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Metallo-Wittig Chemistry of an Alkylidene to Form a Terminal Titanium Oxo Complex

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Abstract

We report the synthesis and structure of a titanium (IV) benzophenone adduct bearing a terminal oxo ligand, $(PNP)Ti=O(OTf)(OCPh_2)$ $(PNP^- = N[2-P^iPr_2-4-methylphenyl]_2)$ (**2**). Complex **2** is readily synthesized in 71% yield from the previously reported titanium alkylidene $(PNP)Ti=CH^tBu(OTf)$ (**1**) and two equivalents of benzophenone, by extruding the olefin $Ph_2C=CH^tBu$. Treatment of benzophenone adduct **2** with a bulky aryloxide salt results in formation of $(PNP)Ti=O(OAr)$ (**3**) $(OAr^- =2,6-bis(diphenylmethyl)-4-tert-butylphenoxide)$, concurrent with salt elimination and displacement of the benzophenone. Complexes **2** and **3** were characterized by single-crystal X-ray diffraction and a variety of spectroscopic techniques, including NMR, UV-Vis-NIR spectroscopies, and TD-DFT calculations.

Introduction

Transition-metal oxo (M=O) complexes have been established over the last several decades as a major area of interest in the organometallic community.[1-2] In particular, transition metal oxo complexes are widely considered to be useful in systems that wish to accomplish selective oxo-transfer reactions in both stoichiometric and catalytic fashions.[3-4] Although transition metal oxo complexes have been extensively studied relative to other classes of metal-ligand multiple bonds, there are still limitations in the isolation of metal complexes bearing a terminal oxo ligand, especially when the metal in question is highly electropositive. This is particularly true in the case of group (IV) transition metals, which have a tendency to oligomerize[5] or undergo cycloaddition reactions.[6-7] Despite these propensities, there still exist examples of terminally bound titanium[8-16], zirconium[17], and hafnium[18] oxo complexes. A majority of these terminal titanium oxo examples are formed by means of oxidizing titanium (II) precursors or masked forms of low-valent titanium. Previously published work by Andersen,[8] Arnold,[9] Parkin,[10] and Chirik[11] demonstrate the versatility of oxidants available to generate terminal titanium (IV) oxo complexes. These oxidants include, but are not limited to, O_2, N_2O, and pyridine N-oxide (PyO). Additionally, work by Rothwell[12] and Floriani[13] utilize H_2O and CO, respectively, as oxygen atom sources with titanium (IV) precursors. More recently, Huang and coworkers demonstrated the synthesis of a titanium (IV) terminal oxo complex *via* cross-metathesis between CO_2 and a titanium (IV) imido.[14] In their report, a bis-ketiminate titanium imido complex $PhN=Ti[OCMeCHCMeN(Ar)]_2$ (Ar=2,6-diisopropylphenyl) was subjected to an atmosphere of CO_2 or CS_2 to generate the corresponding terminal oxo, $O=Ti[OCMeCHCMeN(Ar)]_2$ and sulfido $(S=Ti[OCMeCHCMeN(Ar)]_2)$ systems. Such a reaction compliments Mountford's work involving the metathesis of imides with unsaturated molecules like CO_2.[7] There are several well-known examples of metathesis reactions between early transition metal alkylidenes with organic molecules bearing a carbonyl group.[19] However, we are unaware of any reported group IV transition metal complexes with a terminal oxo ligand that are generated *via* cross-metathesis reactions using an alkylidene ligand. Intuitively, one would expect that using the relative strength of the Ti-O bond in relation to Ti=C species could offer a new path towards the isolation of unusual Ti(IV) complexes bearing a terminal oxo group and this approach could offer a mild entry to coordinatively unsaturated oxo species.

We decided to investigate the generation of a stable titanium complex bearing a terminal oxo ligand by way of a non-oxidation route. More specifically, we desired to develop a clean metathesis sequence that would produce such a complex without oxidation of the PNP-ligand framework. Furthermore, we sought to exclusively synthesize a titanium monomer bearing a *terminal* oxo ligand without the formation of titanium oxo dimers or oligomers. Despite a continuous interest in the generation of a terminal group IV oxo complex, we have yet to isolate a stable titanium compound bearing the pincer PNP scaffold $(PNP^- = N[2-P^iPr_2-4-methylphenyl]_2)$. Previously, we reported the oxidation of the olefin complex $(PNP)Ti(CH_2^tBu)(\eta^2-CH_2=CH_2)$ with 1 atm of N_2O at room temperature to generate the terminal oxo complex $(PNP)Ti=O(CH_2^tBu)$.[20] However, the complex is unstable at room temperature in solution. Herein, we report the synthesis and characterization of a terminal titanium-oxo adduct using benzophenone as the oxygen source. This compound can then be reacted with bulky aryloxide substrates to generate a stable, 5-coordinate titanium oxo-aryloxide complex under relatively mild conditions.

Results and Discussion

We reported the use of benzophenone as an oxygen atom source with the four-coordinate β-diketiminate alkylidene complex $(nacnac)Ti=CH^tBu(OTf)$ $(nacnac^- =[ArNC(^tBu)]_2CH$, Ar= 2,6-diisopropylphenyl) to form the oxo-triflate dimer $[(nacnac)Ti(\mu_2-O)(\mu_2-OTf)]_2$ in quantitative yield.[21] As a result of this dimerization product (via bridging of the oxo and OTf groups), we hypothesized that the use of the pincer ligand, PNP, would preserve a monomeric oxo compound given the higher coordination number at titanium. In addition, we demonstrated previously that the vanadium (III) precursor $(PNP)V(CH_2^tBu)_2$ could be oxidized with N_2O

to form a 5-coordinate vanadium (V) complex bearing a terminal V=O bond, namely (PNP)V=CH^{t}Bu(O).[22] Gratifyingly for us, heating a solution of (PNP)Ti=CH^{t}Bu(OTf) (**1**) and a stoichiometric equivalent of benzophenone in toluene overnight at 100 °C led to the formation of a new titanium species in ~50% yield when judged by ^{31}P{^{1}H} NMR spectroscopy. Adding a second equivalent of benzophenone resulted in complete consumption of **1** with clean formation of a new titanium species we proposed to be (PNP)Ti=O(OTf)(OCPh$_2$) (**2**) on the basis of multinuclear NMR spectroscopy (Scheme 1). Under the latter conditions, the crude reaction mixture was monitored by both ^{31}P{^{1}H} and ^{1}H NMR spectroscopy. In the ^{1}H NMR spectrum, the presence of an olefinic hydrogen signal at 6.12 ppm (corresponding to Ph$_2$C=CH^tBu) suggests that the new species forms by a metathesis-like process involving an alkylidene for oxo exchange. The ^{31}P{^{1}H} spectrum shows two new doublets at 26.23 ppm and 21.23 ppm ($^2J_{PP}$ = 69.9 Hz). Unfortunately, no intermediates are observed by both ^{1}H and ^{31}P NMR spectroscopy. Coordination of benzophenone in **2** is evident by ^{1}H NMR spectroscopy, with three broad resonances at 7.70 ppm, 7.11 ppm, and 7.03 ppm. We suspect that the hindered rotation of benzophenone in complex **2** is responsible for such broadening. The fact that one equivalent of ketone did not yield more that 50% of **2** suggests that binding of the ketone at the post-rate determining step is irreversible, even at 100 ^{o}C (Scheme 1). In other words, the intermediate [(PNP)Ti=O(OTf)] must be a powerful Lewis acid, and its formation is slow relative to binding of the ketone. However, in order to establish the presence of the oxo and degree of aggregation of this species, we obtained single crystals of this complex suitable for X-ray diffraction studies.

Scheme 1. Preparation of complex **2** by cross-metathesis between alkylidene **1** and benzophenone.
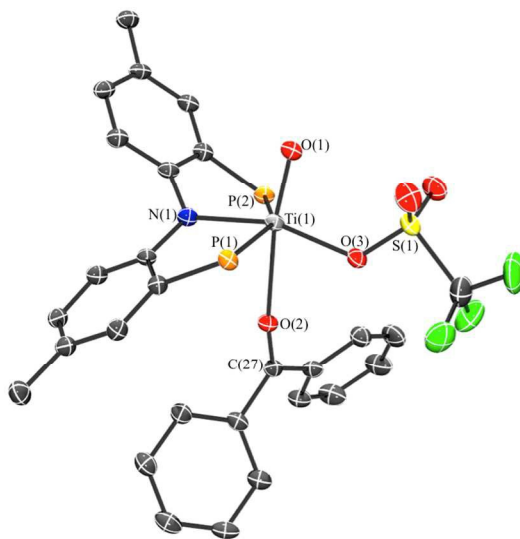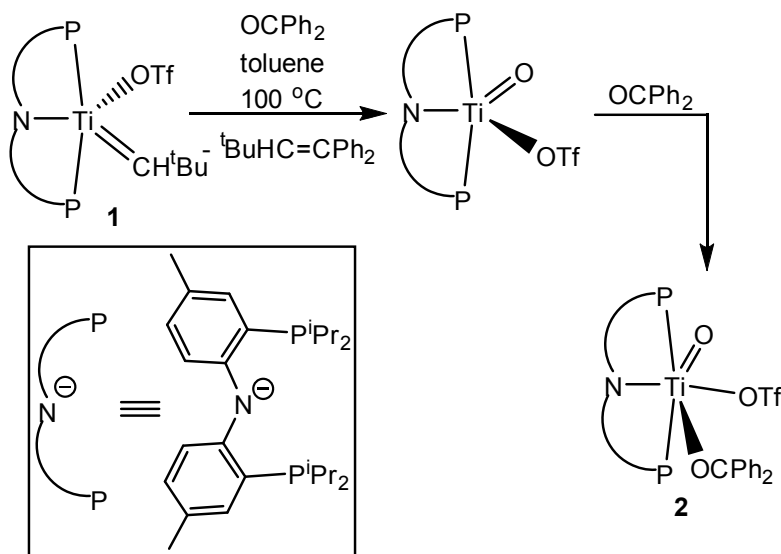

Figure 1. Molecular structure of compound **2**. Thermal ellipsoids are displayed at 50% probability level. Hydrogens and isopropyl groups on P1 and P2 have been omitted for clarity. A diethyl ether molecule co-crystallized with compound **2** was also

omitted. Selected bond lengths (Å) and angles (deg): Ti1–O1, 1.639(2); Ti1–O2, 2.300(2); Ti1–O3, 2.091(2); Ti1–P1, 2.608(1); Ti1–P2, 2.623(1); Ti1–N1, 2.055(2); O2–C27, 1.235(3); O1–Ti1–O2, 168.95(8); O1–Ti1–O3, 95.87(8); O3–Ti1–N1, 160.92(7); P1–Ti1–P2, 150.74(3); O1–Ti1–N1, 101.48(9); N1–Ti1–O2, 87.04(7); O3–Ti1–O2, 76.84(6); O1–Ti1–P1, 102.97(6); N1–Ti1–P1, 75.33(6); O3–Ti1–P1, 93.17(5); O2–Ti1–P1, 85.89(5); O1–Ti1–P2, 87.91(6); N1–Ti1–P2, 75.91(6); O3–Ti1–P2, 112.91(5); O2–Ti1–P2, 87.36(5).

As shown in Figure 1, the molecular structure of **2** reveals formation of a mononuclear titanium complex having a terminal oxo ligand. Due to coordination of the benzophenone, the geometry at titanium is best described as pseudo-octahedral with the oxo and benzophenone ligands coordinated transoid (O=Ti–O(benzophenone) = 168.96(8)°). The PNP ligand framework adopts a meridional configuration, with the tolyl groups lacking co-planarity (C_1 symmetric). The most notable feature, however, is the presence of a terminal Ti=O bond with a length of 1.639(2) Å that falls well within range of previously reported terminally-bound titanium oxo complexes.[8-16] The Ti–O(benzophenone) bond length in **2** is 2.300(2) Å, longer than that of previously reported titanocene (III)[23a,23b] and titanium (IV)[23c] ketone complexes. Furthermore, the C=O bond length for the coordinated benzophenone was determined to be 1.235(3) Å, only slightly longer than that of free benzophenone and significantly shorter than that of a ketyl radical (~1.30 Å).[24] Hence, the ketone is merely coordinated as a Lewis base to the Ti(IV) center.

Compound **2** can be isolated as a stable, purple colored solid, and is thermally stable up to ~100 °C in C_6D_6 solution over several days. To our knowledge, compound **2** is a rare example of a transition metal complex bearing a terminal oxo ligand and a coordinated benzophenone. Few examples of this type exist and have been reported with vanadium[25] and molybdenum.[26] Due to the complex's deep purple color, which is rather unexpected for a d^0 group IV metal, we collected electronic absorption spectra for **2** using UV-Vis-NIR spectroscopy. Intuitively, one would not anticipate the intense color observed to be due to chemical reduction of the ketone moiety to a ketyl radical since the complex contains a titanium (IV) center, but the presence of a lone-pair and low-lying π^* orbital on the ketone moiety could also account for a low-energy transition. An electronic transition responsible for the color is observed at 511 nm (ε = 661 M^{-1} cm^{-1}). However, we could not definitively determine the origin of the absorption based on UV-Vis-NIR spectroscopy alone, since the electronic transition observed at 511 nm could be the result of a forbidden transition between the PNP framework (lone pair on nitrogen) and the titanium center (d orbital), or a forbidden transition between the PNP framework and the π^* of the coordinated benzophenone. Interestingly, Roesky and co-workers studied and characterized a calcium complex bearing a bound benzophenone and a β-diketiminate ligand, and hypothesized that the distinct color change of the complex from clear to red was the result of a charge transfer from the electron rich β-diketiminate ligand or bridging hydroxyl groups to the bound ketone π^*.[27] To assist in determining the electronic transitions associated with compound **2**, time dependent density functional theory (TD-DFT) studies were performed on a full model. We decided to investigate compound **2** using the B3LYP functional because of its relative simplicity and its reliability with respect to the study of transition metal complexes. Geometry optimization of the electron diffraction-based coordinates resulted in little change in bond distances and angles from the original crystal structure, indicating good agreement between experimental and computed values. As a note, the optimized Ti=O bond length using DFT was calculated to be 1.623(1) Å, which is well in agreement with that found in the solid structure of **2**. However, the computed structure displays some noticeable bond elongation with respect to the titanium center and the benzophenone ligand (Ti–O, 2.484(1) Å). Optimization of the structure for compound **2** and the corresponding UV-Vis simulation (in n-hexane solvent) predicts an electronic transition at 513.88 nm to be originated from exciting of an electron from the HOMO (orbital 196, left, Figure 2) to the LUMO+1 (orbital 198, right, Figure 2). The orbital representations proposed to be responsible for this transition are displayed in Figure 2 below.
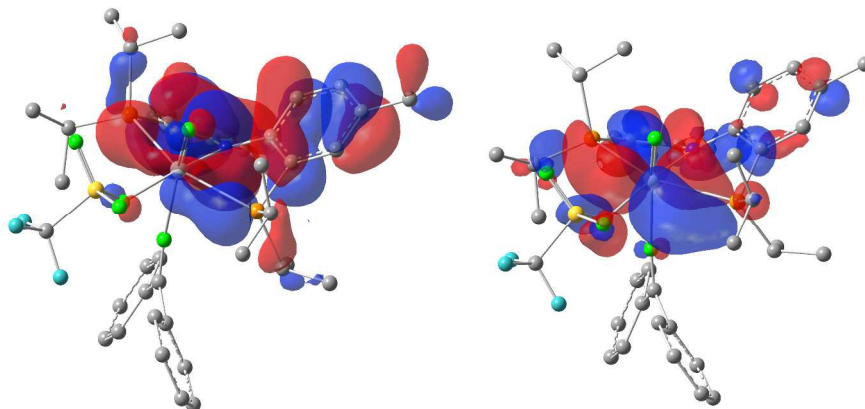

Figure 2: Time Dependent Density Function Theory simulation of the electronic transition in **2** from the HOMO (orbital 196, left) to the LUMO+1 (orbital 198, right). Oxygen atoms are colored green for clarity.

The HOMO orbital (Figure 2, left) shows primarily PNP aryl ligand character. There is however, a small p-orbital contribution found on the terminal titanium oxo, which is perpendicular to the orbitals localized on the PNP tolyl groups. The LUMO+1 orbital (orbital 198, Figure 2, right) is primarily metal based in d* character (d_{xy}). The HOMO representation (pointed along z) is oriented perpendicular to the vacant d orbital, therefore indicating a symmetry forbidden LMCT electronic transition. This feature aligns well with the experimentally determined molar extinction coefficient of ε = 661 M^{-1} cm^{-1} (*vide supra*). Although the LUMO (orbital 197) for compound **2** is primarily localized about the benzophenone ligand (See Supporting Information), TD-DFT studies predict this transition HOMO-LUMO (PNP aryl ligand → π* of the O=C bond in benzophenone) to occur at 648 nm. DFT calculations do in fact suggest that such a transition is symmetry forbidden and that it is not visible by UV-Vis-NIR spectroscopy even when **2** is present at higher concentrations (ε was calculated to be essentially zero).

With compound **2** in hand, we looked into preparing a benzophenone-free, and five-coordinate titanium oxo. Accordingly, we decided to use a sterically encumbering ligand that would not react with the benzophenone. Since benzophenone occupied another coordination site to satisfy a powerful Lewis acid, we decided to transmetallate **2** with the sterically encumbering aryloxide ligand NaOAr (OAr⁻= 2,6-bis(diphenylmethyl)-4-tert-butylphenoxide). This ligand has been demonstrated to stabilize mononuclear niobium complexes containing metal-ligand multiple bonds and could serve as a π-donor ligand.[28] Stirring a solution of **2** and NaOAr in benzene at room temperature overnight leads to a gradual color change from deep purple to orange brown, concurrent with precipitation of a salt. Multinuclear NMR spectroscopic data are in accord with formation of a single new metal complex, namely (PNP)Ti=O(OAr) (**3**), along with the formation of free benzophenone (Scheme 2). The ^{31}P{^{1}H} NMR spectrum contains overlapping doublets at 22.70 ppm and 21.66 ppm. As expected, the $^2J_{PP}$ value for five-coordinate **3** ($^2J_{PP}$ = 73.0 Hz) is slightly larger than that of six coordinate **2** ($^2J_{PP}$ = 69.9 Hz). Interestingly, the aryloxide methine resonances (C*H*Ph$_2$) in the ^{1}H NMR spectrum experience significantly different chemical environments, since they appear at very different chemical shifts at 8.11 ppm and 6.11 ppm. This disparity in the chemical shifts is most likely correlated to the proximity of some of the methine hydrogens in the aryloxide ligand to the terminal oxo ligand (Figure 3). To ascertain the degree of aggregation of this presumed lower-coordinate titanium oxo and to visualize the orientation of the -CHPh$_2$ groups in the –OAr ligand, we obtained single crystal X-ray diffraction data of **3**. Indeed, our structural data confirm the loss of benzophenone and the formation of a five-coordinate, mononuclear titanium oxo complex, **3** (Figure 3).

Scheme 2. Preparation of compound **3** *via* transmetallation with NaOAr and benzophenone displacement from **2**.
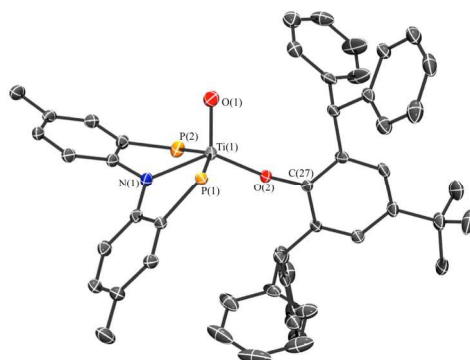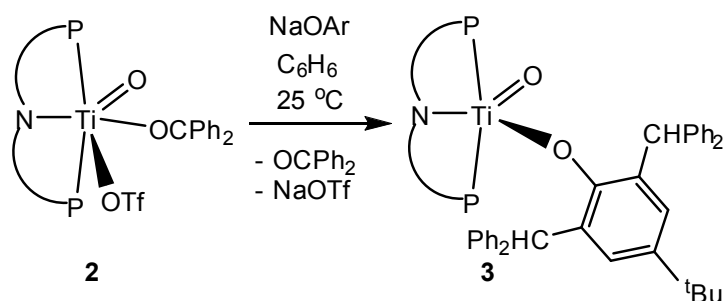
Figure 3. Molecular structure of compound **3**. Thermal ellipsoids are displayed at 50% probability level. Hydrogens and isopropyl groups on P1 and P2 have been omitted for clarity. A toluene molecule co-crystallized with compound **3** was omitted for clarity. Selected bond lengths (Å) and angles (deg): Ti1–O1, 1.656(2); Ti1-O2, 1.868(2); Ti1–P1, 2.587(1); Ti1–P2, 2.592(1); Ti1–N1, 2.111(2); O2–C27, 1.347(3); P1–Ti1–P2, 147.22(3); O1–Ti1–P1, 97.82(7); O1–Ti1–P2, 95.51(7); O1–Ti1–O2, 114.06(9);

O1–Ti1–N1, 112.04(9); O2–Ti1–P1, 101.73(6); O2–Ti1–P2, 99.88(6); O2–Ti1–N1, 133.86(8); N1–Ti1–P1, 73.47(6); N1–Ti1–P2, 73.77(6).

As depicted in Figure 3, the solid-state structure of **3** displays a pseudo-square pyramidal geometry (τ_5 = 0.22)[29] with the O=Ti–O$_{Ar}$ bond angle of 114.06(9)°, a value slightly higher than that of the angles O=Ti–P$_{PNP}$ (97.82(7)°) and O=Ti–N$_{PNP}$ (112.04(9)°). This feature may be attributed to the sterics associated with the aryloxide ligand, particularly with respect to the proximity of the aryloxide phenyl groups to the PNP-based isopropyl groups. The terminal titanium oxo distance (1.656(2) Å), is very similar to the previously synthesized five-coordinate titanium oxo species reported by Arnold (1.654(2) Å),[9] and Guilard *et. al.* (1.613(5) Å),[15] as well as the oxo unit the bis-ketiminate complex (O=Ti[OCMeCHCMeN(Ar)]$_2$) synthesized by Huang (1.620(2) Å).[14] We expect that such an elongation is not necessarily due to the change in coordination number, but instead due to the presence of the strongly π-donating aryloxide ligand. Geometry optimization and TD-DFT UV-Vis simulations were also conducted on compound **3**. Not surprisingly, the transition responsible for the vibrant orange color (466 nm, ε = 1643 M^{-1} cm^{-1}) most likely stems from a HOMO (orbital 245) to a LUMO (orbital 246) transition, and such transition involves is a forbidden LMCT from the aryl framework of the PNP ligand to an empty d_{xy} orbital on the titanium(IV) center (See Supporting Information). Figure 4 displays the computed HOMO and LUMO orbitals of compound **3**. Instead of antibonding interactions between the d_{xy} orbital of the titanium center and the PNP framework in the LUMO, an antibonding configuration is apparent between the Ti(IV) metal center and the aryloxide ligand. Such features are well in agreement with the TD-DFT findings of compound **2** and further confirm that the purple color found in **2** is not likely due to the bound benzophenone.
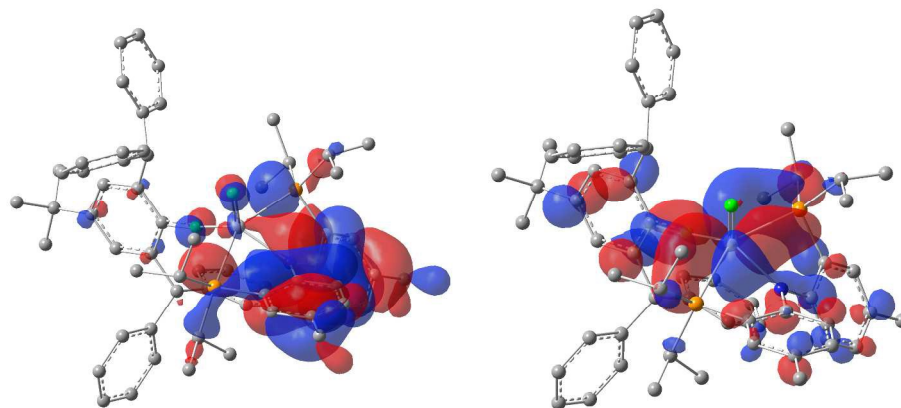

Figure 4: Time Dependent Density Function Theory simulation of the electronic transition in **3** from the HOMO (orbital 245, left) to the LUMO (orbital 246, right). Oxygen atoms are colored green for clarity.

Bulky aryloxide salts proved to be successful transmetallation reagents with **2**. When the aryloxide salt Na(ODipp) (ODipp$^-$ = 2,6-diisopropylphenoxide) was added to a solution of **2** in benzene under similar conditions, a clean conversion from **2** to the proposed species (PNP)Ti=O(ODipp) was detected by ^{31}P{^{1}H} NMR analysis. However, this complex is unfortunately unstable in solution, and we were unable to obtain spectroscopic data as well as structural evidence. Thus, we confirmed that a significant amount of steric bulk is necessary for the stabilization of titanium terminal oxo complexes using this particular pincer scaffold. We believe benzophenone coordination in **2** is indispensable in stabilizing the terminal oxo group. However, the fact that **2** can be formed cleanly under a depleted amount of ketone suggests transient [(PNP)Ti=O(OTf)] to not only be a powerful Lewis acid, but an isolable species since no degradation was observed under these conditions.

In conclusion, we report the synthesis and structural identification of a titanium (IV) oxo complex stabilized by a benzophenone and a pincer scaffold PNP. We also report preliminary reactivity studies of the oxo complex **2**, particularly those involving sterically encumbering aryloxide ligands. The use of a sterically encumbering aryloxide can yield a five-coordinate titanium oxide, concurrent with benzophenone and salt extrusion. The origin of such unique colors (purple for **2**, and bright orange for **3**) was probed using UV-vis-NIR spectroscopy in conjunction with TD-DFT calculations. Our results suggest the observable electronic transitions in **2** and **3** to derive from the PNP framework orbitals to a low-lying d* orbital on titanium.

Experimental Procedure

General Considerations
Unless otherwise stated, all operations were performed in a M. Braun Lab Master double-dry box under an atmosphere of purified nitrogen or using high vacuum standard Schlenk techniques under an argon atmosphere. Benzene, diethyl ether (Et$_2$O), n-pentane, hexanes, and toluene were purchased from Fisher Scientific. Solvents were sparged with argon for 20 minutes and dried using a two-column solvent purification system where columns designated for benzene, n-pentane, hexanes, and toluene were packed with Q5 and alumina respectively and columns designated for Et$_2$O were packed with alumina. All solvents were

stored over 4Å molecular sieves and sodium after being transferred to a glove box. Benzene-d_6 (C$_6$D$_6$, Cambridge Isotope Laboratories), was degassed by three consecutive freeze-pump-thaw cycles in a Schlenk line and placed over sodium or molecular sieves for at least 24 hours prior to use. (PNP)Ti=CH^{t}Bu(OTf) (**1**) (PNP =N[2-P(CHMe$_2$)$_2$-4-methylphenyl]$_2^-$)[30] and NaOAr (OAr$^-$ = 2,6-bis(diphenylmethyl)-4-tert-butylphenoxide)[28a] were prepared according to the reported procedures. Benzophenone (99%, pure) was purchased from Acros Organic and used as received. ^{1}H and ^{13}C{^{1}H} NMR spectra were recorded on a Bruker AVII500B Fourier transform NMR spectrometer equipped with a 5 mm BBO ATM z-gradient probe. ^{31}P{^{1}H}, and ^{19}F{^{1}H} NMR were recorded on a Bruker DRX360 Fourier transform NMR spectrometer. ^{1}H and ^{13}C{^{1}H} chemical shifts are reported referenced to the internal residual proton or carbon resonances of C$_6$D$_6$ (δ = 7.160 ppm (^{1}H) and 128.06 ppm (^{13}C{^{1}H})). ^{31}P{^{1}H} NMR chemical shifts are reported with respect to external H$_3$PO$_4$ (δ 0.0 ppm). ^{19}F{^{1}H} NMR chemical shifts are reported with respect to external HOCOCF$_3$ (δ = −78.5 ppm). UV-Vis spectroscopy was collected on a Cary 5000 UV-Vis-NIR spectrophotometer, with the samples being prepared in an inert atmosphere and measured for absorbance in a dry 10 mm path length quartz cuvette. Elemental analyses were performed by Robertson Microlit Laboratories.

Synthesis of (PNP)Ti=O(OTf)(OCPh$_2$) (2)

Complex **1** (332 mg, 0.467 mmol, 1 eq.) was added to a 20 mL scintillation vial and dissolved in 15 mL of toluene. Benzophenone (285 mg, 1.56 mmol, 3.3 eq.) was then added as a solid to the dark red solution and stirred for 30 minutes at room temperature. The solution was transferred to a thick-walled storage flask and heated overnight at 100 °C. A color change from dark red to purple is observed over the course of several hours. The solution is cooled to room temperature and dried *in vacuo*. The resulting purple oil was extracted with diethyl ether (20 mL), filtered, and the filtrate dried *in vacuo*. The purple solid was dissolved in ~3 mL of n-pentane and stored at −35 °C overnight, where a dark, purple crystalline solid is formed. The dark purple solid was quickly filtered, washed with cold pentane (2 x 5 mL), and dried *in vacuo* to give purple solid **2** (276 mg, 0.335 mmol 71.7%). Crystals suitable for X-ray diffraction were grown from a concentrated ether/pentane solution stored at −35 °C. **^{1}H NMR (23 °C, 500.39 MHz, C$_6$D$_6$):** δ 7.74-7.66 (br s, Ar-C*H* (benzophenone), 4H), 7.20 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HP}$ = 4.2 Hz, Ar-C*H*, 1H), 7.14-7.08 (br m, Ar-C*H* (benzophenone), 2H), 7.08-6.97 (br m, Ar-C*H* (benzophenone), 4H), 6.93 (dd, $^3J_{HH}$ = 8.5 Hz, $^4J_{HP =}$ 2.0 Hz, Ar-C*H*, 1H), 6.84 (dd, $^3J_{HH}$ = 6.2 Hz, $^4J_{HP}$ = 2.4 Hz, Ar-C*H*, 1H), 6.81 (d, $^3J_{HH}$ = 4.1 Hz, Ar-C*H*, 1H), 6.80 − 6.76 (m, Ar-C*H*, 1H), 6.69 (dd, $^3J_{HH}$ = 6.7 Hz, $^4J_{HP}$ = 2.0 Hz, Ar-C*H*, 1H), 2.26 − 2.20 (m, PC*H*(CH$_3$)$_2$, 1H), 2.18 (m, PC*H*(CH$_3$)$_2$, 1H), 2.12 (s, ArC*H$_3$*, 3H), 2.16–2.07 (m, PC*H*(CH$_3$)$_2$, 1H), 2.05 (s, ArC*H$_3$*, 3H), 2.08–1.99 (m, PC*H*(CH$_3$)$_2$ 1H), 1.53 − 1.33 (m, PCH(C*H$_3$*)$_2$, 6H), 1.32 − 1.08 (m, PCH(C*H$_3$*)$_2$, 6H), 1.02 (dd, $^3J_{HP}$ = 16.6 Hz, $^3J_{HH}$ = 7.0 Hz, PCH(C*H$_3$*)$_2$, 3H), 0.95 − 0.77 (m, PCH(C*H$_3$*)$_2$, 6H), 0.72 (dd, $^3J_{HP}$ = 11.0 Hz, $^3J_{HH}$ = 6.9 Hz, PCH(C*H$_3$*)$_2$, 3H). **^{13}C{^{1}H} NMR (23 °C, 125.82 MHz, C$_6$D$_6$):** δ 195.75 (s, O=C*P*h$_2$), 160.00 (d, $^1J_{CP}$ = 20.4 Hz, Ar-C*H*), 157.81 (dd, $^1J_{CP}$ = 19.2 Hz, $^3J_{CP}$ = 3.0 Hz, Ar-C*H*), 138.30 (Ar-C*H*, benzophenone), 133.60 (dd, $^1J_{CP}$ = 15.3 Hz, $^3J_{CP}$ =2.0 Hz, Ar-C*H*), 132.97 (s, Ar-C*H*), 132.64 (d, $^2J_{CP}$ = 4.7 Hz, Ar-C*H*), 132.45 (s, Ar-C*H*), 132.12 (s, Ar-C*H*, benzophenone), 130.24 (s, Ar-C*H*, benzophenone), 129.56 (d, $^2J_{CP}$ = 5.1 Hz, Ar-C*H*), 120.17 (d, $^2J_{CP}$ = 7.2 Hz, Ar-C*H*), 118.30 (d, $^1J_{CP}$ = 31.7 Hz, Ar-C*H*), 117.30 (d, $^2J_{CP}$ = 8.1 Hz, Ar-C*H*), 116.65 (d, $^1J_{CP}$ = 32.2 Hz, Ar-C*H*), 24.46 (d, J_{CP} = 13.0 Hz, PCH(C*H$_3$*)$_2$), 22.92 (d, J = 10.6 Hz PCH(C*H$_3$*)$_2$), 20.89 (s, Ar-C*H$_3$*), 20.74 (d, $^1J_{CP}$ = 18.0 Hz, PCH(C*H$_3$*)$_2$), 20.53 (s, Ar-C*H$_3$*), 20.32 (d, $^1J_{CP}$ = 17.8 Hz, PCH(C*H$_3$*)$_2$), 19.96 (d, $^2J_{CP}$ = 7.0 Hz, PCH(C*H$_3$*)$_2$), 19.09 (d, $^2J_{CP}$ = 5.9 Hz, PCH(C*H$_3$*)$_2$), 18.24 (d, $^2J_{CP}$ = 8.6 Hz, PCH(C*H$_3$*)$_2$), 17.85 (d, $^2J_{CP}$ = 4.4 Hz, PCH(C*H$_3$*)$_2$), 17.75 (d, $^2J_{CP}$ = 8.6 Hz, PCH(C*H$_3$*)$_2$), 16.45 (d, $^2J_{CP}$ = 4.4 Hz, PCH(C*H$_3$*)$_2$), 16.04 (d, $^2J_{CP}$ = 6.6 Hz, PCH(C*H$_3$*)$_2$) (carbon resonances for the triflate group could not be located) **^{31}P{^{1}H} NMR (23 °C, 145.78 MHz, C$_6$D$_6$):** δ 26.23 (d, $^2J_{PP}$ = 69.9 Hz), 21.23 (d, $^2J_{PP}$= 69.9 Hz) **^{19}F{^{1}H} NMR (23 °C, 338.86 MHz, C$_6$D$_6$):** δ -76.41 (s, OSO$_2$C*F$_3$*) **UV-Vis-NIR (hexanes, λ$_{max}$/nm (ε/M^{-1}cm^{-1})):** 274 (sh, 15494), 302 (6762), 511 (br, 661). Anal. Calcd. For C$_{40}$H$_{50}$F$_3$NO$_5$P$_2$STi: C, 58.33; H, 6.12; N, 1.70. Found: C, 58.32; H, 6.16; N, 1.63.

Synthesis of (PNP)Ti=O(OAr) (3)

Complex **2** (53 mg, 0.064 mmol, 1 eq.) was added to a 20 mL scintillation vial and dissolved in 5 mL of benzene. The solution was then stored in the freezer (−35 °C) for 30 minutes, resulting in a frozen purple solid. Then, the solid was taken out of the freezer and gradually warmed to room temperature, during which NaOAr (OAr$^-$=2,6-bis(diphenylmethyl)-4-tert-butylphenoxide) (36 mg, 0.071 mmol, 1.1 eq.) was added in the solid state under vigorous stirring. The reaction was stirred overnight at room temperature. After several hours, the mixture color changed from a dark purple solution to an orange brown suspension. The suspension was then dried *in vacuo*, resulting in an orange solid. The desired complex was extracted with n-pentane (3 x 10 mL) and filtered over a glass frit. The resulting orange filtrate was then concentrated to ~2 mL and stored in the freezer overnight. The orange precipitate was washed with cold pentane (2 x 5 mL) to afford **3** (50 mg, 0.051 mmol) in 79.7% yield. Crystals suitable for X-ray diffraction were grown from a concentrated toluene/pentane solution stored at −35 °C. **^{1}H NMR (23 °C, 500.39 MHz, C$_6$D$_6$):** δ 8.11 (s, C*H*(Ph)$_2$, 1H), 7.91 (d, $^3J_{HH}$ = 7.1 Hz, Ar-C*H*, 2H), 7.70 (d, $^3J_{HH}$ = 6.9 Hz, Ar-C*H*, 1H), 7.62 (d, $^3J_{HH}$ = 7.3 Hz, Ar-C*H*, 2H), 7.57 (d, $^4J_{HP}$ = 2.6 Hz, Ar-C*H*, 1H), 7.34 − 7.26 (m, Ar-C*H*, 4H), 7.17 (m, Ar-C*H*, 2H), 7.15 − 6.96 (m, Ar-C*H*, 12H), 6.94 (dd, $^3J_{HH}$ = 8.6 Hz, $^4J_{HP}$ = 2.1 Hz, Ar-C*H*, 1H), 6.90 (dd, $^3J_{HH}$ = 5.8 Hz, $^4J_{HP}$ = 2.0 Hz, Ar-C*H*, 1H), 6.87 (dd, $^3J_{HH}$ = 8.4 Hz, $^4J_{HP}$ = 2.0 Hz, Ar-C*H*, 1H), 6.79 (dd, $^3J_{HH}$ = 6.0 Hz, $^4J_{HP}$ = 2.0 Hz, Ar-C*H*, 1H), 6.11 (s, C*H*(Ph)$_2$, 1H), 2.23 − 2.18 (m, PC*H*(CH$_3$)$_2$, 1H), 2.17 (s, ArC*H$_3$*, 3H), 2.15 (s, ArC*H$_3$*, 3H), 2.13 − 2.08 (m, PC*H*(CH$_3$)$_2$, 1H), 1.62 − 1.52 (m, PC*H*(CH$_3$)$_2$, 1H), 1.51 − 1.41 (m, PCH(C*H$_3$*)$_2$, 6H), 1.25 − 1.18 (m, PC*H*(CH$_3$)$_2$, 1H), 1.15 (s, 9H), 1.13 (d, $^3J_{HH}$ = 6.9 Hz, PCH(C*H$_3$*)$_2$, 3H), 1.02 (ddd, J_{HP} = 22.1 Hz, $^3J_{HP}$ = 16.2 Hz, $^3J_{HH}$ = 6.9 Hz, PCH(C*H$_3$*)$_2$, 6H), 0.70 (dd, $^3J_{HP}$ = 9.8 Hz, $^3J_{HH}$ = 6.8 Hz, PCH(C*H$_3$*)$_2$, 3H), 0.55 (dd, $^3J_{HP}$ = 15.0 Hz, $^3J_{HH}$ = 7.1 Hz, PCH(C*H$_3$*)$_2$, 3H), 0.48 (dd, $^3J_{HP}$ = 15.4, Hz $^3J_{HH}$ = 7.1 Hz, PCH(C*H$_3$*)$_2$, 3H) **^{13}C{^{1}H} NMR (23 °C, 125.82 MHz, C$_6$D$_6$):** δ 160.62 (dd, $^1J_{CP}$ = 20.4 Hz, $^3J_{CP}$ =

3.6 Hz, Ar-CH), 159.30 (s, Ar-CH), 147.44 (s, Ar-CH), 146.84 (s, Ar-CH), 146.33 (s, Ar-CH), 144.49 (s, Ar-CH), 141.29 (s, Ar-CH), 138.31 (s, Ar-CH), 134.39 (s, Ar-CH), 133.10 (d, $^2J_{CP}$ = 8.1 Hz, Ar-CH), 132.59 – 132.32 (m, Ar-CH), 132.11 (s, Ar-CH), 131.31 (s, Ar-CH), 130.96 (d, $^1J_{CP}$ = 12.7 Hz, Ar-CH), 130.32 (s, Ar-CH), 130.24 (s, Ar-CH), 129.79 (d, $^3J_{CP}$ = 3.7 Hz, Ar-CH), 128.70 (s, Ar-CH), 128.60 (s, Ar-CH), 128.51 (s, Ar-CH), 128.35 (s, Ar-CH), 127.97 (s, Ar-CH), 127.67 (s, Ar-CH), 119.54 (d, $^1J_{CP}$ = 29.4 Hz, Ar-CH), 118.59 (d, $^2J_{CP}$ = 7.2 Hz, Ar-CH), 118.08 (d, $^2J_{CP}$ = 6.8 Hz, Ar-CH), 117.45 (d, $^1J_{CP}$ = 29.9 Hz, Ar-CH), 49.79 (s, CH(Ph)$_2$), 48.81 (s, CH(Ph)$_2$), 31.64 (s, C(CH$_3$)), 25.27 (d, $^1J_{CP}$ = 10.9 Hz, PCH(CH$_3$)$_2$), 22.37 (dd, $^2J_{CP}$ = 7.8 Hz, $^4J_{CP}$ = 2.2 Hz, PCH(CH$_3$)$_2$), 20.80 (d, $^2J_{CP}$ = 6.7 Hz, PCH(CH$_3$)$_2$), 20.24 – 19.82 (m, PCH(CH$_3$)$_2$), 19.49 (s, Ar-CH$_3$), 19.40 (d, $^1J_{CP}$ = 9.8 Hz, PCH(CH$_3$)$_2$), 18.95(s, Ar-CH$_3$), 18.88 (d, $^2J_{CP}$ = 6.7 Hz, PCH(CH$_3$)$_2$), 18.64 (d, $^2J_{CP}$ = 4.6 Hz, PCH(CH$_3$)$_2$), 18.25 (d, $^2J_{CP}$ = 5.8 Hz, PCH(CH$_3$)$_2$), 17.40 (s, PCH(CH$_3$)$_2$), 15.47 (d, $^2J_{CP}$ = 6.7 Hz, PCH(CH$_3$)$_2$). (resonances for quaternary carbons could not be located). **^{31}P{^{1}H} NMR (23°C, 145.78 MHz, C$_6$D$_6$)**: δ 22.70 (d, $^2J_{PP}$ = 72.5 Hz, PNP), 21.66 (d, $^2J_{PP}$ = 73.0 Hz, PNP) **UV-Vis-NIR (hexanes, λ$_{max}$/nm (ε/M^{-1}cm^{-1}))**: 227 (13156), 335 (7210), 466 (br, 1643). Anal. Calcd. for C$_{62}$H$_{73}$NO$_2$P$_2$Ti: C, 76.45; H, 7.55; N, 1.44. Found: C, 78.09; H, 7.38; N, 1.08.

X-ray Crystallographic Studies

Crystallographic data for **2** and **3** are summarized in the Supporting information (Table S3). Suitable crystals for X-ray analysis of **2** and **3** were placed on the end of a Cryoloop coated in NVH oil. X-ray intensity data was collected on a Bruker APEXII CCD area detector employing graphite-monochromated Mo-Kα radiation (λ=0.71073 Å) at a temperature of 100(1)K. Preliminary indexing was performed from a series of thirty-six 0.5° rotation frames with exposures of 10 seconds. Rotation frames were integrated using SAINT,[31] producing a listing of unaveraged F^2 and σ(F^2) values which were then passed to the SHELXTL[32] program package for further processing and structure solution.

For **2**, the intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[33] The structure was solved by direct methods (SHELXS-97).[34] Refinement was by full-matrix least squares based on F^2 using SHELXL-2014.[35] All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model. There were a total of 2.5 diethyl ether molecules present in the asymmetric unit. There was a region of disordered solvent for which a reliable disorder model could not be devised. The X-ray data were corrected for the presence of disordered solvent using SQUEEZE.[36] The use of SQUEEZE corrected the presence of six diethyl ether molecules (250 electrons) in the unit cell, or 1.5 diethyl ether molecules per asymmetric unit.

For **3**, the intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS. The structure was solved by direct methods SHELXS-97. Refinement was by full-matrix least squares based on F^2 using SHELXL-2014. All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined using a riding model.

Computational Studies

The computations were performed using the Research Center for Computational Science, Okazaki, Japan. Density functional calculations were carried out using the Gaussian09 program.[37] DFT methods were performed at B3LYP level by using 6-31G(d) basis set for H, C, N, O, F and S, LanL2DZ basis for P, and LanL2TZ for Ti. The model structures were optimized from the initial structures based on the experimental solid-state geometry of **2** and **3**. For **2**, orbitals were calculated for the complete structure with 40 frozen core electrons. For **3**, orbitals were calculated for the complete structure with 30 frozen core electrons. The optimized structures were considered true minima if they did not exhibit imaginary vibration modes. TD-DFT calculations were performed with n-hexane as the solvent.

Supporting Information

Crystallographic data for compounds **2** (1472932) and **3** (1472933) have been submitted to The Cambridge Crystallographic Data Centre (CCDC). The data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/structures. Tables, NMR spectra for complexes **2** and **3** can be found in the ESI.

Acknowledgements

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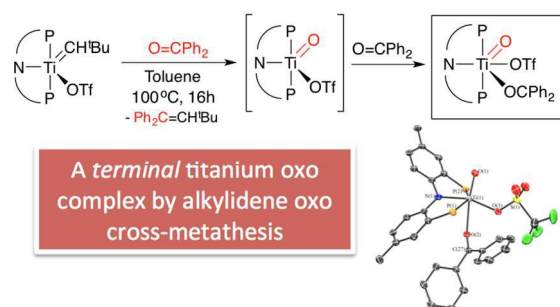
Caption: The synthesis and characterization of a terminal titanium oxo complex generated by alkylidene benzophenone cross-metathesis is reported.