Synthesis and Reactions of Tungsten Oxo Vinylalkylidene Complexes: Reactions of $WCl_2(O)(PX_3)$ (X = OMe, R) Precursors with 3,3-Diphenylcyclopropene[†]

F. Javier de la Mata and Robert H. Grubbs*

Arnold and Mabel Beckman Laboratory of Chemical Synthesis, Division of Chemistry and Chemical Engineering, California Institute of Technology, Pasadena, California 91125

Received May 25, 1995[⊗]

Complexes of the type $WCl_2(O)[PX_3]_3$ ($PX_3 = P(OMe)_3$ (**1**); $PMePh_2$ (**2**)) were synthesized according to procedures previously described in the literature. Upon treatment with 3,3-diphenylcyclopropene, complexes **1** and **2** afforded the corresponding η^2-cyclopropene complexes. Spectroscopic data of $W(\eta^2\text{-diphenylcyclopropene})Cl_2(O)[PX_3]_2$ ($PX_3 = P(OMe)_3$ (**4**); $PMePh_2$ (**5**)) were consistent with an octahedral geometry in which the two mutually trans PX_3 ligands and the cyclopropene ligand occupy equatorial positions cis to the apical oxo ligand. The thermal rearrangement of the η^2-cyclopropene complexes leads to the dimerization product of 3,3-diphenylcyclopropene: 1,1,6,6-tetraphenyl-1,3,5-hexatriene. The presence of carbene species before the dimerization occurs has been demonstrated. Upon treatment with 2 equiv of lithium hexafluoro-*tert*-butoxide, complexes **4** and **5** give the vinyl alkylidene complexes $W({=}CHCH{=}CPh_2)(O)[OC(CH_3)(CF_3)_2]_2[PX_3]$ ($PX_3 = P(OMe)_3$ (**10**); $PMePh_2$ (**7**)). The spectroscopic data of **10** and **7** indicated a distorted trigonal bipyramid, where the oxo and alkylidene ligands are cis to each other and placed in the equatorial plane.

Introduction

Transition-metal alkylidene and metallacyclobutane complexes are important intermediates in acyclic olefin metathesis,[1] ring-opening metathesis polymerization (ROMP),[1] acyclic diene[2] and alkyne[3] polymerizations, carbonyl olefinations,[4] and ring-closing metathesis[5] (RCM). Notable among the isolable complexes[6,7] that catalyze these transformations are titana[8]- and tantalacyclobutane[9] derivatives and certain alkylidene complexes of tungsten,[10−13] molybdenum,[14] rhenium,[15] and ruthenium.[16]

The arylimido tungsten and molybdenum alkylidene complexes are among the most effective early-transition-metal metathesis catalysts synthesized to date.[10−14] Three different types of arylimido tungsten alkylidene complexes have been reported:

(a) Neopentyl complexes[10] such as $W({=}CHCMe_3)(NAr)(OR')_2$. These four-coordinate monomeric species are stabilized by the substantial steric bulk of the imido, alkoxide, and alkylidene ligands.

[†] Contribution No. 9099.

[⊗] Abstract published in *Advance ACS Abstracts,* November 15, 1995.

(1) For general references on the metathesis reaction, see: (a) Grubbs, R. H.; Tumas, W. *Science* **1989**, *243*, 907−915. (b) Ivin, K. J. *Olefin Metathesis*; Academic Press: London, 1983. (c) Grubbs, R. H. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Ed.; Pergamon Press, Ltd.: New York, 1982; Vol. 8, pp 499−551. (d) Leconte, M.; Basset, J. M.; Quignard, F.; Larroche, C. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, pp 371−420.

(2) Wagener, K. B.; Boncella, J. M.; Nel, J. G. *Macromolecules* **1991**, *24*, 2649−2657.

(3) (a) Schlund, R.; Schrock, R. R.; Crowe, W. E. *J. Am. Chem. Soc.* **1989**, *111*, 8004−8006. (b) Park, L. Y.; Schrock, R. R.; Stieglitz, S. G.; Crowe, W. E. *Macromolecules* **1991**, *24*, 3489−3495. (c) Wallace, K. C.; Liu, A. H.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 644−654.

(4) (a) Pine, S. H.; Zahler, R.; Evans, D. A.; Grubbs, R. H. *J. Am. Chem. Soc.* **1980**, *102*, 3270−3272. (b) Brown-Wesley, K. A.; Buchwald, S. L.; Cannizzo, L.; Clawson, L.; Ho, S.; Meinhardt, D.; Stille, J. R.; Straus, D.; Grubbs, R. H. *Pure Appl. Chem.* **1983**, *55*, 1733−1744. (c) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1986**, 531−533. (d) Bazan, G. C.; Schrock, R. R.; O'Regan, M. B. *Organometallics* **1991**, *10*, 1062−1067.

(5) (a) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 5426−5427. (b) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1992**, *114*, 7324−7325. (c) Fu, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **1993**, *115*, 3800−3801. (d) Fujimura, O.; Fu, G. C.; Grubbs, R. H. *J. Org. Chem.* **1994**, *59*, 4029−2031. (e) Kim, S. H.; Bowden, N.; Grubbs, R. H. *J. Am. Chem. Soc.* **1994**, *116*, 10801.

(6) For general references on transition-metal alkylidene complexes, see: (a) Feldman, J.; Schrock, R. R. In *Progress in Inorganic Chemistry*; Lippard, S. J., Ed.; John Willey & Sons: New York, 1991; pp 1−74. (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988. (c) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, pp 221−283. (d) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 119−137. (e) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*; John Wiley & Sons: New York, 1988; Chapter 11.

(7) For general references on metallacycle complexes, see: (a) Ingroso, G. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, pp 639−677. (c) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; Chapter 9.

(8) (a) Gilliom, L. R.; Grubbs, R. H. *J. Am. Chem. Soc.* **1986**, *108*, 733−742. (b) Petasis, N. A.; Fu, D. *J. Am. Chem. Soc.* **1993**, *115*, 7208−7214.

(9) (a) Wallace, K. C.; Liu, A. H.; Dewan, J. C.; Schrock, R. R. *J. Am. Chem. Soc.* **1988**, *110*, 4964−4975. (b) Wallace, K. C.; Schrock, R. R. *Macromolecules* **1987**, *20*, 448−450. (c) Wallace, K. C.; Dewan, J. C.; Schrock, R. R. *Organometallics* **1986**, *5*, 2162−2164.

(10) Schrock, R. R.; DePue, R. T.; Feldman, J.; Schaverien, C. J.; Dewan, J. C.; Liu, A. H. *J. Am. Chem. Soc.* **1988**, *110*, 1423−1435.

(11) (a) Kress, J.; Wesolek, M.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1982**, 514. (b) Aguero, A.; Kress, J.; Osborn, J. A. *J. Chem. Soc., Chem. Commun.* **1985**, 793. (c) Couturier, J.; Paillet, C.; Leconte, M.; Basset, J. M.; Weiss, K. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 628−631.

(12) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 8130−8145.

0276-7333/96/2315-0577$12.00/0

(b) Imido vinylalkylidene complexes[12] such as $W(=CHCH=CPh_2)(NAr)(OR')_2[P(OMe)]_3$; in this case, the smaller size of the alkylidene group requires the presence of trimethyl phosphite in order to stabilize the complex.

(c) Tungsten imido alkylidene complexes have been reported by Van Koten and co-workers,[13] using bidentate phenoxide and alkoxide ligands.

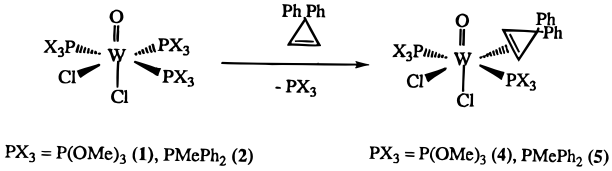
In comparison to the large number of tungsten imido alkylidene complexes, the synthesis of tungsten oxo alkylidene complexes that can be used in metathesis processes was essentially unknown at the outset of this study.[17] Only a couple of tungsten oxo alkylidene complexes are described in the literature,[18,19] but these complexes require Lewis acid activation to be metathesis catalysts.

In this paper we report the synthesis of the first oxo tungsten vinylalkylidene complexes via the reaction of appropriate tungsten(IV) oxo precursors and 3,3-diphenylcyclopropene. We also report some details about their catalytic activity in ROMP and RCM processes.

Results and Discussion

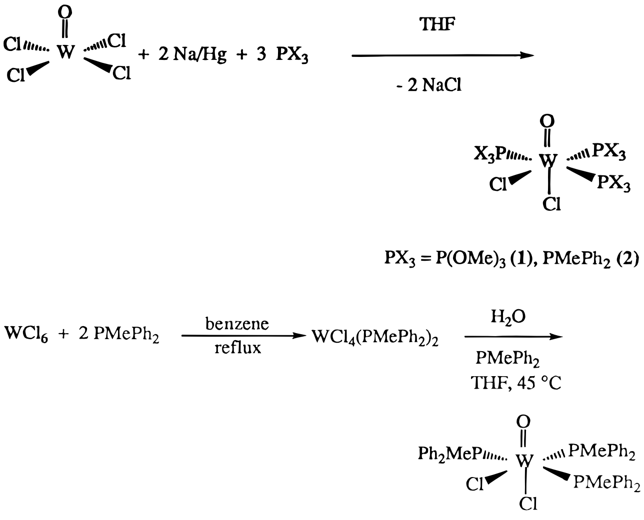
The tungsten(IV) oxo precursors $WCl_2(O)(PX_3)_3$ ($PX_3 = P(OMe)_3$ (**1**); $PMePh_2$ (**2**)) were prepared via known or modified literature procedures[20b] (see Experimental Section) (Scheme 1).

η^2-Cyclopropene Complexes. Synthesis, Characterization, and Stability. Synthesis. The reaction of **1** and **2** with 3,3-diphenylcyclopropene (**3**) was then investigated. In both cases, only one mode of reactivity was identified, leading to the η^2-cyclopropene complexes $W(\eta^2\text{-diphenylcyclopropene})Cl_2(O)[PX_3]_2$ ($PX_3 = P(OMe)_3$ (**4**); $PMePh_2$ (**5**)) (eq 1).



(1)

Scheme 1



This reaction of **1** with **3**, carried out in benzene, methylene chloride, or diethyl ether, was complete in 24 h at room temperature, while **2** and **3** required at least 6 h in benzene at 40 °C. In order to drive the reactions to completion, a slight excess of **3** was necessary. The resulting products, **4** and **5**, are yellow powders that can be purified by recrystallization from methylene chloride/pentane.

Characterization. The ^{1}H-NMR spectrum of **4** in deuterated benzene presents a triplet at $\delta = 5.70$ ($J_{H-P} = 6.3$ Hz) corresponding to the two olefinic protons of the diphenylcyclopropene ligand. This indicates the equivalence of both protons and that they are coupled to two equivalent phosphite ligands.

This ^{1}H-NMR spectrum also shows another triplet found at $\delta = 3.75$ ($J_{H\text{-}P} = 5.4$ Hz) corresponding to the two mutually trans phosphite ligands. The ^{13}C-NMR spectrum of this complex presents a triplet and a singlet for the three-membered ring carbons of the cyclopropene ligand and a triplet for the methyl groups of the phosphite ligand (see Experimental Section for details). The ^{31}P-NMR spectrum is a singlet at $\delta = 116.4$, which shows the equivalence of both phosphite ligands. The spectroscopic data obtained for **5** are analogous to those presented by **4**.

The spectroscopic data obtained for **4** and **5** are very similar to that of the analogous imido η^2-diphenylcyclopropene tungsten complexes prepared earlier,[12] which suggests a distorted octahedral structure: The olefin carbons occupy one position in the equatorial plane, the oxygen atom occupies one of the axial positions cis to the 3,3-diphenylcyclopropene ligand, the two mutually trans PX_3 groups occupy the equatorial positions in each side of the η^2-diphenylcyclopropene ligand, and, finally, the two chloride ligands occupy the remaining equatorial and axial positions (Figure 1).

For the tungsten imido phosphite η^2-diphenylcyclopropene complexes, it has been shown that the chemical shift of the olefinic proton and carbon resonances shifts downfield as the steric bulk of the imido ligand increases, corresponding to a weaker binding of the cyclopropene in the more sterically crowded molecule.[12] In the oxo phosphite complex **4**, the steric bulk of the oxo ligand is lower than that of any imido group. However, the observed chemical shift for the olefinic

---

[13] Van der Schaaf, P. A.; Abbenhuis, R. A.; Van der Noort, W. P. A.; de Graaf, R.; Grove, D. M.; Smeets, W. J. J.; Spek, A. L.; Van Koten, G. *Organometallics* **1994**, *13*, 1433−1444.

[14] (a) Murdzek, J. S.; Schrock, R. R. *Organometallics* **1987**, *6*, 1373−1374. (b) Murdzek, J. S.; Schrock, R. R. *Macromolecules* **1987**, *20*, 2640−2642. (c) Schrock, R. R.; Murdzek, J. S.; Bazan, G. C.; Robbins, J.; DiMare, M.; O'Regan, M. *J. Am. Chem. Soc.* **1990**, *112*, 3875−3886. (d) Bazan, G. C.; Oskam, J. H.; Cho, H.-N.; Park, L. Y.; Schrock, R. R. *J. Am. Chem. Soc.* **1991**, *113*, 6899−6907.

[15] Toreki, R.; Schrock, R. R. *J. Am. Chem. Soc.* **1990**, *112*, 2448−2449. (b) Schofield, M. H.; Schrock, R. R.; Park, L. Y. *Organometallics* **1991**, *10*, 1844−1855.

[16] (a) Nguyen, S. T.; Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1992**, *114*, 3974−3975. (b) Nguyen, S. T.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1993**, *115*, 9858.

[17] These complexes were proposed by Goddard as active, chain-carrying metathesis catalysts for high-valent Mo, W, and Re complexes. Rappé, A. K.; Goddard, W. A. *J. Am. Chem. Soc.* **1982**, *104*, 448−456.

[18] (a) Schrock, R. R.; Rocklage, S.; Wengrovious, J.; Rupprecht, G.; Fellmann, J. *J. Mol. Catal.* **1980**, *8*, 73−83. (b) Wengrovious, J. H.; Schrock, R. R.; Churchill, M. R.; Missert, J. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1980**, *102*, 4515−4516.

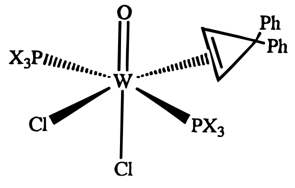
[19] (a) Blosch, L. L.; Abboud, K.; Boncella, J. M. *J. Am. Chem. Soc.* **1991**, *113*, 7066−7068. (b) Bryan, J. C.; Mayer, J. C. *J. Am. Chem. Soc.* **1990**, *112*, 2298−2308.

[20] (a) Butcher, A. V.; Chatt, J.; Leigh, G. J.; Richards, P. L. *J. Chem. Soc., Dalton Trans.* **1972**, 1064. (b) Carmona, E.; Sanchez, L.; Poveda, M. L. *Polyhedron* **1983**, *2*, 797−801. (c) Bradley, D. C.; Hursthouse, M. B.; Malik, K. M. A.; Nielson, A. J.; Short, R. L. *J. Chem. Soc., Dalton Trans.* **1983**, 2651−2656.

Table 1. Selected NMR Spectra Data for Some η^2-Diphenylcyclopropene Complexes[a]

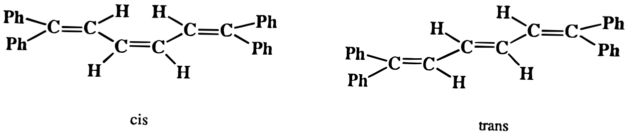
	^1H (t, $HC{=}CH$)		^{13}C (t, $HC{=}CH$)		^{31}P (PRR′2)
η^2-diphenylcyclopropene complex	δ	J_{HP}	δ	J_{CP}	δ
$W(\eta^2\text{-cyclopropene})Cl_2(O)[P(OMe)_3]_2$	5.70	6.3	69.8	13.5	116
$W(\eta^2\text{-cyclopropene})Cl_2(O)[PMePh_2]_2$	4.35	6.0	76.8	7	13
$W(\eta^2\text{-cyclopropene})Cl_2(NPh)[P(OMe)_3]_2$	5.08	5.8	64.8	16	118
$W(\eta^2\text{-cyclopropene})Cl_2(N\text{-}2,6\text{-}Me_2Ph)[P(OMe)_3]_2$	5.29	6.0	66.2	15	110
$W(\eta^2\text{-cyclopropene})Cl_2(NPh)[PMePh_2]_2$	4.19	5.7	72.4	9	5

[a] All spectra were acquired in C_6D_6. [b] Uncomplexed $HC{=}CHCPh_2$: $^1H(CD_2Cl_2)$ δ 7.54 ($HC{=}CH$); ^{13}C (CD_2Cl_2) δ 113.8 ($HC{=}CH$).



$PX_3 = P(OMe)_3$ (**4**), $PMePh_2$ (**5**)

Figure 1. Structure proposed for η^2-cyclopropene complexes.



cis

trans

Figure 2. Cis and trans isomers for 1,1,6,6-tetraphenyl-1,3,5-hexatriene.

protons is consistent with a more weakly bound cyclopropene (Table 1).

Stability. The oxo η^2-diphenylcyclopropene complexes (**4** and **5**) can be stored under argon at room temperature for long time periods without decomposition; both are soluble in aromatic hydrocarbons, tetrahydrofuran, and chlorinated solvents such as methylene chloride or chloroform.

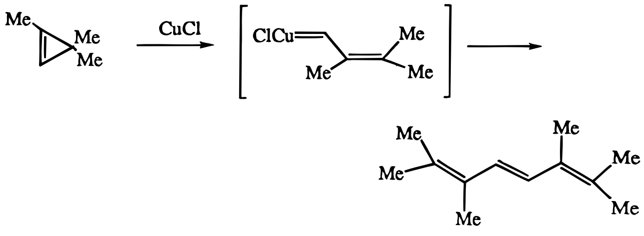
Complexes **4** and **5** have different thermal stabilities. When a benzene solution of **4** is heated at 50 °C over 1 h in the presence of an equivalent of $P(OMe)_3$, regeneration of the starting material **1** and formation of a new product corresponding to *cis*- and *trans*-1,1,6,6-tetraphenyl-1,3,5-hexatriene (**6**) is observed in the ^1H-NMR spectrum (Figure 2).

Complex **5** is more stable; higher temperatures (70 °C) and longer reactions times (5−6 h) are necessary to observe decomposition. Thermal decomposition of **5** also leads to the dimerization of diphenylcyclopropene, but in this case the presence of a vinyl alkylidene species, $W({=}CHCH{=}CPh_2)Cl_2(O)(PMePh_2)_2$, is observed in solution as an intermediate.

The compound $Ph_2C{=}CHCH{=}CHCH{=}CPh_2$ (**6**) had been previously observed by the dimerization of **3** using a ruthenium alkylidene catalyst.[21] The structure of **6** was confirmed by comparison of spectroscopic data with an independent synthesized sample (eq 2). By employing $TiCl_4$/Zn coupling conditions, the trans isomer was obtained in more than 90% yield.[22] In the decomposition of **4** and **5**, the cis:trans ratio varies from batch to batch but the cis isomer is always the major isomer in the mixture. In contrast, decomposition of the ruthenium catalyst gives only the trans isomer.[21]

$$\text{Ph2C=CH-COH} + 4\,TiCl_4 + 8\,Zn \xrightarrow[\text{Reflux, 12 h}]{\text{Dioxane}} Ph_2C{=}CH\text{-}CH{=}CH\text{-}CH{=}CPh_2 \qquad (2)$$

Scheme 2

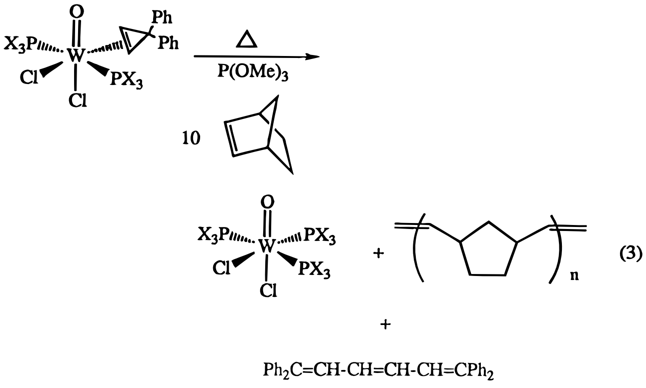


The mechanism involved in this dimerization process is uncertain, but the following evidence suggests the presence of a carbene complex as an intermediate:

(a) When a solution of **5** is heated to 70 °C for 2 h, the formation of a small amount of a vinyl alkylidene species can be observed by NMR spectroscopy. By comparison to known compounds, it can be infered that this alkylidene species might be $W({=}CHCH{=}CPh_2)Cl_2(O)[PMePh_2]_2$.

(b) There are examples in the literature that implicate carbene species in the transition-metal-catalyzed dimerization of cyclopropene[23] (Scheme 2).

(c) When the thermal decomposition of **4** and **5** occurs in the presence of strained olefins such as norbornene, the ROMP product of this olefin is obtained. A viscous, high-molecular-weight polymer is obtained when only 10 equiv of norbornene is added, indicating that initiation is much slower than propagation in this particular case (PDI = 1.83, M_n = 4018) (eq 3).



(3)

(d) If the thermal decomposition of **4** is carried out in the presence of an enamide such as $CH_2{=}CHCH_2C(O)$-

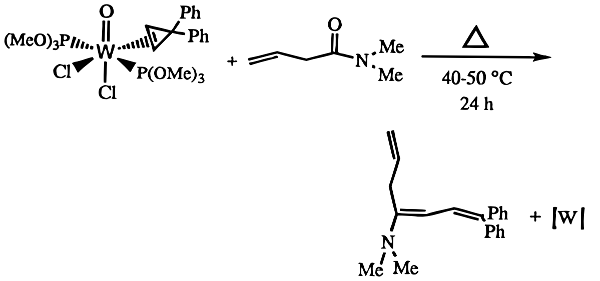
---

(21) Gagne, M. R.; Grubbs, R. H.; Feldman, J.; Ziller, J. W. *Organometallics* **1992**, *11*, 3933−3935.

(22) Mukaiyama, T.; Sato, T.; Hanna, J. *Chem. Lett.* **1973**, 1041.

(23) Techl, H. H. *Chem. Ber.* **1964**, *97*, 2681−2688.

NMe_2, the carbonyl olefination product is obtained[24] (eq 4).



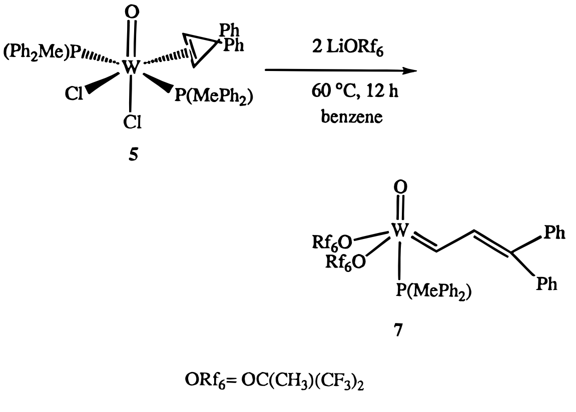
(4)

(e) Thermal decomposition of isolated tungsten oxo vinyl alkylidene complexes also leads to the formation of **6** (see the next section in this paper).

Synthesis, Characterization, and Catalytic Activity of New Tungsten Oxo Alkoxy Vinylalkylidene Complexes

Synthesis and Characterization. The detection of vinyl alkylidene species as intermediates in the decomposition reactions of the previous derivatives provided an impetus for the synthesis of new, potentially stable oxo vinyl alkylidene complexes. Exchange of chloride ligands for bulkier ligands such as suitable alkoxides was proposed to be a way to stabilize the final vinyl alkylidene complexes.

The reaction of 1 equiv of **5** with 2 equiv of $LiOC(CH_3)(CF_3)_2$ ($LiORf_6$) in benzene or toluene at 55−60 °C over 12 h leads to the formation of the tungsten oxo vinyl alkylidene complex $W(=CHCH=CPh_2)(O)(ORf_6)_2(PMePh_2)$ (**7**), which can be isolated as a yellow powder in 70−80% yield (eq 5). Complex **7** can be stored under argon at −30 °C for long time periods without showing signs of decomposition. This complex is soluble in aromatic hydrocarbons, tetrahydrofuran, and chlorinated solvents. When solutions of **7** are heated to more than 80 °C, the complex decomposes and the dimer **6** is observed.



(5)

Complex **7** is isolated as a mixture of two different (syn and anti) rotamers, the designations of which are based on comparison of the value of the I_{HH} coupling constants to those of other analogous imido vinyl alkylidene complexes.[12,25] The ^1H-NMR spectrum presents two double doublets corresponding to the resonances of the vinyl alkylidene ligand, at $\delta = 12.07$ (dd, $J_{H-H} = 14.7$ Hz, $J_{H-P} = 5.4$ Hz) and $\delta = 8.83$ (dd, $J_{H-H} = 14.7$ Hz, $J_{H-P} = 1.8$ Hz) for the anti isomer and $\delta = 11.48$ (dd, $J_{H-H} = 11.4$ Hz, $J_{H-P} = 3.3$ Hz) and $\delta = 8.48$ (dd, $J_{H-H} = 11.4$ Hz, $J_{H-P} = 1.8$ Hz) for the syn isomer.

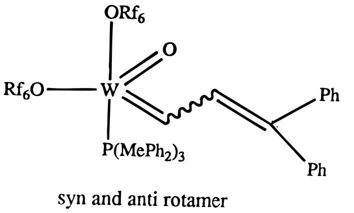


Figure 3. Proposed structure for **7**.

The spectroscopic data of **7** are very similar to those observed in an analogous imido complex $W(=CHCH=CPh_2)(NPh)(ORf_6)_2[PMePh_2]$.[26] The chemical shift and coupling constant corresponding to the H_α and H_β of the vinylalkylidene ligand are practically identical in both complexes. Accordingly, we proposed for our complex **7** a structure analogous to that found by X-ray diffraction for the above-mentioned phenyl imido vinyl alkylidene complex: a distorted trigonal bipyramid, where the oxo and vinylalkylidene ligands are cis to each other in the equatorial plane and the two apical positions are occupied by an alkoxide ligand and the phosphite ligand, making both alkoxides inequivalent (Figure 3).

The complex described above evolved from the study of a series of tungsten oxo vinyl alkylidene systems that started with the reaction of **4** with $LiORf_6$. When this reaction was done in C_6D_6, the formation of two new complexes was observed. After 10 min at room temperature the signals corresponding to a new η^2-diphenylcyclopropene complex (**8**) appear. This complex presents a triplet at $\delta = 5.18$ ($J_{H-P} = 5.7$ Hz), corresponding to the olefinic protons of the cyclopropene ligand, another triplet at $\delta = 3.49$ ($J_{H-P} = 5.4$ Hz), corresponding to two mutually trans phosphite groups, and a singlet at $\delta = 1.57$, corresponding to the methyl protons of the alkoxide group. These spectroscopic data seem to indicate that **8** is the result of the substitution of one chloride ligand by one hexafluoro-*tert*-butoxide ligand, leading to $W(\eta^2\text{-diphenylcyclopropene})(O)Cl(ORf_6)[P(OMe)_3]_2$. Complex **8** can also be observed when **3** is added to a solution containing $W(O)Cl(ORf_6)[P(OMe)_3]_3$ in THF-d_8, confirming the proposed structure of this new olefin complex. The appearance of another product can be detected over the course of time, and in fact after 16 h this new product (**9**) becomes the final product of this reaction at room temperature. This spectrum shows two broad signals at $\delta = 4.95$ and $\delta = 4.10$, corresponding to the protons of the cyclopropene ligand, indicating that both protons are inequivalent, and a broad doublet to $\delta = 3.25$ ppm, corresponding to the presence of only one phosphite group in **9**.

There is not enough data available to unambiguously assign the structure of **9**; however, the inequivalency and chemical shift of the signals of the cyclopropene

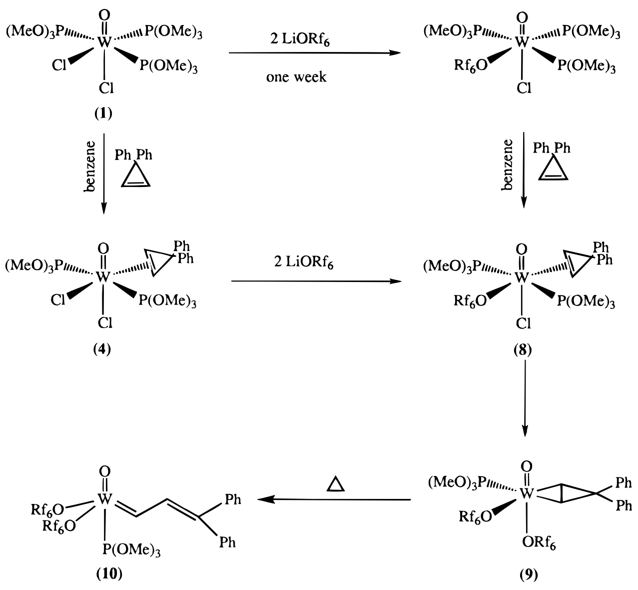
---

[24] The ^1H-NMR data in CD_2Cl_2 for this product: δ 7.6−7.2 (m, 10, $H_{aromatic}$), 6.74 (d, 1, $J_{H-H} = 10.8$ Hz), 6.42 (m, 1), 5.41 (dd, 1, $J = 16.8$, 1.5 Hz), 5.13 (dd, 1, $J = 9.90$, 1.5 Hz), 3.01 (s, 6, NMe_2), 1.43 (d, 2, $J = 17.4$ Hz).

[25] Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832−1843.

[26] De la Mata, F. J.; Claverie, J. P.; Grubbs, R. H., unpublished results.

Scheme 3



ligand are similar to those observed in the ^{1}H-NMR spectra of other well-characterized η^2-diphenylcyclopropene complexes[27] where only one phosphite group is present. Accordingly, we think that **9** could be W(η^2-diphenylcyclopropene)(O)(ORf_6)$_2$[P(OMe)$_3$].

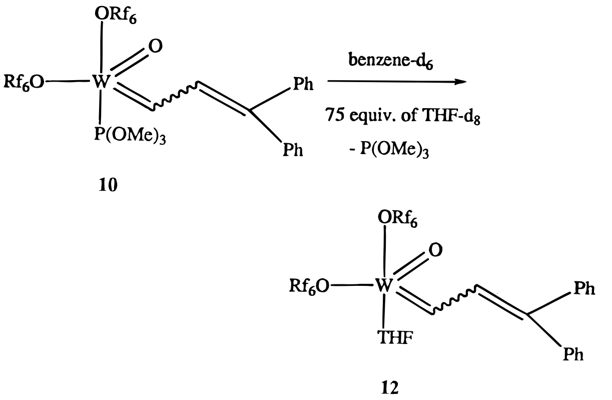
When solutions of **9** are heated to 55−60 °C for 1−2 h, the monophosphite adduct of the corresponding tungsten oxo vinylalkylidene alkoxide complex, W(=CHCH=CPh$_2$)(O)(ORf_6)$_2$[(P(OMe)$_3$] (**10**), is obtained as a mixture of syn and anti rotamers. Again syn and anti designations are based on comparison with analogous imido vinyl alkylidene complexes[12,25] (Scheme 3).

The resonances of the H_α and H_β of the vinylalkylidene ligand (in **10**) appear in the ^{1}H-NMR spectrum as two doublet of doublets, at $\delta = 12.5$ (dd, $J_{H-H} = 14.4$ Hz, $J_{H-P} = 6.6$ Hz) and $\delta = 8.83$ (dd, $J_{H-H} = 14.4$ Hz, $J_{H-P} = 2.1$ Hz) for the anti isomer and at $\delta = 11.75$ (dd, $J_{H-H} = 11.4$ Hz, $J_{H-P} = 4.5$ Hz) and $\delta = 9.03$ (dd, $J_{H-H} = 11.4$ Hz, $J_{H-P} = 2.1$ Hz) for the syn isomer.

The spectroscopic data of **10** are very similar to those of **7** and also to those reported for the corresponding 2,6-diisopropyl imido complex W(=CHCH=CPh$_2$)(NAr)(ORf_6)$_2$[P(OMe)$_3$] (**11**).[12] Accordingly we proposed for **10** the same structure that we have discussed for **7**.

We have found some differences between the two phosphite vinylalkylidene complexes **10** and **11**. For example, the syn isomer is the major isomer in the oxo complex **10**, while the anti one is the main isomer in the imido complex **11**. This could be attributed to the different steric environment presented by the oxo and imido ligands. Another difference concerns the facility of ligand exchange with phosphites. In order to remove P(OMe)$_3$ from **11**, it is necessary to use a phosphite sponge such us CuCl or [RuCp*(OR)]$_2$ in the presence of a weaker ligand.[28] In contrast, ligand exchange in **10** is accomplished by simple addition of suitable ligands. When solutions of **10** are concentrated under vacuum, phosphite dissociation occurs, causing the decomposition of the metal complex. The weakness of the M−P(OMe)$_3$ bond in the oxo complex relative to the imido can be explained by the tendency of the oxo ligand to form a partial triple bond. This makes the oxo ligand a better π-donor that destabilizes the M−P(OMe)$_3$ bond. This lack of stability has impeded the isolation of pure samples of **10** in the solid state, nevertheless **10** can be obtained cleanly in solution and these solutions can be used to study its activity in metathesis and polymerization processes (see the next section).

The reactions of **10** with an excess of THF lead to the corresponding THF adduct W(=CHCH=CPh$_2$)(O)(ORf_6)$_2$(THF) (**12**). This complex can also be prepared by carrying out the alkoxide addition to **4** in a mixture of C_6D_6/THF-d_8, CD_2Cl_2/THF-d_8, or THF-d_8 using the same reaction conditions as before. In all cases, no phosphite-bound alkylidene species are observed at any time, again demonstrating the weakness of the metal−phosphite bond (eq 6).



(6)

Complex **12** also appears as a mixture of syn and anti rotamers, in 1:1 ratio probably due to the low ligand steric bulk. In this case the ^{1}H-NMR spectrum presents two doublets for the resonances of the H_α and H_β in each rotamer, at $\delta = 11.86$ (d, $J_{H-H} = 12.6$ Hz) and $\delta = 9.32$ (d, $J_{H-H} = 12.6$ Hz) for the anti isomer and at $\delta = 10.25$ (d, $J_{H-H} = 10.8$ Hz) and $\delta = 9.28$ (d, $J_{H-H} = 10.8$ Hz) for the syn isomer (Figure 4).

The alkoxide addition to **4** is always accompanied by a small amount of decomposition, which is more evident when THF is present during the reaction. Among the major organic products of these reactions are **6** and $Ph_2C=CHCH_2CH_2CH=CPh_2$, which have been characteized by NMR and GC-MS analyses.[29] Finally, in an analogous manner to other alkoxylations, hexafluoro-*tert*-butyl alcohol is also produced in small amounts.[28]

In order to make more stable oxo vinylalkylidene species, two possible approaches were devised. One is to use bulkier alkoxides to afford a larger stabilization of the final alkylidene product. This approach has been successful and will be reported in a separate paper.[27b] The other way to stabilize these oxo vinyl alkylidene complexes is to change the P(OMe)$_3$ ligand to another ligand which is able to form stronger bonds with the metal center, as we have shown above with the exchange of P(OMe)$_3$ by PMePh$_2$.

---

[27] (a) de la Mata, F. J.; Johnson, L. K.; Grubbs, R. H., unpublished results. (b) de la Mata, F. J.; Fujimura, O.; Grubbs, R. H., unpublished results.

[28] Claverie, J. P. Ph.D. Thesis, California Institute of Technology, 1995.

[29] ^{1}H-NMR data of $Ph_2C=CHCH_2CH_2CH=CPh_2$ (C_6D_6): δ 7.3−7.0 (m, 20, $H_{aromatic}$), 5.96 (m, 2, CH), 2.21 (m, 4, CH_2). GC-MS data: $m/z = 386$.

Table 2. Selected NMR Spectral Data for Some Vinyl Alkylidene Complexes[a]

	H_α			H_β			
diphenylvinyl alkylidene complex	δ	J_{HH}	J_{HP}	δ	J_{HH}	J_{HP}	δ
syn-W(=CHCH=CPh$_2$)(O)(ORf$_6$)$_2$ (**10**) [P(OMe)$_3$]	11.75	11.4	4.5	9.03	11.4	2.1	
anti-W(=CHCH=CPh$_2$)(O)(ORf$_6$)$_2$ (**10**) [P(OMe)$_3$]	12.47	14.4	6.6	8.83	14.4	2.1	
syn-W(=CHCH=CPh$_2$)(NAr)(ORf$_6$)$_2$ (**11**)[b] [P(OMe)$_3$]	11.6	11.0	5.1	8.72	11.0		256
anti-W(=CHCH=CPh$_2$)(NAr)(ORf$_6$)$_2$ (**11**)[b] [P(OMe)$_3$]	12.3	14.4	8.0	8.72	14.4		264
syn-W(=CHCH=CPh$_2$)(O)(ORf$_6$)$_2$ (**12**) (THF)	10.25	10.8		9.32	10.8		
anti-W(=CHCH=CPh$_2$)(O)(ORf$_6$)$_2$ (**12**) (THF)	11.83	12.9		9.28	12.9		
syn-W(=CHCH=CPh$_2$)(O)(ORf$_6$)$_2$ (**7**) (PMePh$_2$)	11.48	11.4	3.3	8.48	11.4	1.8	263.6
anti-W(=CHCH=CPh$_2$)(O)(ORf$_6$)$_2$ (**7**) (PMePh$_2$)	12.07	14.7	5.4	8.83	14.7	2.1	268

[a] All spectra were acquired in C_6D_6 unless indicated otherwise. [b] Reference 12.

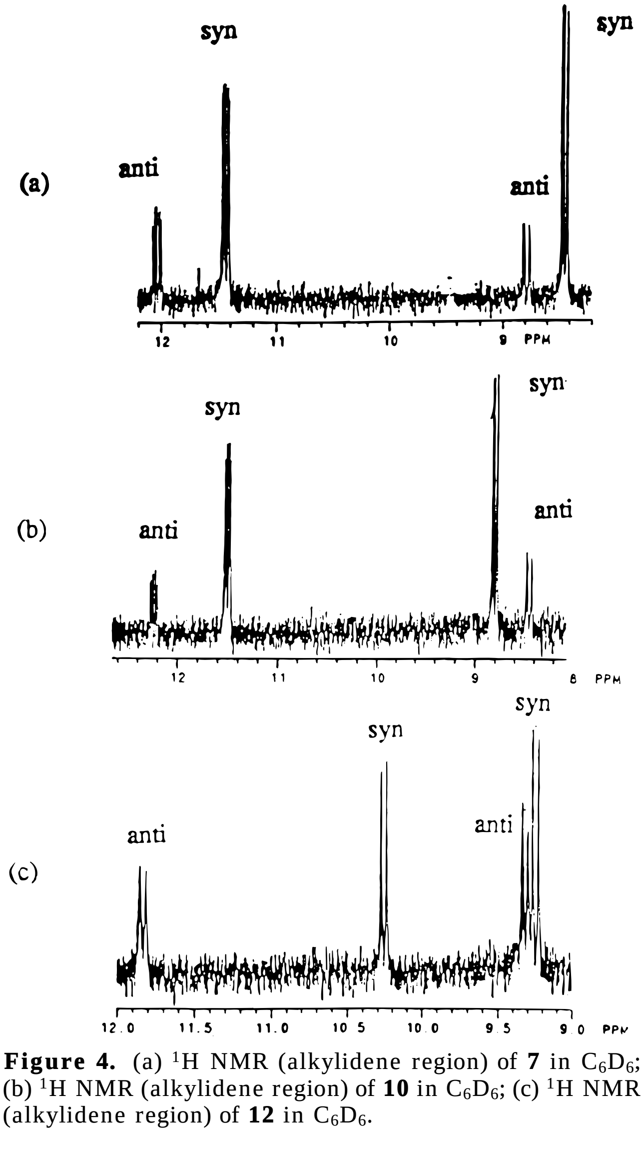


Figure 4. (a) ^1H NMR (alkylidene region) of **7** in C_6D_6; (b) ^1H NMR (alkylidene region) of **10** in C_6D_6; (c) ^1H NMR (alkylidene region) of **12** in C_6D_6.

Catalytic Activity of the Oxo Vinylalkylidene Complexes

The reactivity of these new tungsten oxo vinylalkylidene complexes **7**, **10**, and **12** was studied with various substrates. They show a significant activity in processes such as ROMP and RCM. A complete study about the activity of these new catalysts is currently under investigation[30] and here we provide a preliminary account of our results.

Complexes **10** and **12** were found to be very active catalysts in the ring-opening metathesis polymerization of norbornene at room temperature. These complexes can also ROMP cyclic olefins such as cyclooctene, 1,5-cyclooctadiene, and cyclooctatetraene derivatives. Only the most active metathesis catalysts will polymerize cyclooctatetraene. In contrast to the analogous imido complex **11**, there is no need to use a phosphite sponge to activate the complex. Complex **10** is also active in the ring-closing metathesis reaction of some dienes such as diethyl diallyl malonate or diene-yne derivatives.[31]

Conclusion. Complexes of the type $WCl_2(O)[PX_3]_3$ react with 3,3-diphenylcyclopropene to give η^2-cyclopropene complexes. The thermal decomposition of these η^2-cyclopropene complexes leads to the dimerization product of the diphenylcyclopropene ligand as a mixture of cis and trans isomers. The mechanism of this dimerization remains unknown, but the presence of vinyl alkylidene species before the dimerization occurs has been demonstrated. These η^2-cyclopropene complexes react with suitable alkoxides, first at room temperature and then at higher temperatures (50−60 °C) to give the first tungsten oxo vinylalkylidene complexes which have shown activity as a metathesis catalysts in ROMP and RCM processes.

The results of this study represent a greatly simplified entry into tungsten-based alkylidene olefin metathesis catalysts and demonstrate that oxo alkylidene complexes can serve as single-component, well-defined metathesis catalysts.

Experimental Section

General Considerations. All manipulations were carried out under argon with standard Schlenck techniques or in a nitrogen-filled glovebox equipped with a −40 °C freezer. Argon was purified by passage through columns of Chemalog R3-11 catalyst and Linde 4-Å molecular sieves. NMR spectra were recorded with either a JEOL FX-90Q (89.60-MHz ^1H, 22.53-MHz ^{13}C, 36.20-MHz ^{31}P) or a QE-300 Plus (300.10-MHz ^1H, 75.49-MHz ^{13}C) spectrometer. All coupling constants are reported in hertz. For the ^1H- and ^{13}C-NMR virtual triplet resonances of the trans phosphite/phosphine ligands, the

---

[30] Claverie, J. P.; de la Mata, F. J.; Grubbs, R. H., unpublished results.

[31] Zuercher, W.; Kim, S. H.; Grubbs, R. H., unpublished results.

coupling constant $N = |^2J_{HP} + {}^4J_{HP}|$ is given, where N is the separation of the outer lines of the triplet.[32] GC-MS spectra were recorded at the California Institute of Technology (Hewlett-Packard 5890) or at the University of California at Riverside. Elementary analyses were performed at the California Institute of Technology or by Oneida Research Services, Inc. All reactions were carried out at room temperature unless otherwise indicated.

Materials. Toluene, benzene, diethyl ether, and tetrahydrofuran were purified by methods developed in our research group.[33] 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.

3,3-Diphenylcyclopropene,[34] $WCl_4(O)$,[35] $WCl_2(O)[P(OMe)_3]_3$,[20b] and $WCl_2(O)[PMePh_2]_3$[20b] were synthesized according to literature methods. $P(OMe)_3$ was vacuum-transferred from Na and then subjected to several freeze−pump−thaw cycles. $(CF_3)_2(CH_3)COH$ was purchased, dissolved in Et_2O, deprotonated with 1 equiv of freshly titrated BuLi,[36] and purified by standard techniques.

Procedures. W(η^2-diphenylcyclopropene)Cl_2(O)-[$P(OMe)_3$]$_2$ (4). A 5-mL benzene solution of 3,3-diphenylcyclopropene (0.77 g, 4.02 mmol) was added to a purple solution of $WCl_2(O)[P(OMe)_3]_3$ (2 g, 3.66 mmol) in 20 mL of benzene. The original purple solution turned yellow as the reaction mixture was stirred for 24 h. The solvent was removed under vacuum, and the resulting yellow oil was left under dynamic vacuum for an additional 12 h and then washed with two 15-mL portions of pentane. The yellow solid (2.25 g, 95%) was dried in vacuo and stored at −30 °C: ^{1}H NMR (C_6D_6) δ 7.30−6.90 (m, 10, H_{aryl}), 5.70 (t, 2, J_{H-P} = 6.30 Hz, HC=CH), 3.57 (t, 18, N = 10.80, $P(OMe)_3$); ^{13}C NMR (C_6D_6) δ 151.5 (C*Ph*Ph′: C_{ipso}), 142.6 (CPh*Ph′*: C'_{ipso}), 132.2, 126.3, 125.9 (CPhPh′), 69.8 (t, J_{C-P} = 13.51 Hz, HC=CH), 63.0 (s, CPh_2), 53.8 (t, N = 4.0 Hz, $P(OMe)_3$); ^{13}C NMR (CD_2Cl_2) δ 151.2 (C*Ph*Ph′: C_{ipso}), 141.8 (CPh*Ph′*: C_{ipso}), 131.8, 127.9, 127.6, 127.5, 126.3, 126.0 (CPhPh′: C_o, C'_o, C_m, C'_m, C_p, C'_p), 69.7 (t, J_{C-P} = 13.43 Hz, HC=CH), 62.6 (s, CPh_2), 54.5 (t, $P(OMe)_3$); ^{31}P NMR (C_6D_6) δ 116.4. Anal. Calcd for ($C_{21}H_{30}Cl_2O_7P_2W$): C, 38.99; H, 4.67. Found: C, 38.62; H, 4.41.

W(η^2-diphenylcyclopropene)Cl_2(O)[$PMePh_2$]$_2$ (5). A 10-mL benzene solution of 3,3-diphenylcyclopropene (0.32 g, 1.69 mmol) was added to a purple solution of $WCl_2(O)[PMePh_2]_3$ (1.34 g, 1.54 mmol) in 30 mL of benzene. The reaction mixture was stirred for 4 h at 45 °C. The solvent was removed in vacuo to yielded a pale yellow solid, which was washed with three 15-mL portions of pentane. The resulting yellow product was dried under vacuum and stored at −30 °C in the drybox freezer (1.33 g, 90%). ^{1}H NMR (C_6D_6) δ 7.7−6.91 (m, 30, H_{aryl}), 4.35 (t, 2, J_{H-P} = 6.0 Hz, HC=CH), 2.47 (t, 6, N = 9.6, P*Me*Ph_2); ^{13}C NMR (C_6D_6, only some C_{aryl} chemical shifts are listed) δ 151.4 (C*Ph*Ph′: C_{ipso}), 143.1 (CPh*Ph′*: C_{ipso}), 134.7, 132.7, 132.3, 132.0, 130.9, 130.2 ($C_{aromatic}$), 76.8 (t, J_{C-P} = 6.5 Hz, HC=CH), 66.1 (s, CPh_2), 13.61 (t, N = 35.5, P*Me*Ph_2); ^{31}P NMR (C_6D_6) δ 13.3. Anal. Calcd for ($C_{41}H_{38}Cl_2OP_2W$): C, 57.03; H, 4.43. Found: C, 56.89; H, 4.26.

Ph_2C=CHCH=CHCH=CPh_2 (6): Method A. A 15-mL benzene solution of 3,3-diphenylcyclopropene (0.46 g, 2.37 mmol) was added by cannula to a purple solution of $WCl_2(O)$-[$P(OMe)_3$]$_3$ (0.26 g, 0.47 mmol) in benzene. After being stirred for 2 h at 55 °C, the reaction mixture was passed through a silica gel column. Removal of the solvent in vacuo gave a yellow crystalline solid (0.16 g, 70%). ^{1}H NMR (C_6D_6) trans isomer δ 7.4−7.1 (m, 20, H_{aryl}), 6.67 (m, 4, HCCH=CHCH); cis isomer δ 7.4−7.1 (m, 20, H_{aryl}), 6.25 (dd, 2, J = 8.4, 2.1 Hz, HCCH=CHCH), other doublet of doublets is obscured by the aromatic signals; ^{1}H NMR (CD_2Cl_2) trans isomer δ 7.44−7.25 (m, 20, H_{aryl}), 6.75 (dd, 2, J = 7.7, 3.2 Hz), 6.52 (dd, 2, J = 7.7, 3.2 Hz); cis isomer δ 7.44−7.25 (m, 20, H_{aryl}), 6.10 (dd, 2, J = 8.4, 2.4 Hz), other doublet of doublets is obscured by the aromatic signals. Exact MS: calcd for ($C_{30}H_{24}$) 384.1878; found 384.1884. **Method B.** One Schlenk flask was charged with cinnamaldehyde (0.50 g, 2.4 mmol), a solution of $TiCl_4$ in CH_2Cl_2 (9.6 mL, 9.6 mmol), and Zn (1.25 g, 19.0 mmol), after which dioxane (30 mL) was added to the reaction mixture. The resulting suspension was refluxed for 12 h and then was allowed to settle before it was filtered, giving a yellow solution. Dioxane was removed under vacuum and the resulting yellow residue was washed twice with pentane (5 mL), leading to a yellow powder characterized as **6** (95% trans).

W(=CHCH=CPh_2)(O)[$OC(CH_3)(CF_3)(CF_3)_2$]$_2$($PMePh_2$) (7). A mixture of W(HC=$CHCPh_2$)Cl_2(O)[$PMePh_2$]$_2$ (0.85 g, 0.98 mmol) and $LiOC(CH_3)(CF_3)_2$ (0.39 g, 2.07 mmol) was suspended in benzene (15 mL). This solution was stirred for 2 h at room temperature, then 2 h at 55−60 °C. The yellow suspension was filtered into −70 °C pentane, giving a yellow precipitate that was dried under vacuum (0.61 g, 65%): ^{1}H NMR (C_6D_6) anti rotamer, δ 12.07 (dd, J_{H-H} = 14.7, J_{H-P} = 5.4 Hz, H_α); 8.83 (dd, J_{H-H} = 14.7, J_{H-P} = 2.1 Hz, H_β), 7.5−6.8 (m, 20, H_{aryl}), syn rotamer δ 11.48 (dd, J_{H-H} = 11.4, J_{H-P} = 3.3 Hz, H_α); 8.48 (dd, J_{H-H} = 11.4, J_{H-P} = 1.8 Hz, H_β), 7.5−6.8 (m, 20, H_{aryl}). ^{13}C NMR (C_6D_6), major rotamer, δ 263.6 (d, J_{C-P} = 12.46 Hz, C_α), 142.1 (d, J_{C-P} = 3.9 Hz, $C\gamma$), 141.1, 138.8, 137.7, 132.6, 132.4 (C aromatic), 123.2 (d, J_{C-P} = 4.5 Hz, C_β), 18.7 (s, $OC(CH_3)(CF_3)_2$), 16.9 (s, $OC(CH_3)(CF_3)_2$), 12.6 (d, J_{C-P} = 15.02 Hz, P*Me*Ph_2).

Observation of W(η^2-diphenylcyclopropene)Cl(O)[OC-(CH_3)(CF_3)$_2$][$P(OMe)_3$]$_2$ (8): Procedure A. The cyclopropene complex **4** (20 mg, 0.031 mmol) was dissolved in C_6D_6 (500 mg) and $LiOC(CH_3)(CF_3)_2$ (64 mg, 0.034 mmol) was added. After 5−6 h at room temperature, a new cyclopropene complex **7** is the major product in the reaction mixture as identified by ^{1}H-NMR spectroscopy. ^{1}H NMR (C_6D_6) δ 7.6−6.9 (m, 10, H_{aryl}), 5.18 (t, 2, J_{H-P} = 5.7 Hz, HC=CH), 3.49 (t, 18, N = 10.8 Hz, $P(OMe)_3$), 1.57 (s, 3, $OC(CH_3)(CF_3)_2$). **Procedure B.** The oxo triphosphite complex **1** (20 mg, 0.036 mmol) was dissolved in THF-d_8 and $LiOC(CH_3)(CF_3)_2$ (14 mg, 0.072 mmol) was added. After a week at room temperature, approximately 50% of **1** was converted to another triphosphite complex identified as $WCl(O)(OC(CH_3)(CF_3)_2)[P(OMe)_3]_3$ by NMR spectroscopy. The reaction of this compound with diphenylcyclopropene results in the observation of **8**.

Observation of W(η^2-diphenylcyclopropene)(O)[OC-(CH_3)(CF_3)$_2$]$_2$[$P(OMe)_3$] (9). The cyclopropene complex **4** (20 mg, 0.031 mmol) was dissolved in C_6D_6 and then $LiOC(CH_3)(CF_3)_2$ (12 mg, 0.062 mmol) was added. After 18 h at room temperature, a new organometallic complex **9** was observed as the major product in the reaction mixture. ^{1}H NMR (C_6D_6) δ 7.45−7.05 (m, 10, H_{aryl}), 5.1 (dd broad, 1, *H*C=CH), 4.2 (d broad, 1, HC=C*H*), 3.25 (d, 9, $P(OMe)_3$), 1.93 (s, 3, OC*Me*(CF_3)$_2$), 1.77 (s, 3, OC*Me*(CF_3)$_2$).

W(=CHCH=CPh_2)(O)[$OC(CH_3)(CF_3)_2$]$_2$[$P(OMe)_3$] (10). A mixture of W(HC=$CHCPh_2$)Cl_2(O)[$P(OMe)_3$]$_2$ (25 mg, 0.038 mmol) and $LiOC(CH_3)(CF_3)_2$ (16 mg, 0.085 mmol) was suspended in deuterated benzene. The solution was stirred for 18 h at room temperature and then 2 h at 60 °C. The resulting yellow-brown suspension was filtered to remove the LiCl. The resulting solution contains the vinyl alkylidene **9** and 1 equiv of free $P(OMe)_3$. ^{1}H NMR (C_6D_6), anti rotamer, δ 12.5 (dd, J_{HH} = 14.4, J_{HP} = 6.6 Hz, H_α), 8.83 (dd, J_{HH} = 14.4, J_{HP} = 2.1 Hz, H_β), 7.5−7.0 (m, 10, H_{aryl}), 3.13 (d, 9, J_{HP} = 12.0 Hz,

---

[32] Harris, R. K. *Can. J. Chem.* **1964**, *42*, 2275.

[33] Pangborn, A. B.; Giardello, M. H.; Grubbs, R. H.; Rosen, R. K.; Timmers, F. J. *Organometallics*, submitted for publication.

[34] Moore, J. S.; Nguyen, S. T.; Grubbs, R. H., unpublished results.

[35] $WOCl_4$ may be purchased commercially or synthesized from (a) WO_3 and $SOCl_2$ (Nielson, A. J. In *Inorganic Syntheses*; Kirschner, S., Ed.; John Wiley & Sons: New York, 1985; pp 195−199) or (b) WCl_6 and $(Me_3Si)_2O$ (Gibson, V. C.; Kee, T. P.; Shaw, A. *Polyhedron* **1988**, *7*, 579−580).

[36] Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155−158.

$P(OMe)_3$), 1.86 (s, 3, OC*Me*($CF_3)_2$), 1.69 (s, 3, OC′*Me*($CF_3)_2$); syn rotamer, δ 11.75 (dd, $J_{HH} = 11.4$, $J_{HP} = 4.5$ Hz, H_α), 9.03 (dd, $J_{HH} = 11.4$, $J_{HP} = 2.1$ Hz, H_β), 7.5−7.0 (m, 10, H_{aryl}), 3.22 (d, 9, $J_{HP} = 12.0$ Hz, $P(OMe)_3$), 1.82 (s, 3, OC*Me*($CF_3)_2$), 1.73 (s, 3, OC′*Me*($CF_3)_2$).

Formation of W(=CHCH=CPh$_2$)(O)[OC(CH$_3$)(CF$_3$)$_2$]$_2$(THF) (12). Method A. A mixture of W(HC=CHCPh$_2$)Cl$_2$(O)[P(OMe)$_3$]$_2$ (20 mg, 0.031 mmol) and LiOC(CH$_3$)(CF$_3$)$_2$ (11.6 mg, 0.062 mmol) was suspended in a mixture of C_6D_6/THF-d_8 in a ratio of 10:1. The solution was stirred for 18 h at room temperature and then 2 h at 60 °C. The resulting yellow-brown suspension was filtered to remove LiCl. The resulting solution contains the vinyl alkylidene **12** and free $P(OMe)_3$. ^1H NMR (C_6D_6), anti rotamer, δ 11.83 (d, 1, $J_{HH} = 12.9$ Hz, H_α), 9.28 (d, 1, $J_{HH} = 12.9$ Hz, H_β); syn rotamer, δ 10.25 (d, 1, $J_{HH} = 10.8$ Hz, H_α), 9.32 (d, 1, $J_{HH} = 10.8$ Hz, H_β). **Method B.** THF-d_8 (75 equiv) was added to a solution of **10** in deuterated benzene, leading immediately to the formation of **12**.

Metal Complex Catalyzed ROMP Reactions with Different Strained Olefins. In a typical experiment, a solution of the corresponding olefin in benzene (10 mL of a 0.5 M solution, 5.0 mmol) was added to a stirred solution of the corresponding catalyst in benzene (1 mL of a 0.05 M solution, 50 μmol) under inert atmosphere. After 30 min the reaction mixture was quenched with a drop of benzaldehyde and poured into 100 mL of methanol. The precipitated polymer was collected by filtration, dissolved again in methylene chloride, and passed through a silica column; the solvent then was removed under vacuum and the resulting polymer was dried in vacuo.

Metal Complex Catalyzed RCM Reactions with Different Dienes. In a typical experiment, the corresponding diene (5.0 mmol) was added to a solution of the corresponding catalyst in benzene (50 μmol) under inert atmosphere. When the reaction was complete, the reaction mixture was passed through a silica column to remove the catalyst; the solvent was then removed under vacuum and the organic residue was analyzed by NMR spectroscopy and GC-MS.

Acknowledgment. We gratefully acknowledge support from the NSF, and F.J.M. thanks the Ministerio de Educacion y Ciencia of Spain for a postdoctoral fellowship. Thanks also to Dr. Scott Miller and Jerome P. Claverie for helpful discussions.

OM950389C