single-crystal X-ray diffraction was hampered by their deterioration when placed in oil for mounting, with effervescence of gas accompanying decomposition of the crystals. However, elemental analysis of the orange crystals was consistent with the proposed formulation of Ti₂Pn²⁺(CO)₃.

Scheme 1. Reactivity of Ti₂Pn²⁺(CO)₂ with CO (R = Si₃P₃₃₃)

Figure 12. HOMO and HOMO−1 of Ti₂Pn²⁺(CO)₂ (7).

Figure 13. Selected VT ¹³C{¹H} NMR spectra of Ti₂Pn²⁺(¹³CO)₃ in MeCy-d₁₄ solution (the temperature increases down the page in 20 K increments). The asterisk indicates free CO.

Figure 14. ν(CO) region of the ReactIR spectrum of Ti₂Pn²⁺ with CO at −55 °C.
Ti₂Pn₂(CO)₃, which optimized to structure 8. The Ti−Ti distance in 8 is significantly longer than those found in structures 1−7. The structure is asymmetric with one semibridging and two terminal carbonyls. The two highest occupied orbitals, 65a and 64a (Figure 15) are principally involved in back-donation to the CO ligands. The HOMO, 65a, is focused on the Ti, with just one bound CO contributing a π* orbital. MO 64a binds the other two CO ligands but retains a small amount of Ti−Ti bonding character.

The Ti₂Pn₂ fragment occupations are in accord with the reduction in metal−metal bonding (Table 4). The occupancy of the 15a₁ Ti−Ti bonding orbital is reduced compared with the examples above, showing that in the case of 8 both Ti−Ti bonding orbitals of Ti₂Pn₂ are involved in back-donation. In addition, the occupancies of the LUMO+1 and LUMO+2 (13b₂ and 14b₂) are significant, and these have Ti−Ti antibonding character. The calculated CO stretching wave-numbers (Table 6) suggest that one of the three expected vibrations is coincident with the higher stretching frequency of the dicarbonyl. The second one, of lower energy, is stronger than the lower stretch of the dicarbonyl, and the third is too weak to be observed. These predictions fit well with the dynamic behavior of Ti₂Pn₂(CO)₃ in the spectroscopic studies described above.

If Ti₂Pn₁₂(CO)₃ also has three inequivalent carbonyls, as suggested by the computed structure 8, three ¹³C signals are expected in the low-temperature NMR spectrum. As reported above, at −70 °C only two are observed (Figure 13). The obvious inference is that the two outer CO groups are rendered chemically equivalent on the NMR time scale by means of oscillation of the inner CO between them in what might be described as a “ping-pong” mechanism (see Scheme 1). It is proposed that the exchange between bridging and terminal CO sites occurs indirectly via an intermolecular process.

Ti₂Pn₂O. Decomposition of Ti₂Pn₁₂CO₂ proceeds via a mono(oxo) product, which can be synthesized independently by action of N₂O on Ti₂Pn₁₂.¹⁷ Maintenance of the sandwich structure of the Ti₂Pn₂ fragment leads to a local minimum with C₂v symmetry, structure 9. With η⁸ coordination of Pn to Ti, two other structures were found, one with a triplet state (10) and the other with a singlet state (11).

The structures found for the triplet state by the two methods differed in the Ti−O−Ti angle. ADF calculations optimized to a bent Ti−O−Ti unit, while the Gaussian calculations gave a linear Ti−O−Ti unit. Similar structures were found for the singlet state with η⁶ coordination by the two computational methods (Table 1).

The energies of the three structures are close, and which one is the most stable is method- and temperature-dependent (Table 7). ADF (BP/TZP) shows the sandwich structure to be the most stable. Gaussian (B3LYP/SDD) estimates the SCF energy of the sandwich structure to be the lowest, but the free energy at 298 K shows the triplet η⁶-coordinated structure to be the most stable. This is in agreement with experiment, as the experiment.

### Table 7. Relative Energies (kcal mol⁻¹) of Structures Found for Ti₂Pn₂O

| compound | ΔE(SCF) | ΔH²⁹⁸ ° | ΔG²⁹⁸ ° |
|----------|---------|---------|---------|
| 10       | 0, 0    | 0, 0    | 0, 2    |
| 11       | 12, 4   | 13, 3   | 8, 0    |
| 12       | 12, 19  | 13, 21  | 10, 20  |
sandwich structure is known to convert to the triplet state at room temperature.\textsuperscript{17}

Structure 9 has a Ti–Ti bonding orbital, 17\textsubscript{a1} (Figure 16). The high symmetry of the molecule facilitates identification of orbitals associated with Ti–O bonding, 14\textsubscript{a1} and 12\textsubscript{b2}. All three 2p orbitals of O contribute to its bonding, as illustrated by the binding energies decomposed by the symmetry of the orbitals involved (Table 3). The O atom competes effectively with the pentalene ligands for the Ti 3d orbitals, as evidenced by the increased Ti ring centroid distances (Table 1).

Orbitals containing the metal-based electrons of 10(ADF) and 11 are shown in Figure 17. Orbital 53\textsubscript{a} of 11 shows a bent Ti–Ti bond, the cause of the more acute angle at O in 11 (Table 1).

\textbf{Ti\textsubscript{2}Pn\textsubscript{2}(\textmu-O)(CO).} A possible intermediate in the decomposition of Ti\textsubscript{2}Pn\textsubscript{2}CO\textsubscript{2}, undetected as yet experimentally, is Ti\textsubscript{2}Pn\textsubscript{2}(\textmu-O)CO, in which a CO bond has broken, the detached O bridges the two Ti atoms, and the CO ligand formed is bonded to one of the Ti atoms. Geometry optimization gave a local minimum for such a species, structure 12. The Ti–Ti distance (2.46 Å, 2.43 Å) is still indicative of Ti–Ti bonding but longer than found for 9. The bridging O is placed asymmetrically, further from the Ti to which the CO is coordinated.

The HOMO of 12 (Figure 18) forms a Ti–Ti bond but also has a role in back-bonding to the CO. The CO stretching vibration has a high wavenumber (1954 cm\textsuperscript{-1}, 1945 cm\textsuperscript{-1}), consistent with the small amount of back-bonding indicated by the HOMO. Binding of the bridging oxo ligand is spread over several MOs and has both \(\sigma\) and \(\pi\) character. The \(\pi\) bonding of O competes with the pentalene binding, resulting in an increase in the Ti–Pn ring C distances (Table 1).

The energies of 3 and 12 are very close; ADF calculates 12 to be 1 kcal mol\textsuperscript{-1} less stable than 3, whereas Gaussian predicts 12 to be 11 kcal mol\textsuperscript{-1} more stable than 3.

\textbf{Ti\textsubscript{2}Pn\textsubscript{2}S.} The monosulfide derivative Ti\textsubscript{2}Pn\textsubscript{2}S\textsubscript{2} can be synthesized by the reaction of Ti\textsubscript{2}Pn\textsubscript{2} with Ph\textsubscript{3}PS.\textsuperscript{17} Geometry optimization of Ti\textsubscript{2}Pn\textsubscript{2}S (13) gave a structure with dimensions in good agreement with the X-ray structure of Ti\textsubscript{2}Pn\textsubscript{2}S.\textsuperscript{17}

The Ti–Ti distance in 13 is longer than that calculated for the oxo analogue 9 but indicates Ti–Ti bonding. The HOMO of 13, 13\textsubscript{b1}, is largely localized on the S and lies close in energy to the Ti–Ti bonding orbital 17\textsubscript{a1} (Figure 19). Separation of the bonding interactions by symmetry shows a different pattern from the oxo analogue in that the \(b_1\) interaction is the strongest and the \(a_1\) interaction the weakest, although all three S 3p
orbitals contribute significantly to the bonding (Table 3). The Ti$_2$Pn$_2$ fragment occupancies (Table 4) also indicate less donation from the Ti atoms to the S than is found for O.

**Ti$_2$Pn$_2$S(CO).** There is good NMR evidence that Ti$_2$Pn$_2$S binds CO reversibly.$^{17}$ Geometry optimization of Ti$_2$Pn$_2$S(CO) (14) gives a similar structure to 12. Binding of CO utilizes the Ti–Ti bonding orbital of 13, as found for 12 and shown in Figure 20.

The Ti–Ti distance calculated for 14 is slightly longer than for 12 (Table 1) and the calculated CO stretch slightly lower (Table 6), both comparisons suggesting that donation from the Ti–Ti bonding orbital is greater for 14, consistent with the lower electronegativity of S compared with O. The CO ligand has a rather low free energy of binding (Table 5), consistent with rapid exchange in solution, as evidenced by the NMR spectrum.$^{17}$

The relative energies calculated for 14 and 5 differ from the oxo analogues; both methods predict 14 to be more stable (ADF (BP/TZP) by 14 kcal mol$^{-1}$, Gaussian (B3LYP/SDD) by 9 kcal mol$^{-1}$).

**PnTi(O)$_2$TiPn.** Pn$^\text{′}$(μ-O)$_2$TiPn$^\text{′}$ is one of the products obtained from the reductive disproportionation of CO$_2$ by Ti$_2$Pn$_2$$^\text{′}$, and structural parameters of the optimized structure of PnTi(O)$_2$TiPn (15) (Table 1) are in good agreement with those obtained experimentally.$^{17}$ There is no Ti–Ti bonding, as the Ti atoms are in the IV oxidation state; the Ti–Ti distance of 2.74 Å (Table 1) is constrained by the short bonds to the bridging O atoms. The HOMO and HOMO–1 (Figure 21) represent δ bonds binding the pentalene ligands.
CONCLUSIONS

$\text{Ti}_2\text{Pn}_3$ has three frontier orbitals, two occupied high-lying metal–metal bonding orbitals and one low-lying LUMO, which enable this particular complex to display a range of reactivities not found with other double-sandwich compounds of this class. Its electron-rich nature dominates the chemistry, and it acts as a donor to CO, $\text{CS}_2$, and COS and is able to bind one, two, or three CO groups. The three frontier orbitals are of $a_1$, $b_1$, and $b_2$ symmetry involving all three chalcogen p orbitals. All of the compounds that maintain the double-sandwich structure of $\text{Ti}_2\text{Pn}_3$ maintain significant Ti–Ti bonding character.

EXPERIMENTAL SECTION

Computational Methods. Density functional theory calculations were carried out using two methods. One method employed the Amsterdam Density Functional Package (versionADF2012.01). The Slater-type orbital (STO) basis sets were of triple-$\zeta$ with one polarization function (ADF basis TZP). Core electrons were subjected to fragment analyses in which the MOs of fragments, with functional and SDD basis set. In both sets of calculations, tight correlation corrections of Becke and Perdew (BP86). Density functional theory calculations (ADF) were carried out by A.-C. Schmidt at FAU Erlangen using a Quantum Metropolitan University. Solid-state magnetic measurements were performed at the University of Oxford using an X-band Bruker EMXmicro spectrometer. Simulations were made with the Win-EPR suite. Mass spectra were recorded using a VG Autospec Fisons instrument (EI at 70 eV). Elemental analyses were carried out by S. Boyer at the Elemental Analysis Service, London Metropolitan University. Solid-state magnetic measurements were carried out by A.-C. Schmidt at FAU Erlangen using a Quantum Design MPMS-5 SQUID magnetometer. Accurately weighed samples (ca. 20 mg) were placed into gelatin capsules and then loaded into nonmagnetic plastic straws before being lowered into the cryostat. Samples used for magnetization measurements were recrystallized multiple times and checked for chemical composition and purity by elemental analysis and EPR spectroscopy. Values of the magnetic susceptibility were corrected for the underlying diamagnetic increment using tabulated Pascal constants and the effect of the blank sample holders (gelatin capsule/straw).

Synthesis of $\text{[Ti}_2(\mu-\eta^2-\eta^5-\eta^p-\text{Pn})_3]\text{[B(CF}_3)_4]}$. To a stirred, solid mixture of $\text{Ti}_2\text{Pn}_3$ (132 mg, 0.143 mmol) and $\text{FeCp}_3$ (143 mg, 0.142 mmol) at $-35 \degree C$ was added $\text{Et}_2\text{O}$ (20 mL), precooled to $-78 \degree C$, and the resultant brown mixture was allowed to warm to room temperature after 12 h. The solvent was removed under reduced pressure to afford a brown residue that was washed thoroughly with pentane (4 x 20 mL) to remove $\text{FeCp}_3$, and the washings were re-dried by warming. The residue was then extracted with $\text{Et}_2\text{O}$ (2 x 10 mL) and concentrated to ca. 5 mL, and 5 drops of hexane were added. Cooling this solution to $-35 \degree C$ produced brown-green crystals, which were isolated by decantation and dried in vacuo. Total yield: 125 mg (55% with respect to $\text{Ti}_2\text{Pn}_3$).

$\text{Fe}$ NMR (THF-d$_8$, 375.9 MHz, 303 K): $\delta_f$ = 132.7 (br, f-F), $\delta_p$ = 165.2 (t, $\delta_p$ = 20.2 Hz, f-F), $\delta_F$ = 167.8 (br t, $\delta_F$ = 19.3 Hz, m-F). $^{11}$B($^1$H) NMR (THF-d$_8$, 128.2 MHz, 303 K): $\delta_B$ = 147.5, EPR (solid state, 293 K, X-band): $g_l$ = 2.003, $g_g$ = 1.944, $g_{iso}$ = 1.964. EI-MS: no volatility. Anal. Found (Calcd for $\text{C}_{36}\text{H}_{58}\text{BF}_2\text{Si}_4\text{Ti}_2$): C, 56.72 (56.89); H, 5.83 (5.78) %. Magnetic susceptibility: (Evans method, THF-d$_8$, 303 K) $\mu_{eff}$ = 1.96$\mu_B$/per dimer; (SQUID, 260 K) $\mu_{eff}$ = 1.92$\mu_B$/per dimer. Crystall structure for $\text{[Ti}_2(\mu-\eta^2-\eta^5-\eta^p-\text{Pn})_3]\text{[B(CF}_3)_4]}$ was determined by direct methods and refined by full-matrix least-squares calculations on $\text{Fw}$ data. $\text{Fw}$ correction resulted in a color change from green-brown to orange-brown. NMR titration: 3 CO groups. The three frontier orbitals are of $a_1$, $b_1$, and $b_2$ symmetry, and as a consequence, a single CO molecule binds with one polarization function (ADF basis TZP). Core electrons were subjected to fragment analyses in which the MOs of fragments, with functional and SDD basis set. In both sets of calculations, tight correlation corrections of Becke and Perdew (BP86). In both sets of calculations, tight correlation corrections of Becke and Perdew (BP86).
against all data. An empirical absorption correction was carried out using the Multi-Scan program. The structure was solved using SHELXL-2013 and refined on $F^2$ by full-matrix least-squares refinements using SHELXL-2013. Solutions and refinements were performed using the OLEX2 or WinGX package and software packages within. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were refined using a riding model.

**ASSOCIATED CONTENT**

1. **Supporting Information**

Detailed X-ray, IR, EPR, NMR, and CV data; a text file of computed molecule Cartesian coordinates for all structures in xyz format for convenient visualization; crystallographic data for [Ti$_2$(µ-η$^5$-η$^1$-Pn)$_3$][B(C$_6$F$_5$)$_4$] in CIF format. The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00363.

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**Notes**

The authors declare no competing financial interest.

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