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# Multicomponent Mechanochemical Synthesis of Cyclopentadienyl Titanium tert-Butoxy Halides, $Cp_xTiX_y(O^tBu)_{4-(x+y)}$ (x, y = 1, 2; X = Cl, Br)

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S Supporting Information

ABSTRACT: Titanium *tert*-butoxy halides of the formula $Cp_xTiX_y(O^tBu)_{4-(x+y)}$ (x, y = 1, 2; X = Cl, Br) have been prepared thorough milling the reagents without solvent. In the case of the chloride derivatives, Cp_2TiCl_2 is used as a starting material; in the case of the bromides, a mixture of LiCp, $TiBr_4$, and $Li[O^tBu]$ is used. The stoichiometric ratios of the starting materials are reflected in the major products of the reactions. Single-crystal X-ray structures are reported for Cp_2TiCl-(O^tBu), $Cp_2TiBr_2(O^tBu)$, and $CpTiBr_2(O^tBu)$, as well as for $Cp_2TiCl(O^iPr)$ and a redetermination of $Cp_2TiCl(OMe)$. The *tert*-butoxy derivatives are notable for their nearly linear Ti−O−C angles (>170°) that reflect Ti−O π-bonding, an interpretation supported with density functional theory calculations.

Ti−O−C bond angle = 174°
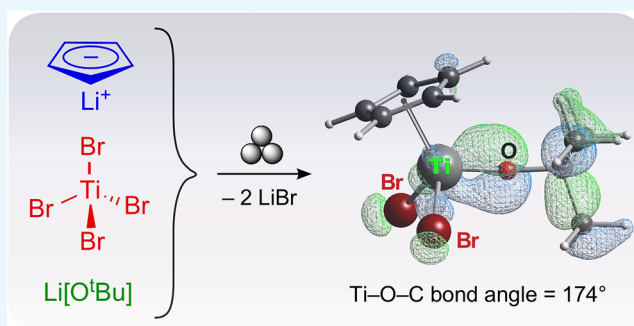
1. INTRODUCTION

The neutral d^0 $Cp'_xML_yL'_{4-(x+y)}$ framework comprises an enormous number of complexes in early transition-metal and actinide chemistry.[1] This is the result of the combinatorial possibilities within the basic metallocene structure, coupled with an extended range of compatible L and L′ ligands. Many applications have been developed for such complexes, mainly in catalysis (e.g., syndiotactic polymerization of styrene,[2] alkyne hydroamination,[3] olefin polymerization,[4−13] including copolymerization, e.g., of ethylene/norbornene,[14,15] polymerization of lactide monomers and ε-caprolactone[16−18]), but there are also uses in organic synthesis[19−22] and for the chemical vapor deposition production of thin-film oxides[23,24] and carbides.[25]

The richness of the synthetic landscape of these complexes can be appreciated by considering a subset of complexes in which the cyclopentadienyl ligand is the unsubstituted C_5H_5, L′ is a halide, and L″ is an alkoxide. Not counting the homoleptic complexes MX_4, $M(OR)_4$, and MCp_4, 12 general compositions can satisfy the $Cp_xMX_y(OR)_{4-(x+y)}$ formula (Figure 1). The very flexibility that makes the metallocene framework so versatile, however, can also complicate the synthesis of specific compositions. Remarkably, for the specific set with M = Ti, X = Cl, and R = ^tBu, all of the possible compounds with the exception of $Cp_2TiCl(O^tBu)$ are known.[26] This is one of the most complete such families, however. With the sole change of Cl to Br, for example, none of the heteroleptic $Cp_xTiBr_y(O^tBu)_{4-(x+y)}$ or $TiBr_x(O^tBu)_{4-x}$ complexes has been described. Even when known, the assembly of particular ligand sets in a Cp_2MLL' complex is not always straightforward. The dichlorides Cp_2MCl_2 are
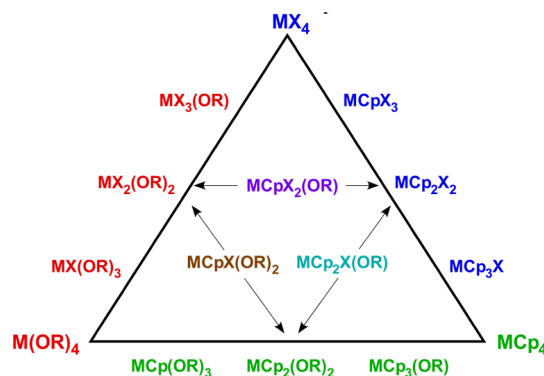

Figure 1. Combinatorial possibilities of mixed group 4 $Cp_xMX_y(OR)_{4-(x+y)}$ complexes, starting from the homoleptic species MX_4, $M(OR)_4$, and MCp_4. Complexes in the interior represent conceptual blends of the compounds on the edges.

commonly used starting materials for bis(cyclopentadienyl) derivatives, but the reaction of Cp_2TiCl_2 and 2 equiv $Li[O^tBu]$ in tetrahydrofuran (THF) yields not only $Cp_2Ti(O^tBu)_2$ (61%) but also $CpTi(O^tBu)_3$ (26%) and $Ti(O^tBu)_4$ (13%).[26f] Similarly, the reaction of Cp_2ZrCl_2 and (Li or Na)$[O^tBu]$ yields an inseparable mixture of $Cp_2ZrCl(O^tBu)$ and $Cp_2Zr(O^tBu)_2$, even with the use of more than 2 equiv of the alkoxide.[23]

The formation and disruption of Ti−O bonds has been of particular interest because although such bonds are typically rather robust (e.g., ca. 90 kcal mol^{-1} in various $Cp_2Ti(OR)_2$ complexes),[27] their strength depends markedly on the metal oxidation state and the identity of other ligands on the metal center.[28−30] In general, increased electron density on the metal center is associated with weaker Ti−O bond strength. Thus, the Ti−O energy in the Ti(IV) complex $Ti(O^tBu)_4$ has been placed at 108 kcal mol^{-1}, whereas in the Ti(III) species $Cp_2TiCl(TEMPO)$ [TEMPO = (2,2,6,6-tetramethylpiperidine-N-oxyl)], the bond strength is calculated at 17 kcal mol^{-1}.[30] The ready scission of the Ti(III)−TEMPO bond has been exploited synthetically for the formation of $CpTiCl(OR)_2$ (R = complexes).[31]

In contrast to the solution-based methods described above, we recently explored the use of mechanochemical methods in the preparation of $Cp_xMCl_y(O^tBu)_{4-(x+y)}$ (M = Ti, Zr, and Hf) complexes.[26f] Mechanochemical synthesis, which typically employs grinding or milling, usually under solvent-free conditions, has been investigated for the preparation of organic,[32] inorganic,[33−36] and organometallic compounds.[37] Such reactions can occur on a much faster time scale than equivalent solution methods.[38] Part of the reason for this is the much higher concentration of reagents in the solid state than is the case in solution. Solvents can also coordinate to reagents and interfere with their subsequent reactivity or stabilize intermediates that require more time to form products.[39] Mechanochemistry may yield unique products that cannot be isolated from solution-based approaches.[40,41] The distribution of products and isomers can also be tuned.[26f,42,43] In addition, the solvent-free approach provides flexibility to use reagents that are not compatible with typical organic solvents, especially ethers. As demonstrated below, this proves to be valuable in work with titanium halides. We report here mechanochemical routes to $Cp_xTiCl_y(O^tBu)_{4-(x+y)}$ (X = Cl, Br) complexes, with solution syntheses of methoxy[44] and isopropoxy derivatives added for comparison.

2. RESULTS AND DISCUSSION

2.1. Synthesis. Preliminary attempts to prepare $Cp_2TiCl(OMe)$[44] (**1**) and the previously unknown $Cp_2TiCl(O^iPr)$ (**2**) through grinding Cp_2TiCl_2 with the appropriate alkali metal alkoxide did not produce clean results, and hence, for these two compounds, we turned to alcoholysis reactions in THF with an added base.[45] This approach has been used with both bis(cyclopentadienyl)[46] and mono(cyclopentadienyl)-titanium[26h] complexes and provides control over substitution, as indicated in eq 1 (n = 2 or 3; R = Me, Et, and ^iPr) for the latter compounds.[26h] For this study, we used Cp_2TiCl_2 as a starting material, which is inexpensive and its chloride ligands are substitutable.

$$CpTiCl_3 + nHOR + nEt_3N$$
$$\xrightarrow{\text{THF}} CpTiCl_{3-n}(OR)_n + n[HNEt_3]Cl \qquad (1)$$
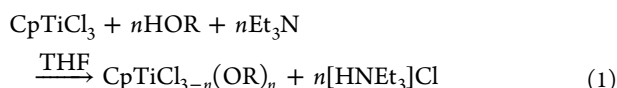
The methoxy derivative **1** has been described before[44] but its synthesis was given without details. The new isopropoxy derivative **2** is an orange solid with the expected ^1H and ^{13}C NMR spectra. The ethoxy derivative has been previously synthesized,[46,47] but it was useful for comparative studies (see below) and was also prepared via the literature solution method.

These solution reactions are slow (ca. 16 h) and even then may be incomplete,[46] and for the synthesis of the tert-butoxy derivative $Cp_2TiCl(O^tBu)$ (**3**), we investigated halide metathesis instead. This approach has been used to form $Cp_2ZrCl(O^tBu)$ in THF,[23] although the solution route fails for $Cp_2HfCl(O^tBu)$.[26f] Mechanochemical activation works successfully with both of the heavier group 4 metals and it was adopted for the preparation of **3**. At the outset, we were not confident that the reaction would be selective, as our previous investigation into tert-butoxide substitution with Cp_2TiCl_2 demonstrated that at ratios of $[O^tBu]^-/Cp_2TiCl_2$ $\geq$ 2, mixtures of products were obtained whose composition depended on whether or not solvent was used in the reaction and if so, whether it was an alkane or an ether.[26f] Nevertheless, we proceeded with the assumption that the composition of the desired product could be generated from the corresponding ratio of starting materials, that is, 1 equivalent of $[O^tBu]^-$ would replace one Cl$^-$ or Br$^-$. With the use of an equimolar ratio of $K[O^tBu]$ to Cp_2TiCl_2, in fact, grinding in a planetary mill for 15 min at 600 rpm did yield solid orange **3** exclusively. This result parallels those with Zr and Hf. The formation of **3**, which completes the set of $Cp_xTiX_y(O^tBu)_{4-(x+y)}$ compounds for X = Cl and R = ^tBu (Figure 1), has been proposed as an intermediary in the formation of $Cp_3Ti(O^tBu)$ from Cp_2TiCl_2 and $K[O^tBu]$ and LiCp (eq 2).[26f] Its isolation raises the reasonableness of this route.

$$Cp_2TiCl_2 \xrightarrow[-[Cl]^-]{[O^tBu]^-} 3 \xrightarrow[-[Cl]^-]{[Cp]^-} Cp_3Ti(O^tBu) \qquad (2)$$
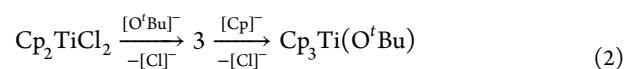
The scarcity of organotitanium bromides stems from a lack of readily accessible starting materials. The solid $TiBr_4$ would be a logical choice but it reacts with ethereal solvents at room temperature (in the case of THF, with ring cleavage).[48] The adduct $TiBr_4(thf)_2$ has been used in the preparation of some titanium complexes, but its preparation requires a low-temperature (−78 °C) reaction between $TiBr_4$ and THF followed by several days of vacuum drying to obtain a solid product. The resulting material is not soluble in THF, CHCl$_3$, or CCl$_4$.[48] Even if it were, such solvents are problematic from an environmental viewpoint and move the traditional route even farther away from a "green" approach to synthesis.[49] Thus, a mechanochemical route seemed especially suitable for the preparation of alkoxybromo derivatives. Rather than starting with Cp_2TiBr_2, which itself can be made from Cp_2TiCl_2 and LiBr,[50] the one-pot synthesis of $Cp_2TiBr(O^tBu)$ (**4**) was accomplished by milling $TiBr_4$, $Li[O^tBu]$, and LiCp in a 1:1:2 M ratio for 15 min (eq 3)

$$TiBr_4 + Li[O^tBu] + 2\ LiCp \xrightarrow{\otimes} Cp_2TiBr(O^tBu)\ (\mathbf{4}) + 3\ LiBr \quad (3)$$
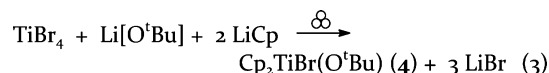
Adjusting the reaction stoichiometry of $TiBr_4$, $Li[O^tBu]$, and LiCp to 1:1:1 and 1:2:1 ratios forms $CpTiBr_2(O^tBu)$ (**5**) and $CpTiBr(O^tBu)_2$ (**6**), respectively. Perhaps not surprisingly, compound **5**, formed from the simplest ratio of reagents, is the bromo complex that is consistently formed most cleanly. In contrast, the formation of **4** is also accompanied by **6** (ca. 56%); crystals **4** can be obtained from hexanes. Compound **6**, in turn, which is produced with a larger amount of the tert-butoxide than is **5**, is usually accompanied by the homoleptic alkoxide $Ti(O^tBu)_4$ (ca. 30%). Such differences reflect the role that kinetic factors play in mechanochemical synthesis, as grinding and milling environments are often far from

Table 1. Crystallographic and Calculated[a] Structures for $Cp_xTiX_y(OR)_{4-(x+y)}$ Complexes

	Ti−Cp (cent) (Å)	Ti−X (Å)	Ti−O (Å)	Ti−O−R (deg)	refs
$Cp_2TiCl(OMe)$ (**1**)	2.091 (ave)	2.405(1)	1.839(2)	141.4(3)	44
$Cp_2TiCl(OMe)$	2.083 (ave)	2.4215(3)	1.8300(19)	138.53(13)	this work
$Cp_2TiCl(OMe)$	2.111 (ave)	2.379	1.844	136.8	calc
$Cp_2TiCl(OEt)$	2.09 (ave)	2.405(1)	1.855(2)	133.2(2)	47
$Cp_2TiCl(OEt)$	2.084 (ave)	2.4044(12)	1.858(3)	133.3(2)	this work
$Cp_2TiCl(OEt)$	2.113	2.378	1.840	140.2	calc
$Cp_2TiCl(O^iPr)$ (**2**)	2.052 (ave)	2.4031(16)	1.802(3)	160.0(3)	this work
$Cp_2TiCl(O^iPr)$	2.116 (ave)	2.387	1.831	147.7	calc
$Cp_2TiCl(O^tBu)$ (**3**)	2.103 (ave)	2.4101(4)	1.7864(9)	172.48(8)	this work
$Cp_2TiCl(O^tBu)$	2.130 (ave)	2.394	1.800	168.0	calc
$Cp_3Ti(O^tBu)$	2.112 (η^5)	2.304(1) (η^1-Cp)	1.794(1)	170.88(9)	26f
$Cp_3Ti(O^tBu)$	2.142 (ave)	2.366 (η^1-Cp)	1.792	175.5	calc
$Cp_2TiBr(O^tBu)$ (**4**)	2.096 (ave)	2.534(2)	1.774(3)	175.8(3)	this work
$Cp_2TiBr(O^tBu)$	2.126 (ave)	2.585	1.797	170.6	calc
$CpTiBr_2(O^tBu)$ (**5**)	2.024	2.433(7) (ave)	1.7274(18)	173.95(19)	this work
$CpTiBr_2(O^tBu)$	2.024	2.430	1.755	178.9	calc

[a]B2PLYP/def2TZVP(Ti,Br,Cl); def2SVP(C,O,H).

equilibrium,[51−54] and it is not uncommon to observe mixtures of the kinetically preferred products from solid-state reactions.

All of the compounds **1−6** are air- and moisture-sensitive and are soluble in hydrocarbons.

2.2. Crystal Structures. Crystals of **1** and **2** that were suitable for X-ray diffraction were grown from toluene; those for **3−5** were grown from hexanes. Comparative listings of selected bond lengths and angles are found in Table 1.

2.2.1. Cp₂TiCl(OMe) (1). An X-ray structure determination of **1** has been reported.[44] The room-temperature (295 K) structure was affected by disorder in the Cp rings that could not be satisfactorily modeled. Interestingly, in the present low-temperature version, which crystallizes in the same space group (*Pbca*), the Cp rings are not disordered but there is a second chlorine position possibly arising from cocrystallized Cp₂TiCl₂; its occupancy is refined (9%) with a Ti−Cl bond similarity restraint. Its presence may be the result of incomplete alcoholysis, a difficulty that has been observed before with this synthetic method.[46] Nevertheless, both the original and our low-temperature redetermination agree on the pseudote-trahedral nature of the molecule, defined by the centroids of the two Cp rings, the chloride, and the oxygen of the methyl group (Figure 2). The Ti−Cl, Ti−O, and Ti-ring centroid distances in the two structures differ by less than 0.01 Å and the Cl−Ti−O angles differ by only 0.19°. The major difference involves the methoxy ligand; the O1−C11 bond distance is 0.05 Å longer in the present structure and the Ti−O−C bond angle has contracted by 2.9°. The low-temperature structure parameters are more in line with those of Cp₂TiCl(OEt).[47] For example, the C−O distance in the ethoxy derivative [1.415(4) Å] is not statistically distinguishable from that in the low-temperature **1** and the Ti−O−C angles, although differing by 5.3°, are closer than the ethoxy/room-temp methoxy values (Δ = 8.2°).

As a result of the unusual ordering of geometric parameters in the previously reported Cp₂TiCl(OEt) structure relative to **1** and **2** (see below), Cp₂TiCl(OEt) was resynthesized (see Experimental Section) and its structure was redetermined (see Supporting Information). Crystals were grown in view of the possibility that a polymorph might exist with a different Ti−O length and/or Ti−O−C angle. Although the new crystals were twinned, unlike those used for the earlier determination, all of
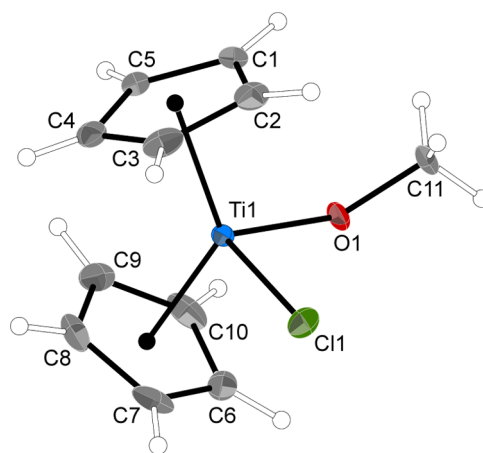

Figure 2. Thermal ellipsoid plot of **1** (50% level); hydrogens have arbitrary radii. A second chloride (2.326 Å from Ti, see text) has been removed for clarity. Selected bond distances (Å) and angles (deg): Ti1−O1, 1.8300(19); Ti1−Cl1, 2.4215(3); O1−C11, 1.419(2); Ti−Cp′ (ring centroid), 2.083 (ave); O1−Ti1−Cl1, 93.61(5); Ti1−O1−C11, 138.53(13); and Cp−Ti−Cp′, 130.9.

the relevant structural parameters of the two structures agree to within 1σ (see Table 1).

2.2.2. Cp₂TiCl(O^iPr) (2). Compound **2** shares the same pseudotetrahedral structure as **1** and Cp₂TiCl(OEt); in the case of **2**, both the Cp rings and O^iPr ligand are disordered. One set of these is depicted in Figure 3. In particular, the alkoxide ligand is disordered across a crystallographically imposed mirror plane, that is, Cl1, Ti1, O1, C7, and C8 all lie in the plane and C6 is disordered above and below it (50:50). The general details of **2** mimic those of **1**, in that the Ti-ring centroid distances differ only by 0.03 Å and the Ti−Cl bond lengths are within 0.02 Å of each other. Some details of the geometry of the isopropoxy ligand suggest a change in the metal ligand bonding compared to that in **1** and Cp₂TiCl-(OEt). The Ti−O bond has shortened to 1.802(3) Å and the Ti−O−C angle has widened to 160.0(3)°, features that could be consistent with some π-bonding character between Ti and the isopropoxy oxygen. The C−O distance of 1.309(6) Å, however, although not an unprecedented value for such a bond,[55] is nearly 0.1 Å shorter than that found in any of the
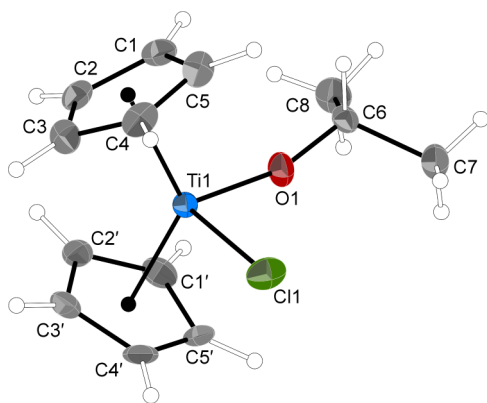
Figure 3. Thermal ellipsoid plot of **2** (30% level); hydrogens have arbitrary radii. Only one conformation of the disordered isopropyl and cyclopentadienyl ligands is shown. Selected bond distances (Å) and angles (deg): Ti1–O1, 1.802(3); Ti1–Cl1, 2.4031(16); O1–C6, 1.309(6); Ti–Cp' (ring centroid), 2.052 (ave); O1–Ti1–Cl1, 94.87(13); Ti1–O1–C6, 160.0(3); and Cp–Ti–Cp', 129.0.

other complexes in this study. It also is not supported by computational modeling (see below), suggesting that the ligand disorder has unrealistically shortened it. Other features may have been altered by the disorder as well.

2.2.3. Cp$_2$TiCl(O^{t}Bu) (3). Compound **3** is not affected by the disorder problems in **1** and **2** and interpretation of its structural features is more straightforward (Figure 4). The
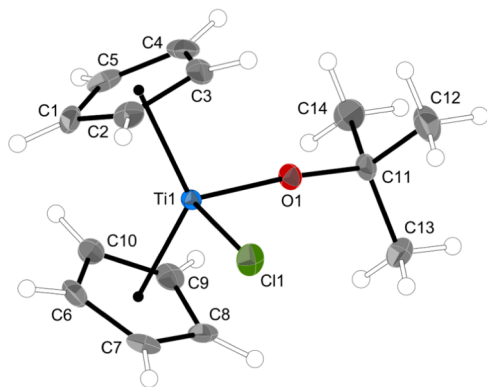

Figure 4. Thermal ellipsoid plot of **3** (50% level); hydrogens have arbitrary radii. Selected bond distances (Å) and angles (deg): Ti1–O1, 1.7864(9); Ti1–Cl1, 2.4101(4); O1–C11, 1.4204(14); Ti–Cp' (ring centroid), 2.103 (ave); O1–Ti1–Cl1, 94.40(3); Ti1–O1–C11, 172.48(8); and Cp–M–Cp', 129.5.

molecule has the same pseudotetrahedral geometry displayed by **1** and **2**, but **3** can probably be compared most directly with the [Cp$_2$Ti(O^{t}Bu)(thf)]$^+$ cation;[56] the Ti–O bond of 1.806(4) Å and Ti–O–C angle of 166.9(3)° of the latter differ by 0.02 Å and 5.6°, respectively, from that of **3**. Comparisons are also possible with the structure of Cp$_2$TiCl(OEt), which has been suggested as representing a sterically unencumbered Cp$_2$TiCl-(OR) complex.[47] The Ti–Cp (centroid) distances and Cp–Ti–Cp' angles in the two complexes differ by only 0.016 Å and 1.0°, respectively. The Ti–Cl distances are also nearly identical (0.005 Å difference) and are ca. 0.04 Å longer than those in Cp$_2$TiCl$_2$.[57]

The differences between **3** and Cp$_2$TiCl(OEt), however, are the most revealing. The Ti–O–C angle in **3** is 172.5°, 39.3° wider than that in Cp$_2$TiCl(OEt), and which to our knowledge

is the widest such angle reported for a Cp$_2$TiCl(OR) complex.[58] It might be thought that, given the bulk of the O^{t}Bu ligand, there could be some steric influence on this value, but the closest intramolecular contact between a methyl carbon atom of the O^{t}Bu group and a Cp carbon is at 3.49 Å (C8···C13). Although the comparison is not exact, in Cp$_2$TiCl(OEt), the methylene carbon displays nearest contacts at 3.15 and 3.23 Å to Cp carbon atoms. More telling is the short (1.786 Å) Ti–O bond distance in **3**, compared to the 1.855 Å distance in the ethoxide. There is clearly no steric impediment to adopting the very short Ti–O distance in **3** and it would seem that the O^{t}Bu group is serving as a strong π donor in this complex.

2.2.4. Cp$_2$TiBr(O^{t}Bu) (4). There are two crystallographically independent but closely similar molecules in the unit cell; only molecule "A" will be discussed here. Not unexpectedly, the bromoalkoxy derivative **4** (Figure 5) is isostructural with the
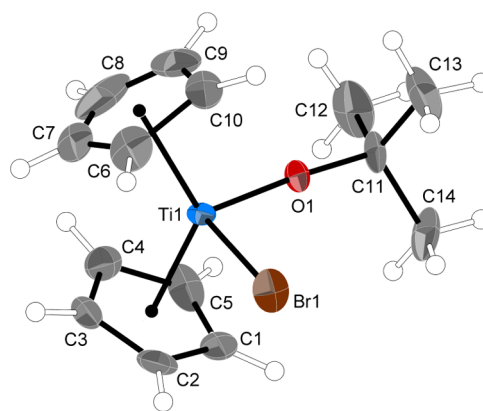

Figure 5. Thermal ellipsoid plot of **4** (50% level); hydrogens have arbitrary radii. Selected bond distances (Å) and angles (deg): Ti1–O1, 1.774(3); Ti1–Br1, 2.534(2); O1–C11, 1.414(5); Ti–Cp' (ring centroid), 2.096 (ave); O1–Ti1–Br1, 84.67(16); Ti1–O1–C11, 175.8(3); and Cp–Ti–Cp', 128.8.

chloroalkoxy derivative **3**. They share the same pseudotetrahedral framework, with closely similar Ti–Cp (centroid) distances (<0.01 Å difference). The Ti–Br bond length in **4** matches that in Cp$_2$TiBr$_2$ exactly[59] and is 0.12 Å longer than the Ti–Cl distance in **3**, which is slightly less than the difference in covalent radii (0.18 Å).[60] The *tert*-butoxy ligand bonding is also similar to that in **3**, as measured by the Ti–O and O–C distances and the Ti–O–C angle (0.012, 0.006 Å, and 3.3° difference, respectively). The differences, although small, are in a direction that indicates that the bromide ligand provides less competition for π-bonding to the metal than does the more electronegative chloride. This is reflected in the contraction of the Ti–O bond and the widening of the Ti–O–C angle in **4** compared to **3**. There is even less reason to posit any steric influence on the wide Ti–O–C angle in **4** (175.8°), as the closest intramolecular contact between a carbon atom of the O^{t}Bu group and a Cp carbon is now at 3.68 Å (C1···C14).

2.2.5. CpTiBr$_2$(O^{t}Bu) (5). Similar to **4**, there are two crystallographically independent but closely similar molecules in the unit cell of **5**; only molecule "A" will be discussed here. Also similar to **4**, compound **5** has a pseudotetrahedral geometry, with one of the Cp rings of **4** replaced with another Br (Figure 6). The molecule possesses approximate, although not crystallographically imposed, C_s symmetry; the atoms C5, Ti1, O1, C6, and C8 are all within 0.03 Å of a least-squares
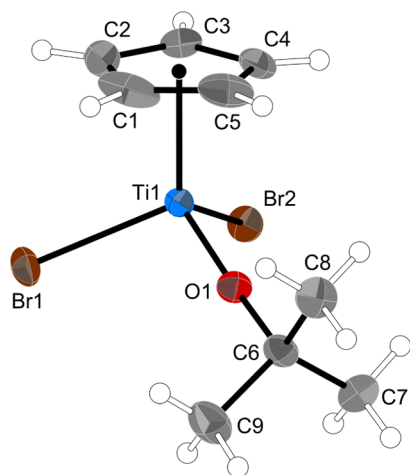
Figure 6. Thermal ellipsoid plot of **5** (50% level); hydrogens have arbitrary radii. Selected bond distances (Å) and angles (deg): Ti1–O1, 1.7274(18); Ti1–Br1, 2.4333(5); Ti1–Br2, 2.4326(5); O1–C6, 1.445(3); Ti–Cp (ring centroid), 2.024 (ave); Br1–Ti1–Br2, 103.05(2); O1–Ti1–Br1, 101.69(7); O1–Ti1–Br2, 101.88(7); and Ti1–O1–C6, 173.95(19).

Figure 7. Ti–O distances vs Ti–O–C angles in mononuclear Ti(IV) *tert*-butoxide complexes. Compounds from the present study are marked in red and are detailed in Table 1. Data are from the Cambridge Crystallographic Database.[65]

plane drawn through their centers. Consistent with the reduced coordination number, all of the distances to the metal have decreased relative to **4**. The Ti–Cp (centroid) distance is smaller in **5** by 0.067 Å and the Ti–Br distances are 0.10 Å shorter. The already short Ti–O distance in **4** is now reduced by 0.047 Å to 1.727 Å. The Ti–O–C angle in **5** is 173.9°, slightly but not appreciably different from the value in **4**.

2.3. Metal–Alkoxide Bonding. The new complexes described here provide a basis for re-examining the long-standing issue of the unusual geometries displayed by terminal transition-metal alkoxides.[61] It was noted over 20 years ago that many such alkoxides of the second- and third-row early transition metals and the lanthanides (e.g., Zr, Nb, Ta, and Sm) possess nearly linear M–O–R angles and short M–O distances, although there is no direct correlation between the distances and angles.[62,63] Several sources for the linear structures have been proposed, including steric crowding (bulkier alkoxides tend to display more linear M–O–R angles), π-bonding between occupied p orbitals of the oxygen and empty metal orbitals, or conversely, ionic interactions (i.e., $M^{\delta+}OR^{\delta-}$).[63] A role has also been assigned to electrostatic repulsion between the α-carbon of the alkoxide and the metal centers.[64] Confounding these explanations are difficulties with solid-state artifacts in crystallographic structures, that is, crystal packing effects and disordered ligands, which can obscure inferences made about bonding arrangements.

Even if a largely ionic interaction is a primary bonding contributor for the heavier metal alkoxides, the situation with the early first-row metals is not necessarily the same. A broad range of M–O–R angles has been observed in first-row alkoxide complexes, although as with the heavier metals, correlation between M–O distances and M–O–C angles is essentially nonexistent. For example, even when restricting examples to complexes comparable to those in the present study, that is, mononuclear Ti(IV) species with terminal *tert*-butoxide ligands, a plot of Ti–O distances versus Ti–O–C angles is effectively a random scatter (Figure 7).

Such randomness affects the plausibility of certain explanations for the observed Ti–O–C angles. For example,
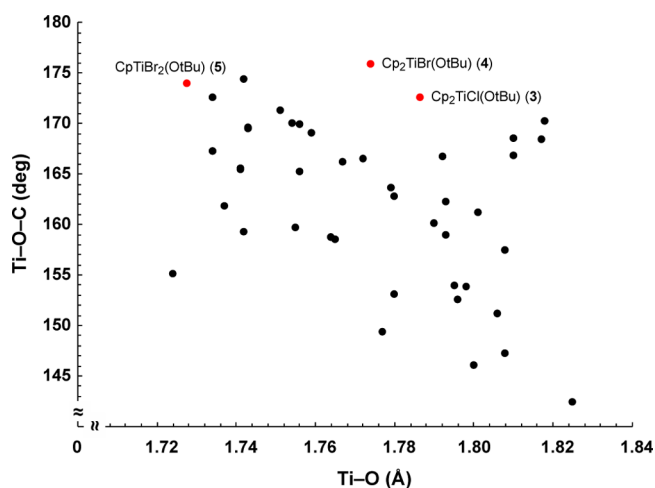
the steric bulk of the $-O^tBu$ ligand, which is obviously a fixed value, is not always accompanied by wide (ca. >160°) Ti–O–C bond angles. In addition, even the longest Ti–O bond in the set of complexes [1.825(4) Å] in $(OPy)_2Ti(O^tBu)_2$ (OPy = 2-pyridylmethoxy[66]) is well below the sum of the covalent radii of Ti and O (2.09 Å), making an ionic contribution to the bonding reasonable for all of the complexes.

The just-mentioned $(OPy)_2Ti(O^tBu)_2$ complex, which possesses two independent (nonsymmetry related) *tert*-butoxide ligands, also illustrates the importance of packing effects on experimentally determined bond distances and angles. Specifically, there are two independent molecules in its asymmetric unit[66] and between the four alkoxide ligands, the Ti–O bonds range from 1.790 Å to the previously noted 1.825 Å; the Ti–O–C angles vary from 142.4° to 162.2°. The large difference in angles ($\Delta = 19.8°$) for the small change in bond lengths ($\Delta = 0.035$ Å) underscores why correlation between the two variables cannot be expected to be strong, if it exists at all.

Even apart from such experimental difficulties, the alkoxide ligand is notoriously ambivalent in its bonding.[67,68] Depending on how the lone pairs on the oxygen interact with the metal, single, double, and (weak) triple covalent bonding can be envisaged or a purely ionic representation can be drawn as well; the latter two forms are consistent with wide M–O–R angles (Figure 8).

We were interested in the opportunity that the present set of complexes offered for illuminating the bonding involved in the $Cp_xTiX_y(OR)_{4-(x+y)}$ series. Calculations on isolated molecules remove the ambiguities of crystal packing effects, of course,
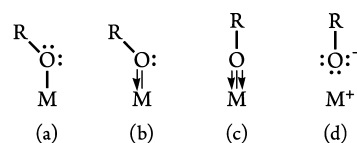

Figure 8. Bonding arrangements for the alkoxide ligand. Forms (a) and (b) represent single and double bonds, respectively; forms (c) and (d) are both compatible with near linear M–O–R bonds.

and also provide the opportunity to look for orbital evidence of M−L π-bonding.

2.4. Computational Results. Even considering the vagaries of crystal packing effects, preliminary density functional theory (DFT) calculations using the M06[69] and APF-D[70] global hybrid functionals provided somewhat disappointing reproductions of the crystallographic structures. Tests with the double hybrid B2PLYP functional,[71] which incorporates perturbative second-order correlation (PT2) obtained from the Kohn−Sham (GGA) orbitals and eigenvalues, were more encouraging and were used for subsequent studies. Not unexpectedly, reproducing angles is more difficult than bond distances (Table 1). Specific points about individual molecules are listed below.

2.4.1. Cp$_2$TiCl(OMe) (1). Although the calculated Ti−O−C angle of 136.8° is 4.6° smaller than that in the original room-temperature structure determination, it is only 1.7° smaller than that in the present redetermined low-temperature geometry, providing confidence that the latter is the more reliable figure.

2.4.2. Cp$_2$TiCl(O^{i}Pr) (2). The wide Ti−O−C angle of 160.0° found in the crystal structure cannot be reproduced by the B2PLYP calculations, which underestimates it by 12.3° [the underestimation is larger (15.4°) with the M06 functional], but the large difference supports the conclusion that the crystallographically observed value, suffering as it does from disorder both in the isopropoxy group and cyclopentadienyl rings, cannot be used uncritically. Other features of the molecule not directly involved in the disorder may be affected as well. The calculated Ti−Cl bond, for example, is 0.16 Å shorter than the crystallographically observed value.

2.4.3. Cp$_2$TiCl(O^{t}Bu) (3). The calculated Ti−O−C angle is smaller than the crystallographic value by 4.5° and the Ti−Cl and Ti−O bonds are in good agreement, with a mismatch of only 0.016 Å (under) and 0.014 Å (over), respectively.

2.4.4. Cp$_2$TiBr(O^{t}Bu) (4). The calculated Ti−O−C angle underestimates the crystallographic value by 5.2°; the Ti−Br and Ti−O bonds are slightly overestimated by 0.051 and 0.023 Å, respectively.

2.4.5. CpTiBr$_2$(O^{t}Bu) (5). The calculated Ti−O−C angle is larger than the crystallographic value by 5.0°; the Ti−Br and Ti−O bonds display good agreement, with a difference of only 0.003 Å (under) and 0.028 Å (over), respectively.

2.5. π-Bonding in Cyclopentadienyl Alkoxide Complexes. When there is no evidence for steric crowding or crystallographic disorder, a wide M−O−C angle accompanied by a shortened M−O bond is consistent with metal−ligand π-bonding.[72] Three of the new compounds reported here, **3**, **4**, and **5**, meet these structural criteria, as they have Ti−O−C angles >170° and Ti−O bonds of <1.80 Å. The bonding in **3** and **5** is discussed in detail.

An inspection of selected orbitals of **3** makes it obvious that two of them display evidence of π-bonding between Ti and O (Figure 9; the x axis is coincident with the Ti−O bond; the Cl lies in the xz plane). In MO#69 [highest occupied molecular orbital (HOMO) − 6, Figure 9a], Ti is involved in sigma bonding to Cl as well as π-type bonding to the oxygen. A natural bond orbital (NBO) analysis of the composition indicates that for oxygen, 98% of its contribution to the MO is from its 2p$_z$ orbital. For Ti, both its 3d$_{z^2}$ and 3d$_{xz}$ orbitals are involved, in a ratio of roughly 3:5. In MO#68 (HOMO − 7, Figure 9b), Ti is again involved in π-type bonding to the oxygen. The contribution from oxygen is 30.5% of the total
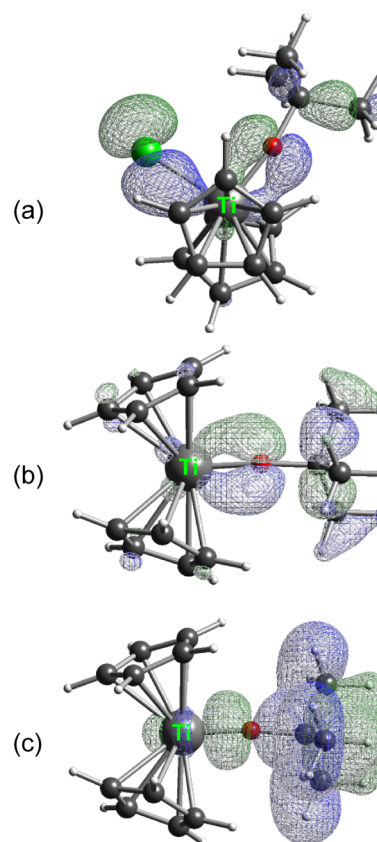

Figure 9. (a) MO#69 of Cp$_2$TiCl(O^{t}Bu). (b) MO#68 of Cp$_2$TiCl-(O^{t}Bu). The isodensity surface for the two orbitals is 0.050. (c) MO#48 of Cp$_2$TiCl(O^{t}Bu); isodensity surface = 0.025.

MO and 99% of this is from the 2p$_y$ orbital. Almost 84% of the contribution of titanium is from the 3d$_{xy}$ orbital, with smaller amounts from 3d$_{yz}$. Much lower in energy (MO#48) are orbitals that represent Ti−O sigma bonding (Figure 9c) and the C−H bonds in the O^{t}Bu ligand. More than 95% of the contribution of oxygen to the MO is from the 2p$_x$ orbital. Most of the contribution of titanium is from the 3d$_{x^2−y^2}$ orbital.

A similar arrangement of orbitals exists for **5**. In MO#76 (HOMO − 8, Figure 10a), Ti is involved in σ-bonding to Cl as well as π-type bonding to the oxygen. NBO analysis of the composition indicates that for oxygen, over 99% of its contribution to MO is from its 2p$_y$ orbital. For Ti, 88% of its contribution is from the 3d$_{xy}$ orbital. Complementary Ti−O π-bonding is found in MO#75 (HOMO − 9, Figure 10b), in which over 99% of the contribution of oxygen is from its 2p$_z$ orbital; almost 85% of the contribution of oxygen is from the 3d$_{xz}$ orbital, with 10.5% from the 4p$_z$. As is the case with **3**, the Ti−O σ interaction is substantially lower in energy (Figure 10c). In MO#57, the overlap is again primarily between the oxygen 2p$_x$ orbital and the Ti 3d$_{x^2−y^2}$ orbital.

The bonding picture presented here is closely related to that developed for the monocyclopentadienyl CpTiMe$_2$((O,S)Ar) complexes.[73] For the arylsulfide CpTiMe$_2$(SAr), a straightforward Lewis structure based on an sp^3-hybridized sulfur atom was sufficient to explain the bonding and geometrical arrangement of the Ti−SAr interaction. For the aryloxide analogue, in contrast, it was not possible to draw a satisfactory bonding picture in terms of a single classical Lewis structure and a resonance blend of forms c (with an sp-hybridized oxygen) and d (Figure 8) was proposed instead. It seems that
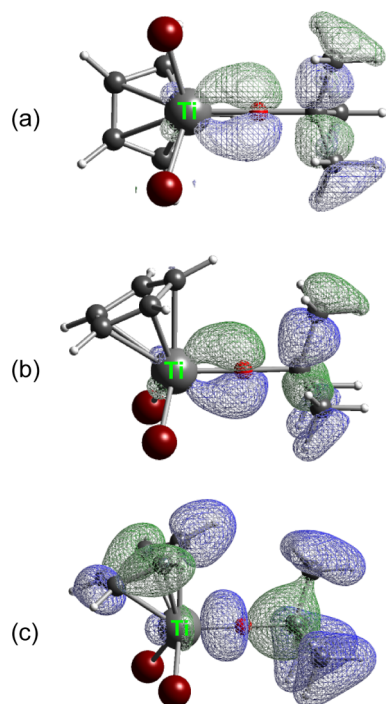
Figure 10. (a) MO#76 of CpTiBr$_2$(O^{t}Bu). (b) MO#75 of CpTiBr$_2$(O^{t}Bu). The isodensity surface for the two orbitals is 0.050. (c) MO#57 of CpTiBr$_2$(O^{t}Bu); isodensity surface = 0.035.

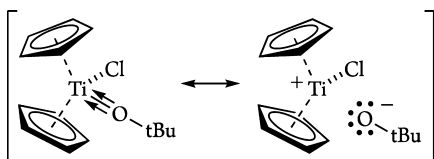the same situation largely applies to the present *tert*-butoxide complexes (Figure 11).

Figure 11. Limiting bonding arrangements for Cp$_2$TiCl(O^{t}Bu). Both extremes support a linear Ti−O−C bond angle.

Estimation of the covalency/ionicity in the Ti−O interaction in the alkoxide complexes is not straightforward. Natural population charges are relatively insensitive to basis set composition[74] and that on Ti is 0.56 and 0.49 for **3** and **5**, respectively. These are higher than the values of 0.12 and 0.06 for Cp$_2$TiCl$_2$ and Cp$_2$TiBr$_2$, respectively, and reflect the electron-withdrawing effect of the more electronegative oxygen and thus a greater ionic contribution to a resonance blend. Although as noted above, the Ti−O bond distances (1.73−1.79 for **3**−**5**) are far shorter than the sum of single-bond covalent radii (2.09 Å), they are close to the sum of double-bond radii (1.74 Å).[75] The Mayer bond order (MBO)[76,77] for the Ti−O bond of **3** and **5** is 1.08 and 1.23, respectively, suggestive of at least a full single bond. In contrast, the "fuzzy" bond order (FBO)[78] (numerically the same as the delocalization index calculated in "fuzzy" atomic space[79] and intended to reflect the number of electron pairs delocalized (shared) between two atomic spaces) of **3** and **5** is 1.80 and 2.07, respectively. As the MBO can tend to underestimate the total bond order and the FBO can overestimate it,[78] assigning an approximate bond order of ~1.5 seems reasonable.

3. CONCLUSIONS

Mechanochemical synthesis can be used to produce Cp$_x$TiX$_y$(O^{t}Bu)$_{4-(x+y)}$ (X = Cl, Br) complexes from the mixture of two or three starting materials, depending on whether bis(cyclopentadienyl) or mono(cyclopentadienyl) compounds are desired. Adjustment of the stoichiometric ratios of the reagents is reflected in the composition of the major products, although the outcomes are cleanest if the ratios are 1:1 (as in the production of **3**) or 1:1:1 (as in the formation of **5**). One noticeable advantage of the mechanochemical approach is that TiBr$_4$, which reacts at room temperature with ethereal solvents, can be used in the solid state without modification. This probably applies to solid TiI$_4$ as well and should make the synthesis of titanium-bromo and -iodo complexes more accessible, while also minimizing the use of solvents with environmental concerns.

All of the *tert*-butoxide complexes display the hallmarks of π-bonding between the titanium and alkoxide ligand, that is, short Ti−O bonds and wide (>170°) Ti−O−C angles. DFT calculations support this interpretation of the bonding, with a total bond order between 1 and 2.

It is notable that the calculations support an increasingly linear Ti−O−C angle in the order Me < Et < O^{i}Pr < O^{t}Bu, which comports with the increasing π-donor ability of the ligands. The X-ray crystal structures in general support this ordering, with the notable exception of the ethoxy complex Cp$_2$TiCl(OEt), whose Ti−O−C angle is the smallest of those studied here. We are at present unsure of the reason for this difference, unless crystal packing effects have a larger than expected influence on the geometry.

4. EXPERIMENTAL SECTION

4.1. General Considerations. All manipulations were performed with the exclusion of air and moisture using high vacuum, Schlenk, or glovebox techniques. All of the solid reagents are slightly to highly moisture-sensitive and/or air-sensitive and should be handled accordingly. Proton and carbon (^{13}C(^{1}H)) NMR spectra were obtained on a DRX-400 spectrometer at 400 (^{1}H) and 100.1 (^{13}C) MHz and were referenced to the residual proton and ^{13}C resonances of C$_6$D$_6$. Elemental analysis was performed by ALS, Tucson, AZ.

4.2. Materials. TiBr$_4$, LiO^{t}Bu, KO^{t}Bu, LiCp, and Cp$_2$TiCl$_2$ were purchased from commercial suppliers and used as received. Toluene and hexanes were distilled under nitrogen from potassium benzophenone ketyl.[80] Anhydrous THF was stored over molecular sieves. MeOH was obtained from MB-SPS. Isopropyl alcohol and triethylamine (TEA) were distilled and dried over CaH$_2$. C$_6$D$_6$ was vacuum-distilled from Na/K (22/78) alloy and stored over type 4A molecular sieves prior to use. Cp$_2$TiCl(OEt) was prepared according to the literature procedure.[47]

4.3. Mechanochemical Protocol. Ball-milling reactions used 50 stainless steel (440 grade) ball bearings [3/16 in. (5 mm), 0.44 g] that were thoroughly cleaned with hexanes and acetone prior to use. Planetary milling was performed with a Retsch PM100 mill, 50 mL stainless steel grinding jar type C, and a safety clamp for air-sensitive grinding. A typical reaction involved 300 mg total sample weight, sealed under an inert atmosphere. The ground mixture was extracted with minimal hexanes (<100 mL) and filtered through a medium porosity ground glass frit. The extraction is designed to dissolve the complex and the filtration removes traces of KCl or KBr. The

filtrate was then dried under vacuum prior to NMR analysis. In the case of $TiBr_4$ reactions, $TiBr_4$ was added to the grinding jar first, followed by LiCp and then $Li[O^tBu]$; this is to prevent the solid-state reaction of the alkoxide with $TiBr_4$.

4.3.1. Cp$_2$TiCl(OMe) (1). This was prepared following the literature procedure.[44] Cp_2TiCl_2 (0.502 g, 2.01 mmol) was added to a Schlenk flask containing 40 mL of THF and a magnetic stirrer bar. This was stirred at room temperature under N_2. To this mixture, TEA (0.52 mL, 3.7 mmol) and MeOH (0.16 mL, 3.9 mmol) were added. The reaction mixture was allowed to stir at room temperature for 16 h. THF was removed in vacuo. The resulting product was then extracted with toluene to yield an orange filtrate. Toluene was removed to afford 0.441 g (90% yield) of an orange solid. ^1H NMR (400 MHz, C_6D_6, 298 K): δ 4.06 ppm (s, 3H, CH_3), δ 5.88 (s, 10H, C_5H_5). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 70.7 (s, OCH_3), δ 117.0 (s, C_5H_5).

4.3.2. Cp$_2$TiCl(O^{i}Pr) (2). Cp_2TiCl_2 (0.500 g, 2.01 mmol) was added to a Schlenk flask containing 40 mL of THF and a magnetic stirrer bar. This was stirred at room temperature under N_2. To this mixture, TEA (0.29 mL, 2.08 mmol) and ^iPrOH (0.16 mL, 2.08 mmol) were added. The reaction mixture was allowed to stir at room temperature for 16 h. THF was removed in vacuo. The resulting product was then extracted with hexanes and filtered through a medium porosity glass-fritted glass filter. Hexane was removed, leaving an orange solid (0.241 g, 44%). ^1H NMR (400 MHz, C_6D_6, 298 K): δ 1.03 (d, 6H, $CH(CH_3)_2$), δ 4.48 (sept, 1H, $J = 6$ Hz, $CH(CH_3)_2$), δ 5.88 (s, 10H, C_5H_5). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 25.5 (s, $CH(CH_3)_2$), δ 84.1 (s, $CH(CH_3)_2$), 116.5 (s, C_5H_5). Anal. Calcd for $C_{13}H_{17}ClOTi$: C, 57.3; H, 6.3; Ti, 17.6. Found: C, 56.2; H, 5.9; Ti, 17.8.

4.3.3. Cp$_2$TiCl(O^{t}Bu) (3). Cp_2TiCl_2 (0.249 g, 1.00 mmol), $K[O^tBu]$ (0.113 g, 1.01 mmol), and 50 ball bearings were added to a grinding jar. The jar was sealed under an inert atmosphere and the reaction mixture was ground at 600 rpm for 15 min. Upon completion, the jar was opened under an inert atmosphere to reveal an orange solid which was then extracted with minimal hexanes and filtered through a fritted glass filter. The resulting orange filtrate was then dried, resulting in an orange solid (0.181 g, 63%). ^1H NMR (400 MHz, C_6D_6, 298 K): δ 1.12 (s, 9H, $OC(CH_3)_3$), δ 5.94 (s, 10H, C_5H_5). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 31.3 (s, CH_3), δ 87.8 (s $OC(CH_3)_3$), 116.6 (s, C_5H_5). Anal. Calcd for $C_{14}H_{19}ClOTi$: C, 58.7; H, 6.7; Ti, 16.7. Found: C, 58.5; H, 6.6; Ti, 16.9.

4.3.4. Cp$_2$TiBr(O^{t}Bu) (4). $TiBr_4$ (0.457 g, 1.24 mmol), $Li[O^tBu]$ (0.101 g, 1.26 mmol), LiCp (0.177 g, 2.46 mmol), and 50 ball bearings were added to a grinding jar. The jar was sealed under an inert atmosphere and the reaction mixture was ground at 600 rpm for 15 min. Upon completion, the jar was opened under an inert atmosphere to reveal an orange solid which was then extracted with minimal hexanes and filtered through a fritted glass filter. The resulting filtrate was then dried, resulting in an orange solid (0.214 g, 52%). The product also contains $CpTiBr(O^tBu)_2$; crystals of **4** can be obtained from hexanes. ^1H NMR of **4** (400 MHz, C_6D_6, 298 K): δ 1.10 (s, 9H $OC(CH_3)_3$), δ 5.92 (s, 10H, C_5H_5). ^{13}C NMR (100 MHz, C_6D_6, 298 K); δ 31.2 (s, $CH(CH_3)_2$), δ 88.4 (s, $CH(CH_3)_2$), 116.2 (s, C_5H_5).

4.3.5. CpTiBr$_2$(O^{t}Bu) (5). $TiBr_4$ (0.576 g, 1.57 mmol), $Li[O^tBu]$ (0.127 g, 1.59 mmol), LiCp (0.114 g, 1.58 mmol), and 50 ball bearings were added to a grinding jar. The jar was

sealed under an inert atmosphere and the reaction mixture was ground at 600 rpm for 15 min. Upon completion, the jar was opened under an inert atmosphere to reveal a yellow-brown solid which was then extracted with minimal hexanes and filtered through a fritted glass filter. The resulting yellow filtrate was then dried, resulting in a yellow solid (0.241 g, 44%). ^1H NMR (400 MHz, C_6D_6, 298 K): δ 1.14 (s, 9H C_4H_9), δ 6.16 (s, 10H, C_5H_5). ^{13}C NMR (100 MHz, C_6D_6, 298 K): δ 30.1 (s, CH_3), δ 92.6 (s $OC(CH_3)_3$), 118.0 (s, C_5H_5). Anal. Calcd for $C_9H_{14}Br_2OTi$: C, 31.25; H, 4.08. Found: C, 31.42; H, 3.96.

4.3.6. CpTiBr(O^{t}Bu)$_2$ (6). $TiBr_4$ (0.382 g, 1.04 mmol), $Li[O^tBu]$ (0.167 g, 2.09 mmol), LiCp (0.0747 g, 1.04 mmol), and 50 ball bearings were added to a grinding jar. The jar was sealed under an inert atmosphere and the reaction mixture was ground at 600 rpm for 15 min. Upon completion, the jar was opened under an inert atmosphere to reveal an orange paste that was then extracted with minimal hexanes and filtered through a fritted glass filter. The resulting yellow filtrate was then placed under vacuum, resulting in an orange oil (0.217 g, 62%). Analysis with ^1H NMR indicates that ca. 31% of the sample consisted of $Ti(O^tBu)_4$. ^1H NMR of **6** (400 MHz, C_6D_6, 298 K): δ 1.19 (s, 18H, C_4H_9), δ 6.22 (s, 5H, C_5H_5). ^{13}C (100 MHz, C_6D_6, 298 K): δ 31.8 (s, $CH(CH_3)_2$), δ 86.8 (s, $CH(CH_3)_2$), 115.0 (s, C_5H_5).

4.4. General Procedures for X-ray Crystallography. A suitable crystal of each sample was located, mounted in a polyimide loop, and mounted on an Agilent SuperNova (Dual, Cu at zero, EosS2) diffractometer. The crystals were maintained at 100 K (223 K for **2**) during data collection. Under Olex2,[81] the structure was solved with the SHELXT[82] structure solution program using direct methods and refined with the SHELXL[83] refinement package using least squares minimization. All nonhydrogen atoms were refined with anisotropic displacement parameters.

4.5. General Procedures for Calculations. All calculations were performed with the Gaussian 09W suite of programs.[84] The double hybrid B2PLYP functional,[71] which incorporates perturbative second-order correlation (PT2) that is obtained from the Kohn–Sham (GGA) orbitals and eigenvalues, was used for geometry optimization. The def2TZVP basis set was used on Ti, Cl, and Br; the def2SVP basis was used on all other atoms.[85] An ultrafine grid was used for all calculations (Gaussian keyword: int = ultrafine).

■ ASSOCIATED CONTENT

ⓈSupporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acsomega.8b00943.

> Crystallographic data for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as 1815544 ($CpTiBr_2(O^tBu)$), 1815545 ($Cp_2TiCl(O^tBu)$), 1815546 ($Cp_2TiCl(OMe)$), 1815547 ($Cp_2TiCl(O^iPr)$), 1815548 ($Cp_2TiCl(OEt)$), and 1815549 ($Cp_2TiBr(O^tBu)$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk) (ZIP)
>
> Optimized coordinates of all structures (XYZ)

Crystal data and summary of X-ray data collection for compounds **1−5**; thermal ellipsoid plot of Cp$_2$TiCl-(OEt); and ^{1}H NMR spectra of **4** and **6** (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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