ORGANOMETALLICS

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Reactivity Studies of a Zirconium Methylidene Complex: Group Transfer and Methylenation Reactions

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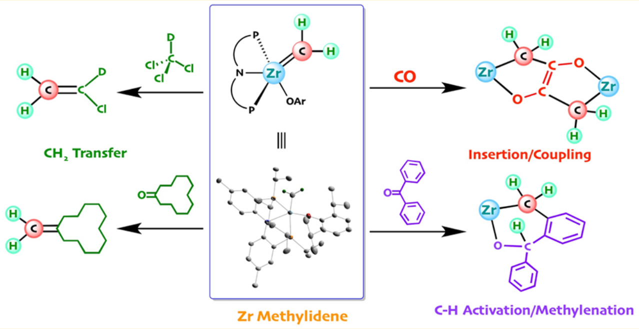
Ⓢ *Supporting Information*



ABSTRACT: The zirconium methylidene complex (PNP)Zr═CH$_2$(OAr) (**1**; PNP = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$, Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$), prepared from photolysis of (PNP)Zr(CH$_3$)$_2$(OAr), can engage in incomplete and complete methylidene group transfer reactions with CO, CDCl$_3$, cyclododecanone, and benzophenone. When CO was treated with **1**, methylenation occurred via the putative metalloketene adduct [(PNP)Zr(OCCH$_2$)(OAr)], which ultimately afforded the C−C coupled enolate dimer [(PNP)Zr(OAr)]$_2$(OCH$_2$C═CCH$_2$O) (**2**). Addition of CDCl$_3$ to **1** rapidly resulted in formation of (PNP)ZrCl$_2$(OAr) (**3**) along with liberation of d_1-vinyl chloride, H$_2$C═CDCl. Complex **3** could be readily prepared independently from (PNP)ZrCl$_3$ and 1 equiv of NaOAr. Wittig reactivity was observed between **1** and cyclododecanone to afford methylenecyclododecane. Similarly, treating **1** with the ketone OCPh$_2$ resulted in methylenation of the ortho position followed by tautomerization to produce the chelated alkyloxide complex (PNP)Zr(OAr)[OCHPh(C$_6$H$_4$)-CH$_2$] (**4**). In addition to the isolation of **4**, complex **1** also engages in a cross-metathesis reaction involving the methylidene and ketone oxygen of benzophenone, as well as in olefin metathesis involving the formed olefin H$_2$C═CPh$_2$. Complexes **2**−**4** have been fully characterized, including solid-state structural analysis, and proposed mechanisms for the formation of species such as **2**−**4** are presented and discussed.

In 1980, Schwartz and Gell reported the synthesis of the first mononuclear zirconium methylidene, Cp$_2$Zr═CH$_2$(PPh$_2$Me), from the oxidation of Cp$_2$Zr(PMePh$_2$)$_2$ with excess H$_2$CPPh$_3$ at 42 °C.[1] Given the propensity of Cp$_2$Zr═CH$_2$(PPh$_2$Me) to decompose under these conditions, the chemistry of the methylidene ligand was largely restricted to hydrolytic reactions involving HO^{t}Bu (by forming CH$_4$) or with reagents such as MeI which would then form ethane upon hydrolysis of the mixture.[1] Nine years later, Grubbs and co-workers recognized the titanium derivative Cp$_2$Ti═CH$_2$(PR$_3$) (PR$_3$ = PMe$_3$, PEt$_3$, PMe$_2$Ph) to be even more reactive, therefore being only stable at −40 °C in the case of the PMe$_3$ adduct (the most stable derivative).[2] Its chemistry with unsaturated molecules such as CO, olefins, and alkynes was also reported.[2]

Using a hindered set of ligand scaffolds, PNP and OAr (PNP$^-$ = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$, OAr$^-$ = O-2,6-^{i}Pr$_2$C$_6$H$_3$), we recently reported the isolation and first structural characterization of a terminally bound zirconium methylidene complex, (PNP)Zr═CH$_2$(OAr) (**1**), which adopts a square-pyramidal structure and has a short Zr═C bond of 2.038(6) Å.[3] The hafnium analogue (PNP)Hf═CH$_2$(OAr) was also reported but not structurally characterized.[3] The precursor to **1**, (PNP)Zr(CH$_3$)$_2$(OAr), is prepared in three simple steps involving (i) transmetalation of Li(PNP) with ZrCl$_4$ (originally reported by Ozerov and co-workers)[4] followed by (ii) transmetalation of (PNP)ZrCl$_3$ with 3 equiv of MeMgCl to form (PNP)Zr(CH$_3$)$_3$ (also reported originally by Ozerov and co-workers)[4] and finally (iii) protonation of the latter with HOAr to produce (PNP)Zr(CH$_3$)$_2$(OAr) and CH$_4$ (Scheme 1).[3] Photolysis of (PNP)Zr(CH$_3$)$_2$(OAr), which absorbs at λ_{max} 310 nm, with 254−355 nm light cleanly promoted α-hydrogen abstraction to afford methylidene **1** in 95% yield. In this work, we wish to report the reactivity of a kinetically stable zirconium methylidene with small molecules such as CO and CDCl$_3$ as well as with aliphatic versus aromatic ketones. In the latter reaction we observe a competitive process involving Wittig-like chemistry versus methylenation of an aromatic C−H bond. Such chemistry complements and parallels reported reactivity studies of tantalum methylidenes.[5,6]

■ RESULTS AND DISCUSSION

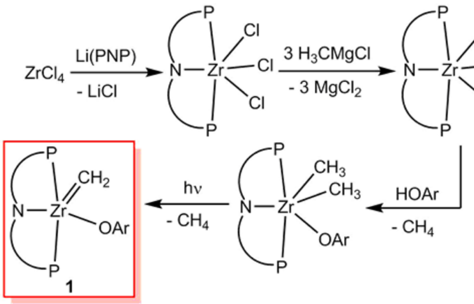
Schrock-like bridging methylidenes[7] have been seldom reported to react with CO to form oligomeric ketene species. With the terminal methylidene **1** in hand, we inquired if this species would react differently when it was confronted with CO. Accordingly, exposure of **1** to 1 atm of CO resulted in clean conversion to a new species when the reaction mixture was examined by ^{1}H and ^{31}P NMR spectroscopy. In the ^{1}H NMR

Special Issue: Hydrocarbon Chemistry: Activation and Beyond

Received: July 26, 2016

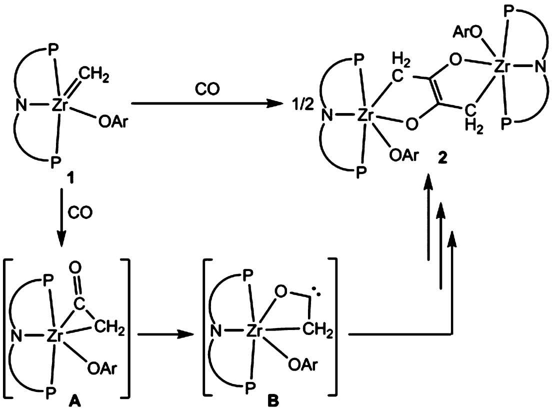
DOI: 10.1021/acs.organomet.6b00594

Scheme 1. Synthesis of the Methylidene Complex 1 from Three Simple Steps Using the Starting Material $ZrCl_4$[a]



[a]The fourth step involves photolysis of $(PNP)Zr(CH_3)_2(OAr)$ in benzene. The ligands PNP and aryl group of the alkoxide have been simplified for clarity (PNP = $N[2\text{-}P^iPr_2\text{-}4\text{-methylphenyl}]_2^-$ and Ar = $2,6\text{-}^iPr_2C_6H_3$).

Scheme 2. Synthesis of Complex 1 and Subsequent Carbonylation to Afford the Ketene Coupled Product 2[a]



[a]The ligands PNP and aryl group of the alkoxide have been simplified for clarity (PNP = $N[2\text{-}P^iPr_2\text{-}4\text{-methylphenyl}]_2^-$ and Ar = $2,6\text{-}^iPr_2C_6H_3$).

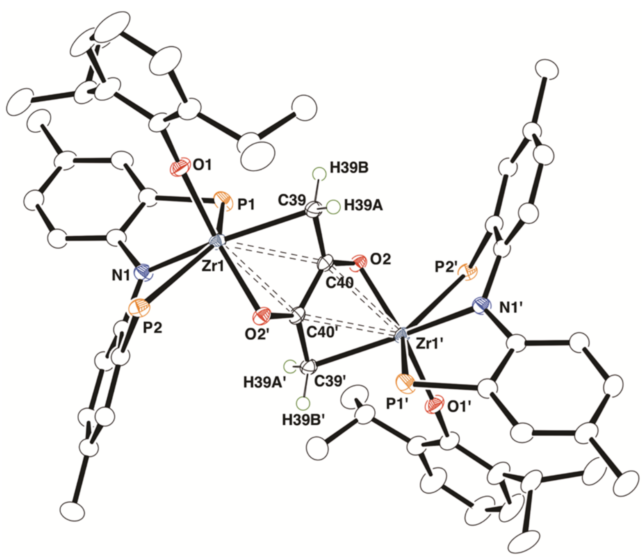
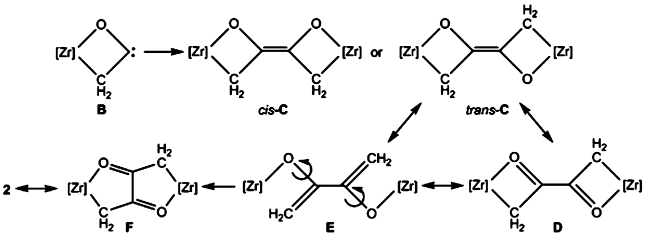


Figure 1. Molecular structure of **2** displaying thermal ellipsoids at the 50% probability level. Solvent (pentane), ^iPr groups of PNP, and H atoms, with the exception of α-hydrogens, have been omitted for clarity. Bond distances (Å) and angles (deg): Zr1−P1, 2.7551(5); Zr1−P2, 2.8095(5); Zr1−N1, 2.2079(15); Zr1−O1, 1.9996(12); Zr1−O2′, 2.0604(12); Zr1−C39, 2.3126(17); Zr1−C40, 2.5315(16); Zr1−C40′, 2.6411(17); C39−C40, 1.462(2); C40−C40′, 1.412(3); P1−Zr1−P2, 140.371(15); P1−Zr1−N1, 69.75(4); P1−Zr1−O1, 93.66(4); P1−Zr1−O2′, 124.26(4); P1−Zr1−C39, 81.27(4); P2−Zr1−N1, 70.81(4); P2−Zr1−O1, 88.09(4); P2−Zr1−O2′, 71.45(3); P2−Zr1−C39, 137.82(4); N1−Zr1−O1, 98.16(5); N1−Zr1−O2′, 106.59(5); N1−Zr1−C39, 147.90(6); O1−Zr1−O2′, 139.83(5); O1−Zr1−C39, 97.14(6); O2′−Zr1−C39, 78.23(5).

spectrum, distinct resonances at 3.69 (overlapping resonances), 6.51, and 6.58 ppm were observed as doublets of doublets consistent with the CH_2 hydrogens being diastereotopic. The $^{31}P\{^1H\}$ NMR spectrum displays four singlets at −2.62, −2.01, 30.46, and 30.73 ppm, and the high-field-shifted ^{31}P resonances indicate the presence of weakly bound phosphines to the metal center from each PNP ligand.[8] These significantly different features in NMR spectra reveal a C_1-symmetrical dinuclear system being retained in solution where the P arms couple weakly, if at all. A solid-state X-ray diffraction study confirmed this new species to be the enolate dimer $[(PNP)Zr(OAr)]_2[O(CH_2)C{=}C(CH_2)O]$ (**2**) (Scheme 2). As shown in Figure 1, complex **2** displays two "$(PNP)Zr^{IV}(OAr)$" units bridged by the tetraanionic and planar dienolate ligand $[O(CH_2)C{=}C(CH_2)O]^{4-}$, where the methylene and oxo groups chelate each metal center while the C=C group (1.412(3) Å) allows for bridging across two metal centers. A list of some important metrical parameters for **2** is given in the caption to Figure 1. The C_4O_2 core, which is situated in a special position with a crystallographic inversion center, is planar. The five-membered ZrC_3O ring is puckered with dihedral angles of 37.5° (Zr−C−C−C) and 51.7° (Zr−O−C−C). The short Zr−C distances between the zirconium center and the new C=C bond (2.5315(16) and 2.6411(17) Å) indicate η^4 coordination of the $[O(CH_2)C{=}C(CH_2)O]$ unit to each metal center in a $\sigma^2\pi^1$ fashion, similar to that observed in zirconacyclopentene complexes.[9] The formation of **2** is proposed to occur via addition of CO across the $Zr{=}CH_2$ multiple bond to form a parent ketene intermediate, $[(PNP)Zr(OAr)(\eta^2\text{-}OCCH_2)]$. As shown in Scheme 2, the bonding of the ketene could also take place through the O=C motif of the ketene (Scheme 2 depicts a C−C bonded ketene) and these systems have been structurally characterized.[7c,10] Such species have been observed in reactions involving CO and bridging methylidenes.[7] From a species such as $[(PNP)Zr(OAr)(\eta^2\text{-}OCCH_2)]$ (**A**), rearrangement to a thermodyamically stable Zr−O bond would occur to form the electrophilic oxy-carbene species $[(PNP)Zr(OAr)(O{-}C{-}CH_2)]$ (**B**) or its canonical form $[(PNP)Zr(OAr)(O^+{=}C^-{-}CH_2)]$ (Scheme 2). O-rich, stabilized carbenes of this type have been observed in dinuclear titanium species.[11] As shown in Scheme 3, in the case of putative **B**, C=C coupling most likely occurs to form dimer *cis*-**C** or *trans*-**C**, which can exist as alternate forms **D** and **E**. To isomerize, species **D** most likely resonates to **E**, which allows for cleavage of the Zr−C bond (the Zr−O bond can also be cleaved, but this is expected to be more thermodynamically difficult), followed by C−C rotation and then ring expansion of the μ-dienolate ligand via the transient Zr(III)−Zr(III) intermediate **F**. Reduction of the $[O(CH_2)C{=}C(CH_2)O]^{2-}$ group in **F** results in formation of the ligand scaffold $\mu\text{-}\eta^4{:}\eta^4\text{-}[O(CH_2)C{=}C(CH_2)O]^{4-}$ in complex **2**. A combination of conjugation and more favorable

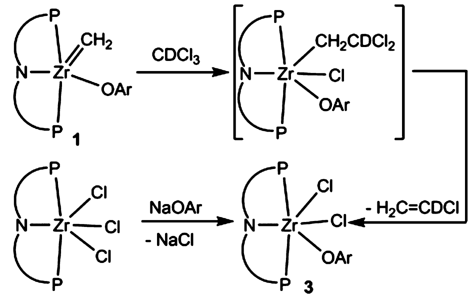
Scheme 3. Proposed Intermediates to the Ketene Coupled Product 2 Stemming from Species A[a]



[a]The ligands PNP and aryl group of the alkoxide have been omitted for clarity.

5-membered metallo rings in **2** most likely promote this type of isomerization.

Scheme 4. Synthesis of Complex 3[a]



[a]The ligands PNP and aryl group of the alkoxide have been simplified for clarity (PNP = N[2-P^{i}Pr$_2$-4-methylphenyl]$_2^-$ and Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$).

We then explored the ability of **1** to deliver the methylidene group to halo-alkanes. Dissolving **1** in $CDCl_3$ results in clean formation of a single new Zr species, (PNP)$ZrCl_2$(OAr) (**3**), along with the vinyl chloride $H_2C{=}CDCl$ (Scheme 4). While **3** could be readily separated from the reaction mixture due to its limited solubility, the formation and quantification of the olefin were established via a combination of ^{1}H NMR and ^{2}H NMR spectroscopy. In the ^{1}H NMR spectrum (Figure S12 in the Supporting Information), complex **3** shows signatures for the aryloxide (3.44 ppm for the methine hydrogens of ^{i}Pr groups), whereas the ^{31}P NMR spectrum (Figure S6 in the Supporting Information) reveals a singlet at 15.98 ppm consistent with such species possessing overall C_s symmetry in solution. A solid-state structure confirmed the presence of two chlorides with retention of the "(PNP)Zr^{IV}(OAr)" unit (Figure 2). Formation of **3** from **1** most likely proceeds via 1,2-CCl addition across the $Zr{=}CH_2$ bond to form a transient dichloroethyl ligand in [(PNP)ZrCl(CH_2CDCl_2)(OAr)], which then eliminates *β*-chloride to form the second chloride ligand with extrusion of vinyl chloride (Scheme 4). As a note, complex **3** could be independently prepared, in a more direct manner in 79% isolated yield, by addition of 1 equiv of NaOAr to (PNP)$ZrCl_3$ (Scheme 4).

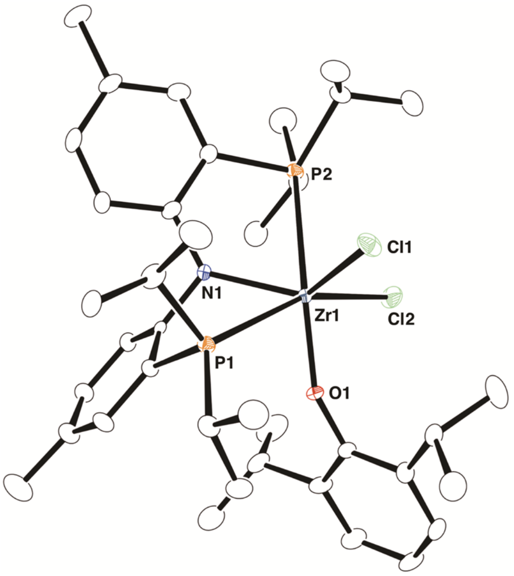
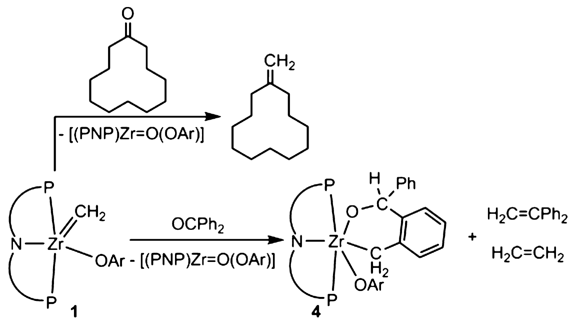


Figure 2. One molecular structure of the two independent molecules **3** in the asymmetric unit displaying thermal ellipsoids at the 50% probability level. H atoms have been omitted for clarity. Bond distances (Å) and angles (deg): Zr1−C1, 2.4772(14); Zr1−Cl2, 2.4005(14); Zr1−P1, 2.8603(15); Zr1−P2, 2.8247(13); Zr1−N1, 2.143(4); Zr1−O1, 1.945(3); Cl1−Zr1−Cl2, 99.05(5); Cl1−Zr1−P1, 160.25(4); Cl1−Zr1−P2, 76.32(4); Cl1−Zr1−N1, 121.15(12); Cl1−Zr1−O1, 83.87(11); Cl2−Zr1−P1, 87.41(5); Cl2−Zr1−P2, 89.78(4); Cl2−Zr1−N1, 125.24(12); Cl2−Zr1−O1, 111.87(10); P1−Zr1−P2, 122.62(4); P1−Zr1−N1, 67.44(11); P1−Zr1−O1, 76.41(11); P2−Zr1−N1, 68.22(11); P2−Zr1−O1, 152.79(10); N1−Zr1−O1, 108.21(15).

Scheme 5. Treatment of 1 with Aliphatic and Aromatic Ketones To Produce Olefins as well as Complex 4

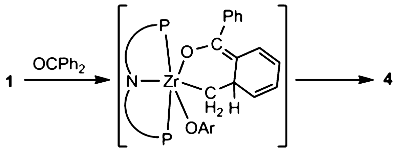


When a ketone such as cyclododecanone is added to **1**, an immediate reaction takes place to yield methylenecyclododecane (Scheme 5). The fate of the [(PNP)Zr=O(OAr)] was never determined, and examination of the reaction mixture revealed the formation of numerous Zr products, despite methylenecyclododecane being produced nearly quantitatively. This result implies that the cross-metathesis of the methylidene for oxo is clean but that the [(PNP)Zr=O(OAr)] product is unstable under these reaction conditions. We recently observed the complex [(PNP)Ti=O(OAr)] to be unstable in solution as well.[12]

Addition of benzophenone to **1** results in a different outcome. Examination of the reaction mixture after 30 min by ^{31}P NMR spectroscopy (Figure S17 in the Supporting Information) reveals formation of multiple metal products akin to those observed in the cyclododecanone reaction. However, in the reaction mixture a new Zr-based product could be identified, given the presence of two doublets having $^2J_{PP}$ = 54 Hz. The ^{1}H NMR spectrum (Figure S16 in the Supporting Information) revealed formation of the olefins $H_2C{=}CPh_2$ and $H_2C{=}CH_2$ among several other products. The presence of $H_2C{=}CPh_2$ suggests **1** to be undergoing Wittig-like reactivity with the ketone, whereas the observation of $H_2C{=}CH_2$

(formed in trace quantities) implies **1** to be reacting via olefin cross-metathesis with $H_2C{=}CPh_2$. Workup of the reaction mixture allowed for the isolation of the new asymmetric complex (PNP)Zr(OAr)[$OCHPh(C_6H_4)CH_2$] (**4**), where the ortho position of the aryl in benzophenone has been methylenated (Scheme 6). Compound **4** is most likely produced via nucleophilic attack of the methylidene at the ortho CH position of benzophenone. Since this disrupts the aromaticity, a 1,3-hydrogen shift must take place to form **4** (Scheme 6).

Scheme 6. Proposed Mechanism in the Formation of 4 from 1 and $OCPh_2$



Complex **4** crystallizes from a pentane solution at −35 °C in the orthorhombic space group $Pca2_1$, and selected bond lengths and angles are given in the caption of Figure 3. The solid-state molecular structure of **4** shows the ortho position being methylated along with a long C−O bond (1.409(7) Å). Interestingly, the space group this complex crystallizes in is achiral despite the presence of a chiral carbon (C39) in the molecule. Although the asymmetric unit contains the two enantiomers with a Flack parameter of −0.04(2), the packing diagram shows both enantiomers to be present with pentane along the 2_1 screw axis, resulting in a polar packing system $Pca2_1$.

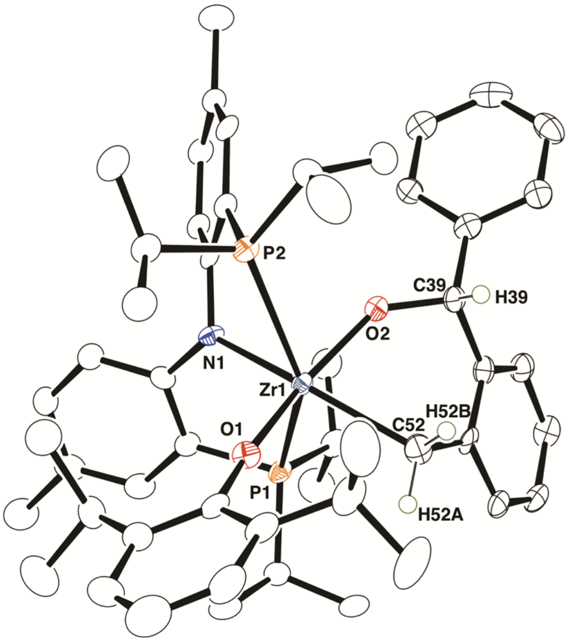


Figure 3. Molecular structure of **4** displaying thermal ellipsoids at the 50% probability level. Solvent (pentane) and H atoms, with the exception of α- and β-hydrogens, have been omitted for clarity. Bond distances (Å) and angles (deg): Zr1−P1, 2.7603(15); Zr1−P2, 2.7968(15); Zr1−N1, 2.202(4); Zr1−O1, 1.983(4); Zr1−O2, 1.963(4); Zr1−C52, 2.323(6); O2−C39, 1.409(7); P1−Zr1−P2, 142.82(5); P1−Zr1−N1, 70.97(12); P1−Zr1−O1, 95.70(13); P1−Zr1−O2, 103.27(12); P1−Zr1−C52, 85.79(17); P2−Zr1−N1, 71.88(11); P2−Zr1−O1, 91.54(12); P2−Zr1−O2, 80.26(12); P2−Zr1−C52, 130.18(17); N1−Zr1−O1, 103.62(19); N1−Zr1−O2, 93.39(18); N1−Zr1−C52, 152.2(2); O1−Zr1−O2, 157.86(17); O1−Zr1−C52, 93.46(19); O2−Zr1−C52, 76.88(19); Zr1−O2−C39, 141.9(3).

■ CONCLUSIONS

The chemistry of the zirconium methylidene functionality has been explored in this report. Whereas **1** reacted with CO to form a transient parent ketene species that coupled to form **2**, the use of haloalkanes such as $CDCl_3$ resulted in complete "CH_2" group transfer to form $H_2C{=}CDCl$ and the dichloride species **3**. Such reactivity is in contrast with the more coordinately saturated tantalum methylidene $Cp_2Ta{=}CH_2(CH_3)$, which is known to be stable in chlorocarbons.[5] Wittig-like reactivity could be observed when **1** was treated with cyclododecanone, while the use of benzophenone resulted in two different pathways: metathesis to form the olefin as well as methylenation of the ortho C−H group to ultimately form **4**. Overall, the reactivity of the methylidene ligand in **1** with benzophenone parallels Arnold's tantalum methylidene $[tolylC(NSiMe_3)_2]_2Ta{=}CH_2(CH_3)$ (tolyl = p-$CH_3C_6H_5$) reactivity with *N*-oxides.

■ EXPERIMENTAL SECTION

General Procedures. All operations were performed in an M. Braun glovebox under a nitrogen atmosphere or using standard Schlenk techniques under an argon atmosphere unless otherwise stated. Anhydrous solvents were purchased from Fisher Scientific or Aldrich. All anhydrous solvents were purified and dried by passage through two columns of activated alumina and Q-5 drying agent in a Grubbs-type solvent system. Hexamethyldisiloxane (HMDSO) was dried by passage through one column of activated alumina. All bulk solvents were kept over sodium and 4 Å molecular sieves. Deuterated benzene (benzene-d_6, Cambridge Isotope Laboratories) was dried and degassed over a potassium mirror prior to use. Deuterated chloroform (chloroform-d_1, Cambridge Isotope Laboratories) was distilled from calcium hydride prior to use. Celite and 4 Å molecular sieves were activated under vacuum overnight at 200 °C. (PNP)Zr=CH_2OAr (**1**) was prepared by the optimized procedure described below. (PNP)Zr$(CH_3)_2$(OAr),[3] $ZrCl_4(THF)_2$,[13] NaOAr (Ar = 2,6-$^iPr_2C_6H_3$),[14] and Li(PNP)[15] were prepared according to the reported procedures. CO (99.3%) was purchased from Airgas and used as received. ^{1}H, ^{2}H, ^{13}C, ^{31}P, HMBC, and HSQC NMR spectra were recorded on Bruker AV-II 500 MHz, AVIII 400 MHz, and DMX 360 MHz spectrometers. ^{1}H and ^{13}C NMR chemical shifts are reported referenced to the internal residual proton or carbon resonances of C_6D_6 (7.16 and 128.06 ppm, respectively). ^{2}H NMR chemical shifts are reported referenced to $CDCl_3$ (7.26 ppm). ^{31}P NMR chemical shifts are reported with respect to external H_3PO_4 (0.0 ppm). Elemental analyses were performed with a FLASH EA 1112 Series CHN analyzer (Thermo Finnigan).

Optimized Synthesis of Complex 1. In a 100 mL Teflon-cocked tube (Pyrex glass), (PNP)Zr$(CH_3)_2$OAr (1.01 g, 1.39 mmol) was suspended in hexane (50 mL). The headspace was evacuated, and the yellow suspension of [(PNP)Zr$(CH_3)_2$OAr] was photoirradiated with a MAX-303 Xe-lamp photoreactor (Asahi Spectra Co.) equipped with a UV mirror module (250−385 nm) for 24 h at room temperature. The solution was degassed under reduced pressure after 1, 3, 6, and 10 h; over this period the reaction mixture changed from a yellow suspension to a yellowish green suspension and then a dark yellow solution. After the photoirradiation, the reaction mixture was evaporated to dryness. The dark yellow residue was dissolved in pentane (10 mL), and the solution was filtered through glass wool in a pipet. The filtrate was dried in vacuo to give a pure dark yellow solid (914 mg, 1.28 mmol, 92%). Spectroscopic data conform to the reported ^{1}H NMR and ^{31}P{^{1}H} NMR spectra.[3]

Synthesis of Complex 2. A 25 mL Schlenk tube was charged with **1** (260 mg, 366 μmol) and hexane (10 mL). The headspace was evacuated, and an atmosphere of CO (1 atm) was introduced at 0 °C. The mixture quickly turned from dark yellow to orange. After it was stirred for 2 h at room temperature, the reaction mixture was evaporated to dryness. The orange residue was dissolved in pentane (1 mL), and the solution was filtered through glass wool in a pipet. The orange filtrate was stored at −35 °C overnight to afford **2** as an orange solid (121 mg, 81.9 μmol, 45%). Orange crystals suitable for X-ray analysis were grown from a concentrated pentane solution at −35 °C over 3 days. ^{1}H NMR (400 MHz, benzene-d_6, 300 K): δ 7.35−7.30 (overlapped m, 2H, Ar-C*H*), 7.12 (s, 1H, Ar-C*H*), 7.11 (s, 1H, Ar-C*H*), 7.08−7.02 (overlapped br, 6H, Ar-C*H*), 7.00−6.88 (overlapped m, 8H, Ar-C*H*), 6.58 (dd, $^2J_{HH}$ = 8.4 Hz, $^3J_{HP}$ = 4.8 Hz, 1H, C*H*$_2$CO), 6.51 (dd, $^2J_{HH}$ = 8.5 Hz, $^3J_{HP}$ = 4.8 Hz, 1H, C*H*$_2$CO), 3.69 (br dd, $^2J_{HH}$ = 8.4 Hz, $^3J_{HP}$ = 5.2 Hz, 2H, C*H*$_2$CO), 3.38 (m, 4H, OArC*H*(CH$_3$)$_2$), 2.41−2.26 (overlapped m, 2H, PC*H*(CH$_3$)$_2$), 2.14 (s, 12H, ArC*H*$_3$), 2.20−2.10 (overlapped m, 2H, PC*H*(CH$_3$)$_2$), 2.70−2.61 (overlapped m, 2H, PC*H*(CH$_3$)$_2$), 1.60−1.36 (overlapped m, 18H, PCH(C*H*$_3$)$_2$), 1.29−1.18 (overlapped m, 55H, PC*H*(CH$_3$)$_2$ and OArCH(C*H*$_3$)$_2$), 0.81 (m, 1H, PC*H*(CH$_3$)$_2$). ^{13}C NMR (126 MHz, benzene-d_6, 300 K): δ160.92 (br, PNP-Ar), 160.69 (br, PNP-Ar), 158.30 (OAr), 143.66 (CH$_2$−*C*(O)=*C*(O)−CH$_2$), 140.16 (OAr), 132.60 (d, J_{CP} = 17 Hz, PNP-Ar), 131.46 (ArO), 129.97 (OAr), 123.82 (br, PNP-Ar), 122.42 (ArO), 76.04 (*C*H$_2$C(O)=C(O)*C*H$_2$), 26.65 (br, OArCH(CH$_3$)$_2$), 26.18 (OArCH(CH$_3$)$_2$), 23.61 (br, PCH(CH$_3$)$_2$), 20.86 (ArCH$_3$), 19.41 (br, PCH(CH$_3$)$_2$). The ^{13}C NMR resonance of the carbonyl carbons in the [CH$_2$C(O)=C(O)CH$_2$] ligand was assigned by a ^{1}H−^{13}C HMBC spectrum. ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K): δ 30.73 (PNP), 30.46 (PNP), −2.01 (PNP), −2.62 (PNP). Anal. Calcd for **2**·2C$_5$H$_{12}$, $C_{90}H_{142}N_2O_4P_4Zr_2$: C, 66.63; H, 8.82; N, 1.73. Found: C, 66.33; H, 8.94; N, 1.67.

Reactivity of Complex 1 with Chloroform-*d*$_1$. In a J. Young valve NMR tube, compound **1** (10.8 mg, 15.2 μmol) was dissolved in chloroform-d_1 (0.5 mL) at −35 °C, resulting in a color change from dark yellow to yellowish orange. After the mixture was shaken for 10 min at room temperature, quantitative formation of **3** was observed by ^{1}H NMR spectroscopy (Figure S12 in the Supporting Information). Likewise, vinyl chloride-d_1 was also observed cleanly by ^{1}H NMR (Figure S12, inset) and ^{2}H NMR spectroscopy (Figure S13 in the Supporting Information). ^{1}H NMR (360 MHz, chloroform-d_1, 300 K): δ 7.06−7.03 (overlapped br, 4H, PNP and OAr Ar-C*H*), 6.99 (d, J_{HH} = 5.4 Hz, 2H, OAr−C*H*), 6.86 (t, J_{HH} = 5.4 Hz, 1H, OAr−C*H*), 6.75 (dd, J_{HH} = 2.5 Hz, 6.1 Hz, 2H, PNP Ar-C*H*), 5.52 (q, $^3J_{HD}$ = 1.5 Hz, $^2J_{HH}$ = 3.2 H, 1H, *H*$_2$C=CDCl), 5.44 (br t, 1H, *H*$_2$C=CDCl), 3.44 (virtual quintet, $^3J_{HH}$ = 4.7 Hz, 2H, OArC*H*(CH$_3$)$_2$), 2.48 (br, 2H, PC*H*(CH$_3$)$_2$), 2.29 (s, 6H, ArC*H*$_3$), 1.28 (br, 12H, PCH(C*H*$_3$)$_2$), 1.21 (dd, $^3J_{HH}$ = 5.4 H, $^4J_{HP}$ = 10.4 H, 12H, PCH(C*H*$_3$)$_2$), 1.11 (d, $^3J_{HH}$ = 4.7 H, 12H, OArCH(C*H*$_3$)$_2$), 1.08 (br, 2H, PC*H*(CH$_3$)$_2$). ^{2}H NMR (76.8 MHz, chloroform-d_1, 300 K): δ 6.34 (dd, $^3J_{HD}$ = 1.5 Hz, 2.6 Hz, H$_2$C=C*D*Cl).

Independent Synthesis of Complex 3. To a white suspension of ZrCl$_4$(THF)$_2$ (433 mg, 1.15 mmol) in toluene (10 mL) was added Li(PNP) (500 mg, 1.15 mmol) as a solid at room temperature, and additional toluene (5 mL) was used to add the remainder of the Li(PNP) in the vial. After it was stirred for 5 h, the reaction mixture changed to a reddish brown suspension which was a mixture of (PNP)ZrCl$_3$[4] and LiCl. To the reddish brown suspension of (PNP)ZrCl$_3$ (without purification) was added NaOAr (231 mg, 1.15 mmol) as a solid at room temperature, and additional toluene (5 mL) was used to add the remaining NaOAr. The reaction mixture gradually turned yellowish orange over the duration of 3 h. After removal of volatiles under vacuum, the yellowish orange residue was dissolved in toluene (5 mL) and the solution was filtered through a medium-porosity glass frit containing Celite, which was washed twice with toluene (2 × 5 mL). The yellowish orange filtrate was evaporated to dryness, and the residue was washed twice with hexane (2 × 2 mL) to give **3** as yellow powder (697 mg, 908 μmol, 79%). Yellow crystals suitable for X-ray analysis were grown from a concentrated pentane solution cooled to −35 °C overnight. ^{1}H NMR (400 MHz, benzene-d_6, 300 K): δ 7.10 (br, 2H, Ar-C*H*), 6.90−6.85 (overlapped br, 5H, Ar-C*H*), 3.87 (br m, 2H, OArC*H*(CH$_3$)$_2$), 2.30 (br, 2H, PC*H*(CH$_3$)$_2$), 2.12 (s, 6H, ArC*H*$_3$), 1.42−1.40 (overlapped br, 12H, PCH(C*H*$_3$)$_2$), 1.21−1.19 (overlapped br, 26H, OArC*H*(CH$_3$)$_2$, PCH(C*H*$_3$)$_2$ and PC*H*(CH$_3$)$_2$). ^{13}C NMR (126 MHz, benzene-d_6, 300 K): δ 158.18 (PNP-Ar), 138.97 (ArO), 133.01 (ArO), 132.27 (ArO), 130.71 (br, PNP-Ar), 128.35 (br, PNP-Ar), 123.71 (ArO), 123.09 (PNP-Ar), 122.20 (PNP-Ar), 120.68 (br, PNP-Ar), 26.90 (OArCH(CH$_3$)$_2$), 25.11 (OArCH(CH$_3$)$_2$), 23.78 (br, 2C, PCH(CH$_3$)$_2$), 20.81 (Ar-CH$_3$), 19.18 (br, PCH(CH$_3$)$_2$), 18.84 (PCH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K) δ 15.98 (s, PNP). Anal. Calcd for **3**, $C_{38}H_{57}NOCl_2P_2Zr$: C, 59.43; H, 7.48; N, 1.82. Found: C, 58.89; H, 7.81; N, 1.20. Multiple attempts to obtain satisfactory elemental analyses failed.

Reactivity of Complex 1 with Cyclododecanone. In a J. Young valve NMR tube, a benzene-d_6 solution (0.5 mL) of **1** (16.8 mg, 23.6 μmol) was treated with cyclododecanone (4.3 mg, 24 μmol) at room temperature, resulting in a color change from dark yellow to reddish brown. After the mixture was shaken at room temperature for 10 min, quantitative formation of methylenecyclododecane was observed by ^{1}H NMR (4.90 ppm, Figure S14 in the Supporting Information) and GS-MS (*m*/*z* 180, [M]$^+$), but both ^{1}H NMR and ^{31}P{^{1}H} NMR spectra showed complicated mixtures of Zr species.

Reactivity of Complex 1 with Benzophenone To Form 4. In a J. Young valve NMR tube, a benzene-d_6 solution (0.5 mL) of **1** (14.9 mg, 20.8 μmol) was treated with benzophenone (3.9 mg, 21.4 μmol) at room temperature, resulting in a color change from dark yellow to reddish brown. After 30 min at room temperature, formation of **4**, 1,1-diphenylethylene, ethylene, and some unidentified products were observed by ^{1}H NMR (Figure S16 in the Supporting Information) and ^{31}P{^{1}H} NMR spectroscopy (Figure S17 in the Supporting Information). These spectra showed a complicated mixture of **4** and other PNP species.

Synthesis of Complex 4. To a dark yellow solution of **1** (200 mg, 281 μmol) in pentane (15 mL) was added benzophenone (56.1 mg, 308 μmol) in pentane (5 mL) at −35 °C, resulting in a color change to brown. The reaction mixture was stirred for 15 min at room temperature, resulting in the gradual formation of a white precipitate. The white insoluble material (∼2 mg) was removed by filtration. The brown filtrate was evaporated to dryness. HMDSO (10 mL) was added to the brown residue. The brown oil was removed, and the brown supernatant was decanted into another vial via pipetting. The brown supernatant was concentrated to ca. 2 mL and stored at −35 °C overnight to yield **4** as a brown powder (74.1 mg, 30% crude yield, 82.9 μmol calculated as **4**). A residual impurity found in **4** prevented us from isolating analytically pure product (observed by ^{1}H NMR and ^{31}P{^{1}H} NMR spectroscopy). Brown crystals suitable for X-ray analysis were grown from a concentrated pentane solution at −35 °C over 3 days. ^{1}H NMR (360 MHz, benzene-d_6, 300 K): selected data δ 7.24−7.11 (overlapped m, PNP, OAr and Ph Ar-C*H*), 7.01−6.90 (overlapped m, PNP, OAr and Ph Ar-C*H*), 6.74 (t, J_{HH} = 5.4 Hz, 1H, Ar-CH), 6.69 (d, J_{HH} = 5.4 Hz, 1H, Ar-CH), 6.43 (s, 1H, OC*H*), 4.06 (d, $^2J_{HH}$ = 9.0 Hz, 1H, ZrC*H*$_2$), 3.58 (br, 2H, OArC*H*(CH$_3$)$_2$), 2.20 (overlapped br, 10H, ArC*H*$_3$ + PC*H*(CH$_3$)$_2$), 1.53 (d, $^2J_{HH}$ = 9.0, 1H, ZrC*H*$_2$), 1.34−1.18 (overlapped m, 21 H, PCH(C*H*$_3$)$_2$), 1.05 (br, 3H, PCH(C*H*$_3$)$_2$), 0.94−0.90 (overlapped virtual t, 9H, PCH(C*H*$_3$)$_2$ and OArCH(C*H*$_3$)$_2$), 0.73 (br, 3H, PCH(C*H*$_3$)$_2$). ^{13}C NMR (126 MHz, benzene-d_6, 300 K): δ 161.56 (d, J_{CP} = 20 Hz, PNP-Ar), 159.08 (d, J_{CP} = 19 Hz, PNP-Ar), 158.37 (Ar), 149.45 (Ar), 144.17 (Ar), 140.52 (Ar), 138.03 (Ar), 133.19 (br, Ar), 132.41 (Ar), 131.67 (Ar), 126.91 (Ar), 126.54 (Ar), 126.41 (Ar), 125.94 (Ar), 123.61 (Ar), 120.52 (Ar), 82.99 (OCHPh), 76.84 (CH$_2$Ph), 26.93 (OArCH(CH$_3$)$_2$), 25.72 (OArCH(CH$_3$)$_2$), 25.04 (br, PCH(CH$_3$)$_2$), 24.73 (br, 2C, PCH(CH$_3$)$_2$), 24.07 (br, PCH(CH$_3$)$_2$), 22.88 (br, ArCH$_3$), 22.76 (ArCH$_3$), 21.53 (br, PCH(CH$_3$)$_2$), 21.43 (br, PCH(CH$_3$)$_2$), 20.83 (br, PCH(CH$_3$)$_2$), 20.24 (br, PCH(CH$_3$)$_2$), 19.60 (br, PCH(CH$_3$)$_2$), 19.18 (br, PCH(CH$_3$)$_2$), 18.80 (br, PCH(CH$_3$)$_2$), 16.08 (br, PCH(CH$_3$)$_2$). ^{31}P{^{1}H} NMR (162 MHz, benzene-d_6, 300 K): δ 24.02 (d, $^2J_{PP}$ = 54 Hz, PNP), 14.54 (d, $^2J_{PP}$ = 54 Hz, PNP). ^{1}H−^{13}C HSQC NMR

DOI: 10.1021/acs.organomet.6b00594

chemical shifts (500 MHz, benzene-d_6, 300 K): selected data $\delta(^1H)$ ($\delta(^{13}C)$) 6.43 (82.99), 4.06 (76.84), 3.58 (76.84).

X-ray Crystallographic Studies. Crystallographic data are summarized in Tables S1−S3 in the Supporting Information. Suitable single crystals for X-ray analysis of **2**−**4** were placed on the end of a Cryoloop coated in NVH oil. The X-ray intensity data collection was carried out on a Bruker APEXII CCD area detector for **2** and **4** and a Bruker D8QUEST CMOS area detector for **3** using graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) at 100(1) K. Preliminary indexing was performed from a series of 24 (**2**) or 36 (**3** and **4**) 0.5° rotation frames with exposures of 10 s. Rotation frames were integrated using SAINT,[16] producing a listing of nonaveraged F^2 and $\sigma(F^2)$ values which were then passed to the SHELXTL[17] program package for further processing and structure solution. The intensity data were corrected for Lorentz and polarization effects and for absorption using SADABS.[18] All calculations were performed using SHELXS[19] and SHELXL.[20] The structures were solved by Patterson and Fourier transform methods. All reflections were used during refinement. Non-hydrogen atoms were refined anisotropically, and hydrogen atoms were refined using riding models. For **2**, one of the ^{i}Pr groups of PNP for each molecule was disordered over two positions. Two sites occupied by pentane were identified in the asymmetric unit. One site was ordered and fully occupied. The second site was considerably disordered and was treated by SQUEEZE as a diffuse contribution.[21,22] In the resulting void space, a contribution of 40 e per unit cell was found and taken to represent 0.5 pentane in the asymmetric unit, giving a total of 3 pentane molecules for each Zr_2 complex. For **3**, these data were treated as a pseudomerohedral twin and solved as monoclinic $P2_1$. Treatment of these data with an orthorhombic space group ($P2_12_12_1$) did not give a good solution of this structure. Two crystallographically independent, but chemically equivalent, molecules are present in the asymmetric unit. One of the ^{i}Pr groups of PNP for each molecule was disordered over two positions. The thermal ellipsoids of these disorders were fixed by SHELXL restraint commands, DELU and ISOR. For **4**, the pentane molecule was disordered over two positions. The thermal ellipsoids were fixed by SHELXL restraint commands, DELU and SIMU. These results were checked using the IUCR's CheckCIF routine. The alerts in the output are related to the disordered groups and co-crystallized solvents.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00594.

Crystallographic data and tables, experimental details, and multinuclear NMR spectral data (PDF)

Crystallographic data (CIF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

We thank the University of Pennsylvania and the National Science Foundation (CHE30848248 and CHE31152123) for financial support of this work. T.K. and M.K. thank the Japanese Society for the Promotion of Science (JSPS) for a postdoctoral fellowship (14J11968).

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