Synthesis and characterization of tungsten oxo alkylidene complexes via the reaction of $WCl_2(O)[PX_3]_3$ ($PX_3 = P(OMe)_3$, PMe_2Ph, $PMePh_2$) with 4,8-dioxaspiro[2,5]oct-1-ene (ketalcyclopropene)

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Abstract

This paper describes the synthesis and characterization of the first tungsten oxo ketalvinyl alkylidene complexes via the reaction of $WCl_2(O)[PX_3]_3$ ($PX_3 = P(OMe)_3$ 1, PMe_2Ph 2, $PMePh_2$ 3) with 4,8-dioxaspiro[2,5]oct-1-ene (ketalcyclopropene). Complex 1 reacts with ketalcyclopropene affording almost quantitatively the corresponding s-*cis*-vinyl alkylidene complex $W(=CH-CH=CR)Cl_2(O)[P(OMe)_3]$ 4 ($R = COCH_2CH_2CH_2O-$). NMR data for this complex support a pseudo octahedral structure where the oxygen ligand occupies an axial position. In order to maximize π-bonding the alkylidene ligand must be cis to the oxo ligand and the chelating ketal functionality is placed trans to the oxo ligand. The $P(OMe)_3$ and chloride ligands lie in the equatorial plane with the $P(OMe)_3$ ligand situated cis to the alkylidene ligand. Complexes 2 and 3 also react with a slight excess of ketalcyclopropene affording vinyl alkylidene complexes that adopt different coordination modes. The two chloride ligands in complex 4 can be exchanged by reaction with different lithium alkoxides yielding tungsten oxo alkoxo ketalvinyl alkylidene complexes that present different geometry depending on the alkoxide ligands.

Keywords: Tungsten; Ketalcyclopropene; Alkylidene; Oxo

1. Introduction

The ring-opening of cyclopropenes to give vinyl alkylidenes constitutes a new entry to transition-metal alkylidene complexes, the first synthesis of isolable transition-metal vinyl alkylidene complexes from cyclopropenes was reported in 1989 and involved the reaction of 3,3-disubstituted cyclopropene with bis(cyclopentadienyl) titanium(II) and -zirconium(II) precursors [1]. The generality of this reaction is thus of interest, especially given the importance of transition-metal alkylidenes as well-defined catalysts for olefin metathesis reactions (for general references on the metathesis reaction, see Ref. [2]). Two important reactions included in this category are ring-opening metathesis polymerization (ROMP) (for leading references, see Refs. [2,3]) and ring-closing metathesis (RCM) [4,5].

Recent work has shown that 3,3-diphenylcyclopropene can be used as a precursor in the synthesis of an important number of vinyl alkylidene complexes of several transition metals, such as titanium and zirconium [1], tungsten [6–8], rhenium [9], iridium [10],

rhodium [11] or ruthenium [12]. A few other disubstituted cyclopropenes have been used and gave analogous results. 4,8-Dioxaspiro [2,6–8] oct-1-ene (referred to throughout the remainder of this paper as ketalcyclopropene) was used as the carbene source for the synthesis of a new class of imido alkylidene complexes of tungsten [6].

In general, η^2-diphenylcyclopropene complexes are more stable than η^2-ketalcyclopropene complexes, which undergo ring-opening to give ketalvinyl alkylidene derivatives more easily. However, the chemistry of imido tungsten derivatives with ketalcyclopropene is quite complex, as several forms of ketalvinyl alkylidene complexes were noted [4] (Fig. 1).

As shown in Fig. 1, in addition to syn and anti rotamers of the s-*trans*-vinyl alkylidene ligand A, the chelating s-*cis*-vinyl alkylidene ligand B and the ring-opened chelating chloro alkylidene C were also observed.

In comparison with the large number of tungsten imido alkylidene complexes described in the literature, the synthesis of tungsten oxo alkylidene complexes that

can be used in metathesis processes has been much less explored (these complexes were proposed by Rappé and Goddard as active, chain-carrying metathesis catalysts for high-valent Mo, W and Re complexes [13]). Some of these oxo alkylidene complexes require Lewis acid activation to be metathesis catalysts [14,15], and only very recently has the preparation and characterization of well-defined, metathetically active oxo alkylidene complexes of tungsten been reported [8,16].

Reported herein is that $WCl_2(O)[PX_3]_3$ (X = R, OMe) reacted with ketalcyclopropene, upon loss of phosphine or phosphite, to give the first examples of oxo ketalvinyl alkylidene complexes.

2. Results and discussion

Recently, the synthesis of oxo vinyl carbene tungsten complexes via the reaction of $WCl_2(O)[PX_3]_3$ (X = R, OMe) with 3,3-diphenylcyclopropene [8] has been reported. This showed that these oxo alkylidene complexes present some advantages over the corresponding arylimido derivatives. The smaller size of the oxo ligand improves the stability of $WCl_2(E)[PX_3]_3$ (E = O, NAr) complexes. For example, $WCl_2(O)[PMePh_2]_3$ can be isolated easily and cleanly, but $WCl_2(NAr)[PMePh_2]_3$ (Ar = 2,6-Me_2-Ph, 2,6-^{i}Pr$_2$-Ph) can only be observed in solution by ^{1}H NMR spectroscopy.

Reactions of the appropriate precursors [17] $WCl_2(O)[PX_3]_3$ (X$_3$ = (OMe)$_3$ 1, Me_2Ph 2, Me^{i}n$_2$ 3) with ketalcyclopropene lead to the formation of vinyl alkylidene species, but some differences are found depending on the precursor. Ketalcyclopropene reacted with $WCl_2(O)[P(OMe)_3]_3$ at room temperature in OEt$_2$ affording the corresponding s-cis-vinyl alkylidene complex W(=CHR$_B$)Cl$_2$(O)[P(OMe)$_3$] 4-B as a dark red solid in 95% yield (Eq. (1)). (In the remainder of this paper, for simplicity and analogously with similar imido derivatives (see Ref. [6]), the formula of the ketalvinyl alkylidene unit in the oxo ketalvinyl alkylidene complexes described herein will be represented as (=CHR$_Y$), where Y = A, B or C and denotes the structure of the alkylidene (see Fig. 1).)

(1)
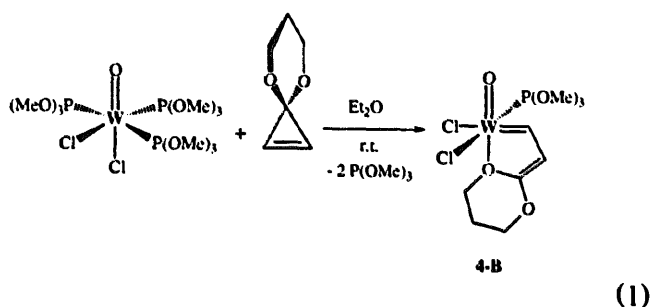
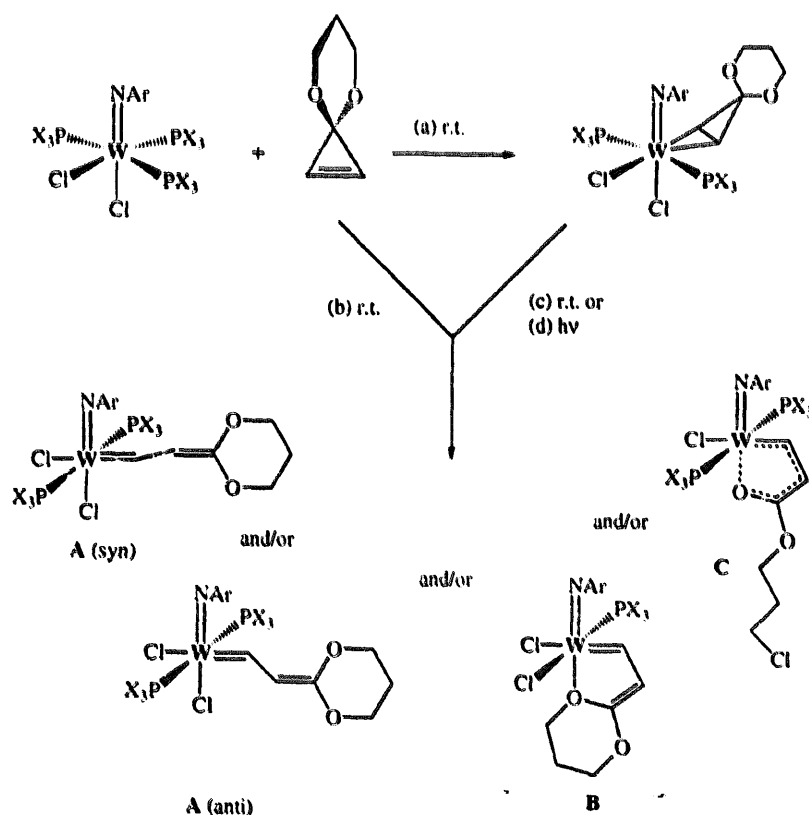Complex 4-B, which can be stored in the solid state under argon at $-10°C$ for months but decomposes at

Fig. 1. Different coordination modes of the ketalvinyl alkylidene ligand in imido tungsten complexes.

room temperature in several hours, is soluble in tetrahydrofuran and chlorinated solvents such as methylene chloride and chloroform, slightly soluble in aromatic solvents and insoluble in saturated hydrocarbons.

The η^2-ketalcyclopropene complex was not observed even when the reaction was followed by ^1H NMR spectroscopy, and only one form of ketalvinyl alkylidene complex was noted.
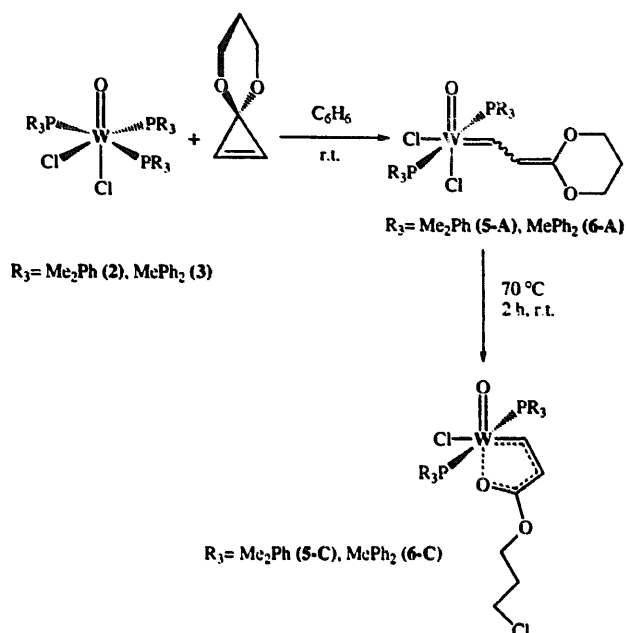
The ^1H NMR spectrum of **4-B** in CD_2Cl_2 presents two signals at δ 12.32 (dd, $J_{HH} = 10.2\,Hz$, $J_{HP} = 5.1\,Hz$, H_α) and δ 5.91 (dd, $J_{HH} = 10.2\,Hz$, $J_{HP} = 1.5\,Hz$, H_β) for the protons of the ketalvinyl alkylidene ligand. The coupling constant between H_α and H_β is smaller than those of s-*trans*-vinyl alkylidene ligands and suggest the s-cis disposition of the double bonds in the alkylidene moiety [6-8]. These observations suggest chelation by the ketalvinyl alkylidene group to tungsten that is also supported by the incorporation of only one $P(OMe)_3$ ligand, as was indicated by the appearance of doublet resonances for H_α and C_α, which indicates the displacement of the other donor ligand by the chelating alkylidene ligand. In addition, the downfield shift of one set of ether methylene protons of the ketal ring $(OC_xH$, 4.7 ppm; OC_xH', 4.56 ppm) was consistent with the coordination by the adjacent oxygen atom to tungsten [6].

In order to maximize the π-bonding in **4-B**, the alkylidene ligand must be cis to the oxo ligand and the alkylidene substituents must lie in the $O-W-C_\alpha$ plane [18]; this would place the chelating ketal functionality trans to the oxo ligand. The $P(OMe)_3$ and chloride ligands must lie in the equatorial plane with the phosphite ligand situated either cis or trans to the alkylidene ligand. The nonequivalence of the geminal protons of the ketal methylene group that lie closest to tungsten supports the asymmetric structure in which the $P(OMe)_3$ ligand occupies a position cis to the alkylidene ligand.

The complete analysis of these and the rest of the spectroscopic data (see Section 4) for **4-B**, and comparison with the analogous imido complexes described earlier in the literature [6], allows one to propose the structure shown in the Eq. (1) for this oxo ketalvinyl alkylidene complex.

Catalytic activity of this complex in metathesis processes was studied and, as expected, showed a very small activity. It polymerized only very strained cyclic olefins, such as norbornene; however, it did not show any activity either in the polymerization of less strained olefins, such as cyclooctatetraene, or in RCM reactions.

Complexes **2** and **3** also reacted with a slight excess of ketalcyclopropene leading to mixtures that contained new alkylidene species (Scheme 1). When these reactions were followed by ^1H NMR spectroscopy in C_6D_6, the η^2-cyclopropene complex was not observed either, but the formation of vinyl alkylidene species could be observed on the basis of their spectroscopic data. After

$R_3 = Me_2Ph$ (2), MePh$_2$ (3)

$R_3 = Me_2Ph$ (5-A), MePh$_2$ (6-A)

70 °C
2 h. r.t.

$R_3 = Me_2Ph$ (5-C), MePh$_2$ (6-C)

Scheme 1.

24 h at room temperature the yellow-orange solution contained a mixture of starting material and a new ketalvinyl alkylidene complex. The large values of $^3J_{H\alpha-H\beta}$ coupling constants of these alkylidene complexes (see Section 4) indicate the formation of syn and anti rotamers of the s-*trans*-ketalvinyl alkylidene complexes $W(=CHR_A)Cl_2(O)[PX_3]_2$ $(X_3 = Me_2Ph$ 5-A, $MePh_2$ 6-A). In addition, the appearance of doublet of triplets resonances for the H_α indicates the presence of two phosphine ligands and rules out the presence of chelating alkylidene ligands.

A complete conversion to 5-A and 6-A could not be achieved, and forcing the reaction by increasing the temperature to 70–80 °C over 2 h resulted in the formation of green solutions from which dark green solids were isolated. The NMR spectra of these dark green solids showed the presence of new ketalvinyl alkylidene complexes identified as the ring-opened chelating chloro-alkylidenes 5-C and 6-C.

The nature of these complexes is proposed on the basis of their spectroscopic data, especially the value of the $H_\alpha-H_\beta$ spin–spin coupling constants and their colour in comparison with the analogous imido derivatives reported earlier, for one of which the X-ray structure was solved [6].

The H_α and C_α resonances are coupled to two mutually trans phosphine ligands (see Section 4) and are shifted slightly upfield of the same resonances of 5-A and 6-A. The coupling of these resonances to phosphorus is smaller than the analogous coupling observed in the s-trans alkylidene derivatives, 5-A and 6-A, indicating a lengthening of the $W-C_\alpha$ bond and that the

coupling between H_α and H_β is relatively small (8.1 Hz in both cases) due to the s-cis arrangement of the alkylidene double bonds. In the ^{13}C NMR spectrum, only one methylene carbon adjacent to oxygen was observed; the methylene carbon adjacent to chlorine appeared about 20 ppm upfield.

^1H and ^{13}C NMR spectra of 5-C showed that the two methyl groups of PMe_2Ph are diasterotopic owing to the prochiral character of the tungsten atom. The same behavior was observed for the two phenyl groups of $PMePh_2$ in 6-C.

2.1. Reaction of $W(=CHR_B)Cl_2(O)[P(OMe)_3]$ (4-B) with alkoxides

Complex 4-B reacted with two equivalents of $LiOC(CH_3)(CF_3)_2$ in THF but we could not characterize any of the organometallic products formed. When the reaction was followed by ^1H NMR spectroscopy in THF-d_8, the formation of a new carbene complex was observed after 5 min, which stayed in solution for about 1 h and afterwards decomposed. This new complex showed two doublets at 9.62 ppm ($J_{HH} = 9.90$ Hz) and 5.75 ppm for the α and β protons of the vinyl alkylidene unit. The chemical shift of these signals, the value of the coupling constants and the absence of phosphite coordinating to the tungsten metal center lead to formulate this complex as $W(=CHR_A)(O)(OC(CH_3)(CF_3)_2)_2(thf)$ 7-A (Eq. (2)).


$$Rf_6 = C(CH_3)(CF_3)_2$$

(2)
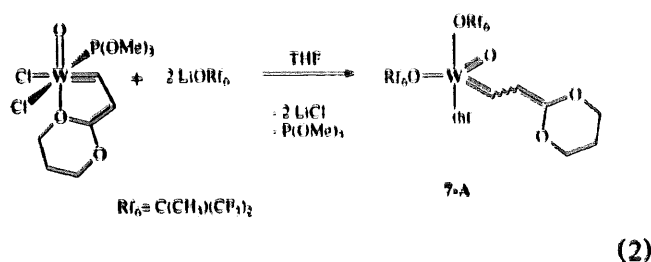
This behavior seems similar to what was observed in analogous oxo vinyl alkylidene complexes obtained with 3,3-diphenylcyclopropene as the carbene source [8], where the phosphite ligand is loosely bonded to the metal so that THF can displace it and form the corresponding THF adduct, which is quite unstable and decomposes after 2 or 3 h.

Despite its low stability, complex 7-A can be used as an effective metathesis catalyst for the ROMP of strained olefins, such as norbornene or cyclooctene, and for the RCM of diethyl diallyl malonate, when the complex was generated in situ in the presence of such substrates.

Bulkier alkoxides should lead to a greater stability of the final ketalvinyl alkylidene complex, thus complex 4-B reacts with one equivalent of the dilithium salt of TBEC (TBEC-H_2 = (1S,2S)-2′,2′,2″,2″-tetrakistri-

fluoromethyl-1,2-bis(2-hydroxyethyl)-cyclopentane) to give $W(=CHR_A)(O)(TBEC)[P(OMe)_3]$ 8-A which can be isolated as a yellow solid in 85% yield (Eq. (3)). A full description of the synthesis and catalytic activity of this complex will be reported separately [19]. Also in this case, THF can displace phosphite from 8-A leading to the corresponding THF adduct. The high solubility of the dilithium salt of TBEC in all organic solvents allows the reaction to be carried out in THF-free conditions.

(3)
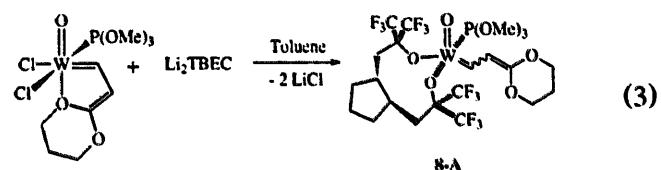
Other alkoxides, different from those reported above, have been tested, but only when $LiOC_6F_5$ was used were new ketalvinyl alkylidene complexes observed. Reaction of 4-B with two equivalents of $LiOC_6F_5$ in a 8:1 mixture of CD_2Cl_2–THF-d_8 proceeded cleanly to form new alkylidene species. The ^1H NMR spectrum of the reaction mixture showed the presence of two different species in a 20:1 ratio (Eq. (4)).

(4)
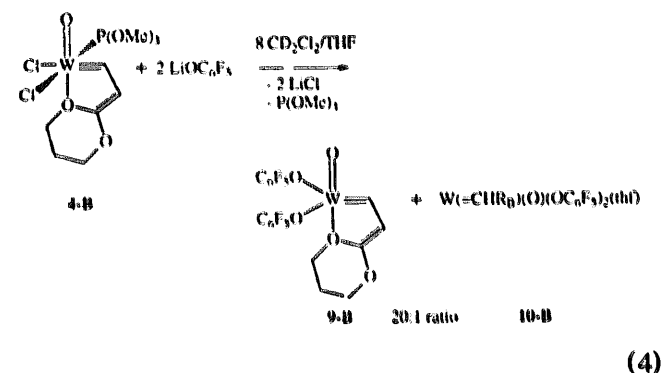
The major compound presents two doublets at 9.86 ppm ($J_{HH} = 9.9$ Hz) and 5.22 ppm for the α and β protons of the vinyl alkylidene unit, two triplets for the methylenic groups bonded to each oxygen at δ 4.85 ($J_{HH} = 5.7$ Hz) and δ 4.28 ($J_{HH} = 5.7$ Hz) and a quintuplet for the third methylenic group at δ 2.16 ($J_{HH} = 5.7$ Hz).

The equivalence of the two hydrogen atoms in each methylenic carbon for this complex, as well as the values of the chemical shift and coupling constants of the carbene signals and the absence of coordinated phosphite, lead one to propose this alkylidene complex as $W(=CHR_B)(O)(OC_6F_5)_2$ 9-B. It has also been observed that the presence of larger amounts of THF-d_8 in the solvent mixture yield greater amounts of the second complex found in this reaction $W(=CHR_B)(O)(OC_6F_5)_2(thf)$ 10-B; in the extreme, when the reaction

was carried out in pure THF-d_8, an approximately 1:1 ratio of both compounds was obtained. The second complex also presents in its ^{1}H NMR spectrum two doublets for the α and β protons of the ketalvinyl alkylidene unit at 10.28 ppm ($J_{HH} = 9.6$ Hz) and 5.58 ppm; the two protons of each methylenic group are now inequivalent and appear as multiplets at δ 4.9, 4.5 and 2.0 ppm. This data seems to be in agreement with the formulation proposed for **10-B**.

In solution, **9-B** and **10-B** are stable; however, they decompose very rapidly when attempts were made to isolate them in the solid state, which impeded their full characterization.

3. Conclusion

$WCl_2(O)[PX_3]_3$ precursors react with ketalcyclopropene to give new tungsten oxo vinyl alkylidene complexes that present different structures depending on the coordination mode of the ketalvinyl alkylidene unit to the metal center. The 'η^2-ketalcyclopropene' complexes could not be observed in any case, confirming their lower stability with respect to the analogous η^2-diphenylcyclopropene derivatives, which facilitates the formation of the final tungsten vinyl alkylidene complexes.

This and previous work [8,16] have shown that is possible to develop a chemistry for tungsten oxo derivatives similar to that developed for tungsten imido complexes, which opens new possibilities in the synthesis of well-defined Group VI metathesis catalysts.

4. Experimental details

All manipulations were carried out under argon with standard Schlenk techniques or in a nitrogen-filled glove box equipped with a $-40\,^\circ$C freezer. Argon was purified by passage through columns of Chemalog R3-11 catalyst and Lynde 4Å molecular sieves. ^{1}H and ^{13}C NMR spectra were recorded with a QE-300 Plus (300.10 MHz ^{1}H, 75.49 MHz ^{13}C) spectrometer. ^{19}F NMR spectra (470.56 MHz) were recorded on a Bruker 500 AM spectrometer. All coupling constants are reported in hertz.

Toluene, diethyl ether, methylene chloride and tetrahydrofuran were purified by standard methods. Pentane was stirred over concentrated H_2SO_4, dried over CaH_2 and $MgSO_4$, and then transferred onto sodium-benzophenone ketyl. Benzene-d_6 and THF-d_8 were dried over sodium-benzophenone ketyl and methylene chloride-d_2 was dried over P_2O_5, vacuum transferred and then degassed by repeated freeze–pump–thaw cycles.

$WCl_2(O)[P(OMe)_3]_3$ [17], $WCl_2(O)[PMe_2Ph]_3$ [17], $WCl_2(O)[PMePh_2]_3$ [17], ketalcyclopropene (for details

of the synthesis and reactivity of ketalcyclopropene see Ref. [20]) and Li$_2$TBEC [19] were synthesized according to literature methods. $P(OMe)_3$, PMe_2Ph and $PMePh_2$ were purchased from commercial sources and then purified by distillation. $(CF_3)_2(CH_3)COH$ and C_6F_5OH were purchased from commercial sources, dissolved in OEt_2, deprotonated with one equivalent of freshly titrated Li^{n}Bu [21] and purified by standard techniques.

4.1. $W(=CHR_B)Cl_2(O)[P(OMe)_3]$ 4-B

A 5 mL OEt_2 solution of ketalcyclopropene (0.36 g, 3.2 mmol) was added to a purple solution of $WCl_2(O)[P(OMe)_3]_3$ (2.0 g, 3.11 mmol) in 30 ml of OEt_2. The original purple solution turns to a red suspension as the reaction mixture was stirred for 1 h. The solvent was removed by filtration and the solid washed with pentane (3×10 ml) affording a red microcrystalline solid (1.42 g, 90%) that was dried in vacuo and stored at $-30\,^\circ$C. ^{1}H NMR (CD_2Cl_2): δ 12.32 (dd, 1, $J_{HH} = 10.2$ Hz, $J_{HP} = 5.1$ Hz, H_α), 5.91 (dd, 1, $J_{HH} = 10.2$ Hz, $J_{HP} = 1.5$ Hz, H_β), 4.7–4.4 (m, 4, $-OCH_2-CH_2-CH_2O-$), 3.81 (d, 9, $J_{HP} = 11.4$ Hz, $P(OMe)_3$), 2.11 (m, 2, $-OCH_2CH_2CH_2O-$). ^{1}H NMR (C_6D_6): δ 12.35 (dd, 1, $J_{HH} = 10.2$ Hz, $J_{HP} = 5.4$ Hz, H_α), 5.91 (dd, 1, $J_{HH} = 10.2$ Hz, $J_{HP} = 1.5$ Hz, H_β), 4.39 (m, 2, $-OCH_2-CH_2-CH_2O-$), 3.32 (d, 9, $J_{HP} = 11.1$ Hz, $P(OMe)_3$), 3.22 (m, 2, $-OCH_2-CH_2-CH_2O-$), 1.06 (m, 1, $-OCH_2CHH'CH_2O-$), 0.86 (m, 1, $-OCH_2CHH'CH_2O-$). ^{13}C NMR (CD_2Cl_2): δ 265.1 (d, $J_{CP} = 17.4$ Hz, C_α), 170.0 (d, $J_{CP} = 4.8$ Hz, Cγ), 91.4 (d, $J_{CP} = 6.04$ Hz, C_β), 68.22 (OCH$_2$), 67.1 (OCH$_2'$), 23.5 ($-CH_2CH_2CH_2-$), $P(OMe)_3$ signal is overlapped by the solvent. ^{31}P NMR (CD_2Cl_2): δ 148.6. Anal. Found: C, 21.42; H, 3.38. $C_9H_{17}Cl_2O_6PW$. Calc.: C, 21.31; H, 3.35%.

4.2. Observation of $W(=CHR_A)Cl_2(O)[PX_3]_2$ ($X_3 = Me_2Ph$ 5-A, $MePh_2$ 6-A)

A 0.5 ml benzene-d_6 solution of ketalcyclopropene (0.035 mmol) was added to an NMR tube containing $WCl_2(O)[PX_3]_3$ ($X_3 = Me_2Ph$ **2**, $MePh_2$ **3**) (0.03 mmol). After 24 h at room temperature, new ketalvinyl alkylidene complexes $W(=CHR_A)Cl_2(O)$-$[PX_3]_2$ ($X_3 = Me_2Ph$ **5-A**, $MePh_2$ **6-A**) are among the products of the reaction mixture and can be observed and identified by ^{1}H NMR spectroscopy. ^{1}H NMR spectrum of **5-A** (C_6D_6): δ (syn and anti rotamers) 12.67 (dt, 1, $J_{HH} = 13.5$ Hz, $J_{HP} = 2.7$ Hz, H_α), 12.51 (dt, 1, $J_{HH} = 14.1$ Hz, $J_{HP} = 3.0$ Hz, H_α). ^{1}H NMR spectrum of **6-A** (C_6D_6): δ (syn and anti rotamers) 12.5 (dt, 1, $J_{HH} = 13.8$ Hz, $J_{HP} = 2.8$ Hz, H_α), 12.05 (dt, 1, $J_{HH} = 14.1$ Hz, $J_{HP} = 3.0$ Hz, H_α).

4.3. W(= CHR$_C$)Cl(O)[PX$_3$]$_2$ (X$_3$ = Me$_2$Ph 5-C, MePh$_2$ 6-C)

A 5 ml toluene solution of ketalcyclopropene (2.6 mmol) was added to a Schlenk flask containing WCl$_2$(O)[PX$_3$]$_3$ (X$_3$ = Me$_2$Ph 2, MePh$_2$ 3) (2.2 mmol). The suspension was stirred for 24 h at room temperature and then heated to 70 °C for an additional 2 h period affording a dark green solution. Solvent was removed under vacuum and the remaining solid washed with pentane (3 × 20 ml) leading to a dark green solid (55% yield) characterized as W(=CHR$_C$)Cl(O)[PX$_3$]$_2$ (X$_3$ = Me$_2$Ph 5-C, MePh$_2$ 6-C). The data for 5-C are ^{1}H NMR (C$_6$D$_6$): δ 12.9 (dt, 1, J_{HH} = 8.1 Hz, J_{HP} = 1.2 Hz, H$_\alpha$), 7.8–6.9 (m, 10, aromatic protons), 5.61 (d, 1, J = 8.1 Hz, H$_\beta$), 3.58 (t, 2, J = 6.0 Hz, OCH$_2$), 3.10 (t, 2, J = 6.3 Hz, CH$_2$Cl), 1.65 (t, 6, J_{HP} = 4.2 Hz, PMeMe′Ph), 1.61 (t, 6, J_{HP} = 4.2 Hz, PMeMe′Ph), 1.46 (q, 2, J = 6.15 Hz, -CH$_2$CH$_2$CH$_2$-). ^{13}C NMR (C$_6$D$_6$, only selected C$_{aryl}$ resonances listed): δ 257.3 (t, J_{CP} = 7.2 Hz, C$_\alpha$), 175.4 (C$_y$), 99.9 (C$_\beta$), 61.6 (OCH$_2$), 41.1 (CH$_2$Cl), 32.0 (CH$_2$CH$_2$CH$_2$), 13.6 (t, J_{CP} = 24.25 Hz, PMeMe′Ph), 11.9 (t, J_{CP} = 24.3 Hz, PMeMe′Ph). ^{31}P NMR (C$_6$D$_6$): δ 2.84. Anal. Found: C, 40.22; H, 4.63. C$_{22}$H$_{30}$Cl$_2$O$_3$P$_2$W. Calc.: C, 40.07; H, 4.55%. The data for 6-C are ^{1}H NMR (C$_6$D$_6$): δ 12.92 (dt, 1, J_{HH} = 8.1 Hz, J_{HP} = 1.3 Hz, H$_\alpha$), 7.9–6.9 (m, 20, aromatic protons), 5.44 (d, 1, J = 8.1 Hz, H$_\beta$), 3.09 (t, 2, J = 6.2 Hz, OCH$_2$), 3.05 (t, 2, J = 5.9 Hz, CH$_2$Cl), 2.06 (t, 6, J = 3.9 Hz, PMePh$_2$), 1.38 (q, 2, J = 6.1 Hz, -CH$_2$CH$_2$CH$_2$-). ^{13}C NMR (C$_6$D$_6$, only selected C$_{aryl}$ resonances listed): δ 255.6 (t, J_{CP} = 7.4 Hz, C$_\alpha$), 175.8 (C$_y$), 134.24 (t, J_{CP} = 5.7 Hz, PMePhPh′, C$_{ipso}$), 133.86 (t, J_{CP} = 5.7 Hz, PMePhPh′, C$_{ipso}$), 102.1 (C$_\beta$), 61.08 (OCH$_2$), 41.4 (CH$_2$Cl), 32.21 (CH$_2$CH$_2$CH$_2$), 16.8 (t, J_{CP} = 16.1 Hz, PMePh$_2$). ^{31}P NMR (C$_6$D$_6$): δ 16.7. Anal. Found: C, 49.19; H, 4.42. C$_{32}$H$_{34}$Cl$_2$O$_3$P$_2$W. Calc.: C, 49.05; H, 4.34%.

4.4. Observation of [W(= CHR$_A$)(O)(OC-(CH$_3$)(CF$_3$)$_2$)$_2$(thf)] 7-A

A mixture of 4-B (0.02 g, 0.04 mmol) and LiOC(CH$_3$)(CF$_3$)$_2$ (0.015 g, 0.08 mmol) was dissolved in 0.5 ml of THF-d_8. The reaction was followed by ^{1}H NMR spectroscopy and after 5 min at room temperature, signals corresponding to the ketalvinyl alkylidene 7-A and free P(OMe)$_3$ can be observed in the spectrum. ^{1}H NMR (THF-d_8): δ 9.62 (d, 1, J_{HH} = 9.9 Hz, H$_\alpha$), 5.75 (d, 1, J_{HH} = 9.9 Hz, H$_\beta$).

4.5. W(= CHR$_A$)(O)(TBEC)[P(OMe)$_3$] 8-A

A 10 ml toluene solution of dilithium salt of TBEC (0.57 g, 1.3 mmol) was added via canula to a red toluene solution of W(=CHR$_B$)Cl$_2$(O)[P(OMe)$_3$] (0.65 g,

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1.3 mmol). The solution was stirred for 12 h at room temperature and then 2 h to 65 °C. The resulting yellow-brown solution was filtered to remove the LiCl and concentrated under vacuum, then transferred over pentane to −78 °C affording a yellow powder that was separated by filtration, dried under vacuum and characterized as 8-A (0.94 g, 85%). Two isomers are observed, each of which are present as syn and anti rotamers; the diagnostic NMR signals are as follows. ^{1}H NMR (C$_6$D$_6$): major isomer (anti rotamer) δ 12.69 (dd, J_{HH} = 14.0 Hz, J_{HP} = 4.9 Hz, H$_\alpha$), 6.69 (dd, J_{HH} = 14.0 Hz, J_{HP} = 1.2 Hz, H$_\beta$), (syn rotamer) δ 12.06 (dd, J_{HH} = 11.5 Hz, J_{HP} = 3.8 Hz, H$_\alpha$), 6.91 (dd, J_{HH} = 11.5 Hz, J_{HP} = 1.2 Hz, H$_\beta$). Minor isomer (anti rotamer) δ 12.13 (dd, J_{HH} = 14.1 Hz, J_{HP} = 5.1 Hz, H$_\alpha$), (signal corresponding to H$_\beta$ is overlapped); (syn rotamer) δ 11.91 (dd, J_{HH} = 11.4 Hz, J_{HP} = 3.8 Hz, H$_\alpha$), 6.40 (dd, J_{HH} = 11.4 Hz, H$_\beta$). ^{13}C NMR (C$_6$D$_6$): major isomer δ 258.1 (d, J_{CP} = 20.5 Hz, C$_\alpha$), 152.7 (d, J_{CP} = 5.4 Hz, C$_y$), 96.6 (d, J_{CP} = 6.2 Hz, C$_\beta$), 64.9 (OCH$_2$), 64.5 (OCH$_2$). ^{31}P NMR (C$_6$D$_6$): major isomer δ 146.8. ^{19}F NMR (C$_6$D$_6$): major isomer δ −72.4, −73.7, −73.8, −77.9 (four inequivalent CF$_3$ groups). Anal. Found: C, 30.86; H, 3.41. C$_{22}$H$_{29}$F$_{12}$O$_8$PW. Calc.: C, 30.58; H, 3.38%.

4.6. Preparation of W(= CHR$_B$)(O)(OC$_6$F$_5$)$_2$ 9-B

A mixture of W(=CHR$_B$)Cl$_2$(O) [P(OMe)$_3$] (0.02 g, 0.04 mmol) and LiOC$_6$F$_5$ (0.015 g, 0.08 mmol) was dissolved in 8CD$_2$Cl$_2$-THF-d_8 mixture (0.5 ml). This solution turns quickly from red to yellow and at the same time the precipitation of LiCl occurs. The ^{1}H NMR spectrum of this solution taken after 5 min showed the complete conversion of the starting materials to a new ketalvinyl alkylidene complex identified as 9-B. ^{1}H NMR (CD$_2$Cl$_2$-THF-d_8): δ 9.86 (d, 1, J_{HH} = 10.2 Hz, H$_\alpha$), 5.22 (d, 1, J_{HH} = 10.2 Hz, H$_\beta$), 4.85 (t, 2, J = 6.0 Hz, OCH$_2$), 4.28 (t, 2, J = 5.7 Hz, OCH$_2$), 2.16 (q, 2, J = 5.7 Hz, -CH$_2$CH$_2$CH$_2$-). ^{13}C NMR (CD$_2$Cl$_2$-THF-d_8): δ 253.84 (s, C$_\alpha$), 167.9 (s, C$_y$), 143–135 (m, C$_6$F$_5$), 84.32 (s, C$_\beta$), 23.7 (s, -CH$_2$CH$_2$CH$_2$-), rest of the signals are overlapped by the solvent.

4.7. Preparation of W(= CHR$_B$)(O)(OC$_6$F$_5$)$_2$(thf) 10-B

The reaction described immediately above in THF-d_8 afforded the formation of a mixture of two ketalvinyl alkylidene species in approximately 1:1 ratio that cannot be separated. Both of them were identified as 9-B and 10-B by ^{1}H NMR spectroscopy. ^{1}H NMR (THF-d_8): δ 10.28 (d, 1, J_{HH} = 9.6 Hz, H$_\alpha$), 5.58 (d, 1, J_{HH} = 9.6 Hz, H$_\beta$), 4.88 and 4.48 (m, 4, OCH$_2$), 2.0 (m, 2, J = 5.7 Hz, -CH$_2$CH$_2$CH$_2$-).

Acknowledgements

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