Synthesis of Tungsten Vinyl Alkylidene Complexes via the Reactions of $WCl_2(NAr)(PX_3)_3$ (X = R, OMe) Precursors with 3,3-Disubstituted Cyclopropenes

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Abstract: Several $WCl_2(NAr)(PX_3)_3$ complexes were synthesized, including $WCl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_3$ (**1**), $WCl_2(NPh)[P(OMe)_3]_3$ (**2**), $WCl_2(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]_3$ (**3**), and $WCl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_3$ (**4**). NMR spectroscopic data for these complexes and a single-crystal X-ray diffraction study of **4** supported a meridional arrangement of the three PX_3 ligands, all lying cis to the apical imido ligand. The lability of one PX_3 ligand in complexes **1–4** was demonstrated by reactions with ethylene and phenyl- and diphenylacetylene to give the corresponding π-acceptor (L) complex $WCl_2(L)(NAr)(PX_3)_2$. In solution, some of the $WCl_2(L)(NAr)(PX_3)_2$ complexes, especially those with $P(OMe)_3$ ligands, were in equilibrium with $WCl_2(L)(NAr)(PX_3)$ and free PX_3; complete removal of 1 equiv of PX_3 was achieved upon addition of CuCl. Complexes **1–4** and also $WCl_2(NPh)(PMePh_2)_3$ reacted with 3,3-diphenylcyclopropene and 4,8-dioxaspiro[2.5]oct-1-ene (referred to subsequently as diphenyl- and ketalcyclopropene) to give a number of η^2-cyclopropene complexes and/or vinyl alkylidene complexes. Concentrated diethyl ether solutions of the reactants and use of the sterically smaller tungsten precursors enabled the clean formation of the η^2-cyclopropene complexes $W(\eta^2\text{-cyclopropene})Cl_2(NAr)(PX_3)_2$. Spectroscopic data and a single-crystal X-ray diffraction study of $W(\eta^2\text{-diphenylcyclopropene})Cl_2(NPh)[P(OMe)_3]_2$ indicated an octahedral geometry in which the two mutually trans PX_3 ligands and the cyclopropene occupy equatorial positions cis to the apical imido ligand and the substituents of the cyclopropene lie syn to the imido ligand. The η^2-cyclopropene complexes were converted to the corresponding vinyl alkylidene complexes $W(=CHCH=CR_2)Cl_2(NAr)(PX_3)_2$ thermally, photochemically, and chemically (catalysis by $HgCl_2$). For the reactions of the sterically more bulky tungsten precursors with cyclopropenes, direct isolation of the vinyl alkylidene complexes was possible. A crystal structure of an alkoxide derivative $W(=CHCH=CPh_2)[N\text{-}2,6\text{-}C_6H_3\text{-}(i\text{-}Pr)_2][OCMe(CF_3)_2]_2[P(OMe)_3]$ confirmed the formation of a diphenylvinyl alkylidene ligand with an s-trans arrangement of the double bonds. In addition to an s-trans isomer, the ketalvinyl alkylidene ligand also formed two different s-cis isomers with one oxygen atom of the ketal ring chelating to tungsten. A crystal structure showed that, in one of these isomers, the ketal ring has been opened by a chloride ligand from tungsten, and a mechanism is proposed for this rearrangement.

Introduction

Traditionally, nucleophilic alkylidene complexes of transition metals have been synthesized almost exclusively via α-hydrogen abstraction routes.[1] However, in recent years the rearrangement of cyclopropenes has shown promise as a new entry to transition-metal vinyl alkylidene complexes.[2-4] For example, the first synthesis of isolable transition-metal vinyl alkylidene complexes from cyclopropenes was reported in 1989 and involved the reaction of 3,3-disubstituted cyclopropenes with bis(cyclopentadienyl)titanium(II) and -zirconium(II) precursors.[2a] Exclusive formation of the vinyl alkylidene product $Cp_2(Me_3P)Ti(=CHCH=CRR')$ was observed upon reaction of 3,3-diphenyl- and 3-methyl-3-phenylcyclopropene with $Cp_2Ti(PMe_3)_2$.

Given the ability of nucleophilic alkylidene complexes to catalyze a number of important reactions, including acyclic olefin metathesis,[5] ring-opening metathesis polymerization,[5] alkyne polymerizations,[6] carbonyl olefinations,[7] and acyclic-diene me-

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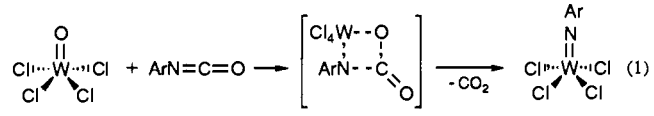
tathesis polymerizations[8] and ring-closing reactions,[9] the further development of alternative routes to alkylidene complexes would be useful. In the following investigation, the reactivity of 3,3-disubstituted cyclopropenes with $WCl_2(NAr)(PX_3)_3$ [Ar = Ph, 2,6-C_6H_3-Me_2, 2,6-C_6H_3-(*i*-Pr)$_2$; PX_3 = $PMePh_2$, PEt_2Ph, $P(OMe)_3$] complexes was determined. The synthesis of $WCl_2(NPh)(PR_3)_3$ complexes was first reported in 1983,[10] and their selection as precursors for this study was based upon their ability to form a variety of π-acceptor complexes of the form $WCl_2(L)(NPh)(PR_3)_2$ (L = CO, CN-*t*-**Bu**, MeC(O)H, olefins, acetylenes; PR_3 = $PMePh_2$, PMe_3) via the substitution of one phosphine ligand.[11] The formation of the π-acceptor complex is sensitive to the steric bulk and donating ability of the phosphine ligand, with the displacement of $PMePh_2$ being particularly facile, presumably due to steric crowding in the equatorial plane.[11a,b] Here we report that, upon loss of a phosphine or phosphite ligand, the $WCl_2(NAr)(PX_3)_3$ precursors react with 3,3-disubstituted cyclopropenes to give η^2-cycloproprene complexes and/or vinyl alkylidene complexes, depending on the reaction conditions and the steric bulk of the metal precursor. The vinyl alkylidene complexes that are produced are analogs of known tungsten neopentylidene complexes, such as $W(=CHCMe_3)Cl_2(NPh)L_2$ (L = PMe_3, PEt_3), whose synthesis by α-hydrogen abstraction routes and also by alkylidene transfer from $Ta(=CHCMe_3)L_2Cl_3$ was reported in 1982.[12]

Results and Discussion

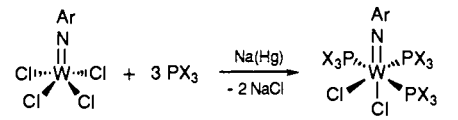
Synthesis, Characterization, and Reactivity of $WCl_2(NAr)(PX_3)_3$ Complexes. Synthesis. The thermal ring-opening of 3,3-disubstituted cyclopropenes to give tungsten vinyl alkylidene complexes required the synthesis of several new $WCl_2(NAr)(PX_3)_3$ derivatives containing both substituted arylimido ligands and labile PX_3 ligands (*vide infra*). Substituted arylimido precursors $WCl_4(NAr)$ [Ar = 2,6-$C_6H_3Me_2$, 2,6-C_6H_3-(*i*-Pr)$_2$] were synthesized via the established method of reacting $WCl_4(O)$ with the corresponding isocyanate (eq 1).[10] However, in comparison



(1)

to the generation of $WCl_4(NPh)$ by this route, longer reaction times and higher temperatures were required for complete formation of the substituted arylimido derivatives. For example, the synthesis of $WCl_4(NPh)$ was reported in refluxing benzene, while the syntheses of WCl_4(N-2,6-$C_6H_3Me_2$) and WCl_4[N-2,6-C_6H_3(*i*-Pr)$_2$] were accomplished in refluxing toluene and *p*-xylene, respectively.[13] The lowering of the reaction rates when sterically demanding isocyanates are employed is consistent with the postulated [2+2] cycloaddition of the tungsten oxo bond and the isocyanate (eq 1),[14] and it also corresponds with the report that $WCl_4(NCMe_3)$ cannot be made by this method.[15]

Since one $PMePh_2$ ligand of $WCl_2(NPh)(PMePh_2)_3$ is readily displaced at room temperature,[11] initial efforts to obtain substituted arylimido derivatives focused on the synthesis of $WCl_2(NAr)(PMePh_2)_3$ [Ar = 2,6-$C_6H_3Me_2$, 2,6-C_6H_3-(*i*-Pr)$_2$] complexes via the sodium amalgam reduction of the $WCl_4(NAr)$ precursors in the presence of $PMePh_2$.[10] Although resonances consistent with the formation of WCl_2(N-2,6-$C_6H_3Me_2$)$(PMePh_2)_3$ were observable by ^1H NMR spectroscopy,[16] initial attempts to cleanly isolate this complex in reasonable yields were unsuccessful. For reactions involving the (2,6-diisopropylphenyl)imido precursor, NMR signals characteristic of $WCl_2(NAr)(PMePh_2)_3$ were not observed. Presumably, unfavorable steric interactions between the arylimido alkyl substituents and the bulky $PMePh_2$ ligands, which are known to favor coordination in a meridional arrangement cis to the imido group,[10,17] were responsible for the poor yields in these reactions. When PEt_2Ph, a more donating and slightly smaller phosphine than $PMePh_2$,[18] was used, the synthesis and clean isolation of WCl_2(N-2,6-$C_6H_3Me_2$)$(PEt_2Ph)_3$ (**1**) was achieved (eq 2).



(2)

For PX_3 = PEt_2Ph, Ar = 2,6-C_6H_3-Me_2 (**1**)

For PX_3 = $P(OMe)_3$, Ar = Ph (**2**); 2,6-C_6H_3-Me_2 (**3**); 2,6-C_6H_3-(*i*-Pr)$_2$ (**4**)

Due to the sensitivity of the stability of $WCl_2(NAr)(PR_3)_3$ complexes to the size of the phosphine ligand, the synthesis of phosphite analogues was pursued. It was hoped that the small size of $P(OMe)_3$ in combination with its weak donating ability, relative to that of phosphines,[19] would enable the synthesis of isolable complexes containing both bulky arylimido substituents and labile donor ligands.[20] This proved to be the case: $WCl_2(NAr)[P(OMe)_3]_3$ [Ar = Ph (**2**), 2,6-C_6H_3-Me_2 (**3**), 2,6-C_6H_3-(*i*-Pr)$_2$ (**4**)] complexes were synthesized via the sodium amalgam reduction of their respective $WCl_4(NAr)$ precursors in the presence of $P(OMe)_3$ and isolated in good yields (eq 2). The formation of a light purple-gray solution, typically after about 1 h of rapid stirring, provided a clear indicator of the complete formation of $WCl_2(NAr)[P(OMe)_3]_3$. The reaction was stopped at this point, as additional stirring led to poor yields and difficulties in clean isolation of the product. The syntheses of the phosphine analogues do not exhibit the same sensitivity to reaction times,[10] and therefore, it is likely that the π-accepting capability of the

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(16) WCl_2(N-2,6-$C_6H_3Me_2$)$(PMePh_2)_3$: ^1H (C_6D_6) δ 1.97 (s, 6, NAr: *Me*$_2$), 1.93 (br t, 6, mutually trans P*Me*Ph_2's), 1.54 (d, 3, J_{HP} = 7.81 Hz, P*Me*Ph_2 trans to Cl).

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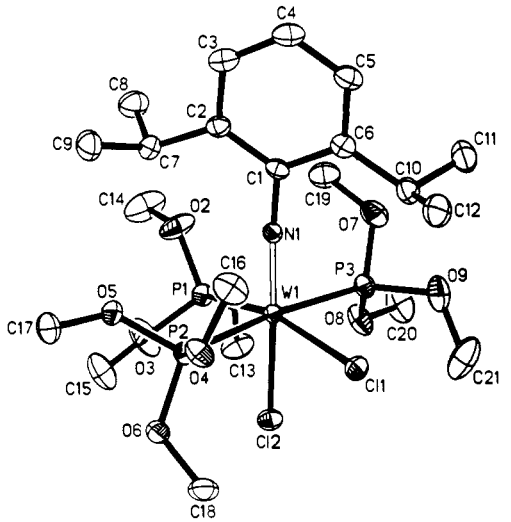


Figure 1. ORTEP plot of $WCl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_3$ (**4**). Thermal ellipsoids are drawn at the 50% probability level.

Table I. Selected Bond Lengths and Angles for **4**

Bond Lengths (Å)			
W(1)–Cl(1)	2.495(1)	W(1)–Cl(2)	2.475(1)
W(1)–P(1)	2.451(1)	W(1)–P(2)	2.486(1)
W(1)–P(3)	2.497(1)	W(1)–N(1)	1.767(3)
Bond Angles (deg)			
Cl(1)–W(1)–Cl(2)	85.0(1)	Cl(1)–W(1)–P(1)	163.0(1)
Cl(2)–W(1)–P(1)	78.1(1)	Cl(1)–W(1)–P(2)	83.4(1)
Cl(2)–W(1)–P(2)	89.1(1)	P(1)–W(1)–P(2)	97.7(1)
Cl(1)–W(1)–P(3)	89.5(1)	Cl(2)–W(1)–P(3)	88.6(1)
P(1)–W(1)–P(3)	88.6(1)	P(2)–W(1)–P(3)	172.7(1)
Cl(1)–W(1)–N(1)	98.0(1)	Cl(2)–W(1)–N(1)	177.0(1)
P(1)–W(1)–N(1)	98.9(1)	P(2)–W(1)–N(1)	90.9(1)
P(3)–W(1)–N(1)	91.8(1)	W(1)–N(1)–C(1)	173.5(2)

phosphite ligand enables reduction beyond the tungsten(IV) oxidation state.

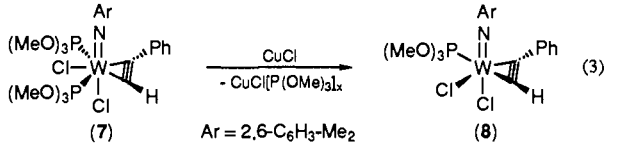
Characterization. Spectroscopic data for the $WCl_2(NAr)[P(OMe)_3]_3$ complexes is consistent with the expected meridional arrangement of the $P(OMe)_3$ ligands.[10] For example, a virtual triplet and a doublet appear in the ^1H and ^{13}C NMR spectra of these species and correspond, respectively, to the two mutually trans phosphite ligands and the phosphite ligand trans to a chloride ligand. In the ^{31}P NMR spectra, coupling between the inequivalent phosphite ligands gives rise to doublet and triplet resonances in a 2:1 ratio. The structure of these complexes was further confirmed by an X-ray crystallographic study of $WCl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_3$ (**4**).[21] An ORTEP diagram of this complex is shown in Figure 1, and selected bond distances and angles are given in Table I. The arrangement of the ligands about the metal center exhibits several distortions from a perfect octahedral geometry: The equatorial chloride ligand and the phosphite ligand trans to it [Cl(1) and P(1)] both lie on the opposite side of the equatorial plane from the imido group, a wide angle [97.7(1)°] exists between two of the cis phosphite moieties [P(1) and P(2)], and the imido group is bent away from these same two phosphite ligands [W(1)–N(1)–C(1) = 173.5(2)°]. These distortions appear to relieve steric crowding between the arylimido substituents and the equatorial ligands, an observation that is consistent with the previous proposal that $WCl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2](PMePh_2)_3$ could not be synthesized due to unfavorable steric interactions between the imido substituents and the $PMePh_2$ ligands. The W(1)–P(1) bond length of the phosphite lying trans to a chloride ligand [2.451(1) Å] is shorter than the W(1)–P(2) and W(1)–P(3) bond lengths of the two mutually trans phosphite ligands [2.486(1) and 2.497(1) Å], and this difference is reflected in the ^{31}P NMR chemical shifts and coupling constants. That is, the triplet resonance for P(1) [143.4 ppm, J_{PW} = 566 Hz] is shifted farther downfield and exhibits a larger tungsten–phosphorus coupling constant than the doublet resonance for P(2) and P(3) [128.0 ppm, J_{PW} = 456 Hz].

π-Complex Formation.[22] The lability of the phosphine/phosphite ligands of complexes **1–4** was determined by the reactions of these complexes with ethylene and with phenyl- and diphenylacetylene. Diphenylacetylene reacted at room temperature with $WCl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_3$ (**1**) to give $W(PhC{\equiv}CPh)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_2$ (**5**). The high lability of a PEt_2Ph ligand of **1** is apparent when this reaction is contrasted with the synthesis of the analogous PMe_3 complex $W(PhC{\equiv}CPh)Cl_2(NPh)(PMe_3)_2$, which required 20 h of refluxing in benzene.[11c]

The phosphite complexes **2–4** readily underwent substitution reactions, generally at room temperature, with even relatively poor π-acceptors such as ethylene. In the ^1H NMR spectrum of the ethylene complex $W(H_2C{=}CH_2)Cl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_2$ (**6**), two multiplets were observed for the ethylene protons (syn and anti to the imido ligand) at 3.25 and 2.85 ppm. According to difference nOe measurements, the upfield ethylene multiplet (2.85 ppm) corresponds to the protons lying syn to the imido ligand. In the ^{13}C NMR spectrum, an upfield shift to 42.3 ppm (Δ = 80.9 ppm) was observed for the ethylene carbon resonance upon complexation. This value lies in between the chemical shifts reported for $W(H_2C{=}CH_2)Cl_2(NPh)(PMe_3)_2$ (39.4 ppm)[11f] and $W(H_2C{=}CH_2)Cl_2(NPh)(PMePh_2)_2$ (48.0 ppm)[11b] and thus indicates that, in $WCl_2(L)(NAr)[P(OMe)_3]_2$ complexes, there is strong back-donation to the π-acceptor ligand (L), despite the potentially poor donating/competing π-accepting ability of the ancillary phosphite ligands.

The room-temperature reaction of $WCl_2(N\text{-}2,6\text{-}C_6H_3\text{-}Me_2)[P(OMe)_3]_3$ (**3**) and PhC≡CH in toluene resulted in the formation of the corresponding acetylene complex $W(PhC{\equiv}CH)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]_2$ (**7**) in good yield. Slow rotation about the imido group in **7** was evidenced by the observation of a broad singlet for the imido methyl protons. Otherwise, the NMR spectral data of **7** corresponds closely with that of the analogous phosphine complexes of phenylacetylene $W(PhC{\equiv}CH)Cl_2(NPh)(PMe_3)_2$[11c] and $W(PhC{\equiv}CH)Cl_2(NPh)(PMePh_2)_2$.[11b]

However, in contrast to the analogous phosphine complexes,[11] an equilibrium between **7** and the monophosphite adduct $W(PhC{\equiv}CH)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]$ (**8**) was observed in solution.[23] The addition of CuCl, a phosphine/phosphite "sponge",[12] resulted in the clean and selective formation of **8** (eq 3), which was characterized by its ^1H, ^{13}C, and ^{31}P NMR spectra.

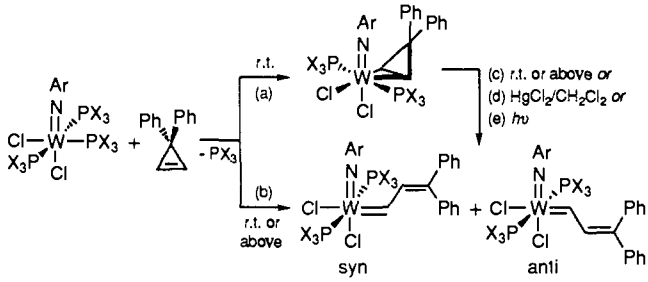


(21) The structure of the analogous trimethylphosphine complex $WCl_2(NPh)(PMe_3)_3$ has been reported. See: Reference 10a.

(22) Detailed studies of π-complex formation have been published for $WCl_2(NPh)(PR_3)_3$ complexes (PR_3 = $PMePh_2$ or PMe_3; ref 11), and therefore the discussion here is mainly limited to a comparison of the reactivity of the known phosphine complexes with the new phosphite analogs.

(23) Additional experiments indicated that mono(phosphite/phosphine) adducts of acetylene complexes could be observed in other cases, also. For example: (a) $W(PhC{\equiv}CPh)Cl_2[N\text{-}2,6\text{-}C_6H_3\text{-}(i\text{-}Pr)_2][P(OMe)_3]_2$ was observed in solution as a mixture of the bis- and mono(phosphite) adducts: ^{13}C NMR (CD_2Cl_2) bis[$P(OMe)_3$] adduct, δ 151.2 (t, J_{CP} = 15.70 Hz, Ph*C*≡*C*Ph); mono[$P(OMe)_3$] adduct, δ 174.9 (d, J_{CP} = 9.06 Hz, Ph*C*≡*C*′Ph cis to $P(OMe)_3$), 163.4 (d, J_{CP} = 31.50 Hz, PhC≡*C*′Ph trans to $P(OMe)_3$); ^{31}P (tol-d_8) δ 140.7 (free $P(OMe)_3$), 123.9 (J_{PW} = 336.9 Hz, mono[$P(OMe)_3$] adduct), 113.7 (J_{PW} = 358.9 Hz, bis[$P(OMe)_3$] adduct). (b) $W(HC{\equiv}C\text{-}t\text{-}Bu)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_2$ was observed as mainly the mono(PEt_2Ph) adduct in solution: ^1H (CD_2Cl_2) bis(PEt_2Ph) adduct δ 9.41 (d of d, J_{HP} = 22.36 Hz (trans), 6.05 Hz (cis), *H*C≡C-*t*-Bu); mono(PEt_2Ph) adduct δ 10.33 (d, J_{HP} = 18.05 Hz (trans), J_{HW} = 9.26 Hz, *H*C≡C-*t*-Bu); ^{31}P (CD_2Cl_2) δ 31.8 (J_{PW} = 190 Hz, mono(PEt_2Ph) adduct).

Scheme I



Loss of one phosphite resulted in a downfield shift of the remaining tungsten-bound phosphite ligand in the ^{31}P NMR spectrum and an increase in the phosphorus–tungsten coupling constant, and it also caused a downfield shift of the acetylenic carbons in the ^{13}C NMR spectrum, all consistent with stronger donation by the phosphite and acetylene ligands to the 16-electron complex **8**.[24] The decrease in steric crowding upon loss of a phosphite ligand enabled free rotation of the imido aryl ring, as was indicated by the appearance of a sharp singlet for the imido methyl protons. According to ^{1}H and ^{13}C NMR data, the phosphite ligand lies trans to the acetylenic proton (J_{HP} = 20.03 Hz for PhC≡C*H*) and cis to the acetylenic phenyl group (J_{CP} = 7.55 Hz for PhC≡CH).

In general, these reactions with simple π-acceptor ligands demonstrated several points: (1) One donor ligand in complexes **1–4** is readily displaced at room temperature. (2) The phosphite complexes are capable of strong back-donation to π-acceptor ligands. (3) The major difference between the reactivity of the phosphine and phosphite tungsten(IV) complexes is the higher lability of a second phosphite ligand upon π-complex formation. This latter observation is consistent with the relative donating/π-accepting abilities of phosphine and phosphite ligands. More specifically, the electron density of the metal center of the tris(phosphine) precursors $WCl_2(NAr)(PR_3)_3$ should be greater than that of the resulting π-acceptor (L) complexes $WCl_2(L)(NAr)(PR_3)_2$, thus electronically favoring loss of phosphine from the tris(phosphine) precursor. In contrast, the combined donating/π-accepting ability of a phosphite ligand and the π-acceptor ligand (L) should be more comparable, electronically making the loss of a phosphite ligand from the tris(phosphite) and π-acceptor complexes equally likely and perhaps determined by the relative sizes of the phosphite and π-acceptor ligands.

η^2-Cyclopropene Complexes. Synthesis and Stability. The reactions of the $WCl_2(NAr)(PX_3)_3$ precursors with 3,3-diphenylcyclopropene[25] and 4,8-dioxaspiro[2.5]oct-1-ene[26,27] (referred to throughout the remainder of this paper as diphenylcyclopropene and ketalcyclopropene, respectively) were investigated, and two modes of reactivity were identified: η^2-cyclopropene coordination and vinyl alkylidene formation (Schemes I and II). In general, the stability of the η^2-cyclopropene complexes decreased as the steric bulk of the ancillary ligands increased, and for the same imido and phosphite ancillary ligands, the η^2-diphenylcyclopropene complexes were more stable than the corresponding η^2-ketalcyclopropene complexes.

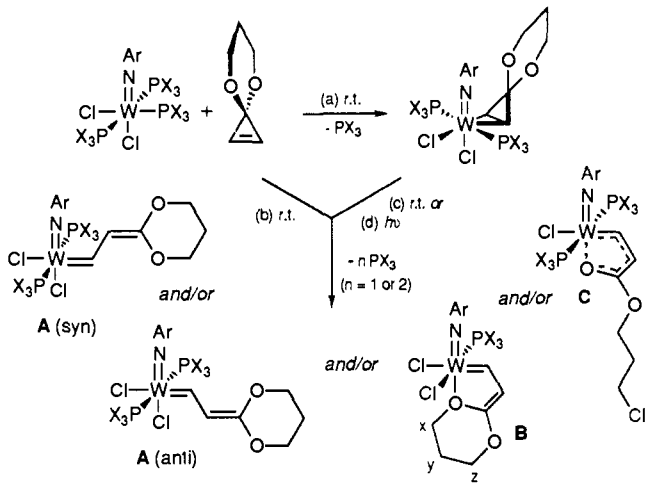
(24) (a) Templeton, J. L.; Ward, B. C. *J. Am. Chem. Soc.* **1980**, *102*, 3288–3290. (b) Templeton, J. L. *Adv. Organomet. Chem.* **1989**, *29*, 1–100.

(25) 3,3-Diphenylcyclopropene was prepared according to an optimized synthesis (Moore, J. S.; Nguyen, S. T.; Grubbs, R. H. Unpublished results) based on the following literature references: (a) Skattebol, L. *Acta Chem. Scand.* **1963**, *17*, 1683–1693. (b) Binger, P. *Synthesis* **1974**, 190–192.

(26) For details of the synthesis and reactivity of 4,8-dioxaspiro[2.5]oct-1-ene (ketalcyclopropene), see: (a) Boger, D. L.; Brotherton, C. E.; Georg, G. I.; Davidsen, S. K.; Heathcock, C. H. *Organic Syntheses*; Vedejs, E., Ed.; Organic Syntheses, Inc.: USA, 1987; pp 32–41. (b) Boger, D. L.; Brotherton, C. E. *J. Am. Chem. Soc.* **1986**, *108*, 6695–6713. (c) Butler, G. B.; Herring, K. H.; Lewis, P. L.; Sharpe, V. V., III; Veazey, R. L. *J. Org. Chem.* **1977**, *42*, 679–682.

(27) Ketalcyclopropene forms an η^2-olefin complex upon reaction with $Cp_2Ti(PMe_3)_2$. See: Binger, P.; Muller, P.; Herrmann, A. T.; Philipps, P.; Gabor, B.; Langhauser, F.; Kruger, C. *Chem. Ber.* **1991**, *124*, 2165–2170.

Scheme II



Many of the η^2-cyclopropene complexes were not stable at room temperature when dissolved in standard NMR solvents (e.g., C_6D_6, tol-d_8, THF-d_8, and CD_2Cl_2), thus limiting the conditions under which they could be synthesized. The preparation of η^2-cyclopropene complexes from the phosphite precursors **2–4** was most readily accomplished in diethyl ether, as the starting tris(phosphite) complexes were moderately soluble in diethyl ether and the resulting η^2-cyclopropene complexes were only sparingly soluble. Thus, when the cyclopropenes were added to concentrated, heterogeneous purple mixtures of the tris(phosphite) complexes in diethyl ether, the yellow η^2-cyclopropene complexes began to precipitate almost immediately (Schemes Ia and IIa). The highly concentrated reaction conditions enabled clean reactivity, while the low solubility of the η^2-cyclopropene complexes in diethyl ether generally prevented conversion to the vinyl alkylidenes on the time scale of the reaction. The preparations of η^2-cyclopropene complexes from the phenylimido tris(phosphite) precursor $WCl_2(NPh)[P(OMe)_3]_3$ (**2**) were especially sensitive to concentration effects. In dilute C_6D_6 solutions, the cyclopropenes were rapidly transformed to unidentified products without loss of **2**. After the formation of the η^2-cyclopropene complexes in diethyl ether was complete, the resulting yellow or tan powders were purified by filtration and washing with diethyl ether or pentane. Although recrystallization was not feasible for the least stable derivatives, it was possible to obtain X-ray-quality crystals of $W(\eta^2$-diphenylcyclopropene$)Cl_2(NPh)[P(OMe)_3]_2$ (**10**) upon cooling a saturated toluene/benzene solution of this complex to 0 °C (*vide infra*).

Spectroscopic Data. Characteristic of η^2-olefin complex formation, upfield shifts were observed for the olefinic proton and carbon resonances of the cyclopropenes upon complexation, along with corresponding 24–36-Hz decreases in the value of J_{CH} (Table II). These resonances appeared as triplets due to coupling with the two trans phosphine/phosphite ligands. The trends in stability were supported by the NMR spectroscopic data: For the phosphite complexes, the upfield shift of the η^2-cyclopropene olefinic proton and carbon resonances decreased as the steric bulk of the imido ligand increased, corresponding to weaker binding of the cyclopropene in the more sterically crowded molecule.

In these η^2-cyclopropene complexes, syn and anti orientations of the cyclopropene substituents relative to the imido ligand are equally likely on an electronic basis.[28] However, only one rotamer was normally observed and isolated, and all of the data point toward it being the syn rotamer. For example, for the η^2-diphenylcyclopropene complexes **9** and **10**, substantial upfield shifts to 5.51 and 6.31 ppm, respectively, were observed for the *ortho* protons of the imido ring. These upfield shifts are best explained by the shielding of these resonances by one of the phenyl rings of the η^2-cyclopropene, requiring that the cyclopropene

Table II. Selected NMR Spectral Data for η^2-Cyclopropene Complexes[a,c,d]

η^2-cyclopropene complex	^{1}H (t, *HC*=C*H*)[b] δ	^{1}H (t, *HC*=C*H*) J_{HP}	^{1}H (t, HC=C*H*) δ	^{1}H (t, HC=C*H*) J_{HP}	^{13}C (t, HC=*CH*) δ	^{13}C (t, HC=*CH*) J_{CH}	^{13}C (t, HC=*CH*) J_{CP}	^{13}C (t, HC=*CH*) J_{CW}	^{31}P (PX_3) δ	^{31}P (PX_3) J_{PW}
W(HC=CHCPh$_2$)Cl$_2$(NPh)(PMePh$_2$)$_2$ (**9**)	4.19	5.68	3.75	5.63	72.4	195	9	45	5	208
W(HC=CHCPh$_2$)Cl$_2$(NPh)[P(OMe)$_3$]$_2$ (**10**)	5.08	5.82	4.50	6.01	64.8	193	16	37	118	364
W(HC=CHCPh$_2$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe)$_3$]$_2$ (**11**)	5.29	5.98	4.74	5.79	66.2	194	15	40	110	379
W(HC=CHCOCH$_2$CH$_2$CH$_2$O)Cl$_2$(NPh)(PMePh$_2$)$_2$ (**12**)	3.66	5.86	3.30	5.71	67.5	188	9	42	5	212
W(HC=CHCOCH$_2$CH$_2$CH$_2$O)Cl$_2$(NPh)[P(OMe)$_3$]$_2$ (**13**)	4.82	5.62	4.14	5.98	59.9	210	15	37	120	361
W(HC=CHCOCH$_2$CH$_2$CH$_2$O)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe)$_3$]$_2$ (**14**)	4.96	5.71	4.27	5.91	61.5	194	15	31	113	376

[a] All spectra were acquired in CD_2Cl_2 unless noted otherwise. [b] In C_6D_6. [c] Uncomplexed HC=CHCPh$_2$: ^{1}H (CD_2Cl_2) δ 7.54 (*HC*=C*H*); ^{13}C (CD_2Cl_2) δ 113.8 (J_{CH} = 230, HC=*CH*). [d] Uncomplexed HC=CHCOCH$_2$CH$_2$CH$_2$O: ^{1}H (CD_2Cl_2) δ 7.85 (*HC*=C*H*); ^{13}C (CD_2Cl_2) δ 126.0 (J_{CH} = 224, HC=*CH*).

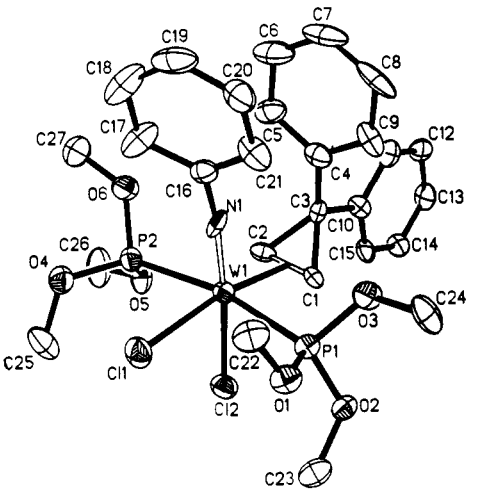


Figure 2. ORTEP plot of W(HC=CHCPh$_2$)Cl$_2$(NPh)[P(OMe)$_3$]$_2$ (**10**). Thermal ellipsoids are drawn at the 50% probability level.

substituents lie syn to the imido ligand. Consistent with this explanation, similar upfield shifts of the phenylimido *ortho* protons were not observed in the corresponding η^2-ketalcyclopropene complexes **12** and **13**. However, a syn arrangement of the imido ligand and the ketal substituent of the cyclopropene was indicated by difference nOe spectroscopy of W(η^2-ketalcyclopropene)Cl$_2$(NPh)[P(OMe)$_3$]$_2$ (**13**). Specifically, irradiation of the 3.72 ppm resonance corresponding to one set of ether methylene protons resulted in a 4.5% enhancement of the phenylimido *ortho* protons. Irradiation of the olefinic protons did not enhance the *ortho* proton resonance of the arylimido ligand and vice versa.

Crystal Structure. A syn arrangement of the imido ligand and the cyclopropene substituents was further supported by an X-ray diffraction study of W(η^2-diphenylcyclopropene)Cl$_2$(NPh)-[P(OMe)$_3$]$_2$ (**10**). An ORTEP diagram of this complex is shown in Figure 2, and selected bond lengths and angles are given in Table III. This molecule is best described as a distorted octahedron with the olefinic carbons occupying one position in the equatorial plane. In addition to relieving steric crowding between the equatorial ligands, the displacement of the olefinic carbons ~12.5° beneath the equatorial plane also reduces unfavorable steric interactions between the imido phenyl ring and the cyclopropene phenyl ring that lies syn to tungsten. Adjustments that further accommodate the steric bulk of this cyclopropene phenyl ring include the bending of the imido ligand away from the cyclopropene substituents, resulting in a W(1)–N(1)–C(16) angle of 170.8(6)°, and the bending of the cyclopropene phenyl rings away from the imido ligand (e.g., the C(2)–C(3)–C(4) angle is 11.1° larger than the C(2)–C(3)–C(10) angle). Due to strong π-back-donation by tungsten, there is a substantial lengthening of the double bond [1.452(12) Å] and an accompanying large increase of the apical angle of the complexed cyclopropene ring [57.0(6)°] as compared to that of free cyclopropene [1.294 Å, 50.4°], resulting in a large decrease in ring strain.[4a,29]

Table III. Selected Bond Lengths and Angles for **10**

Bond Lengths (Å)			
W(1)–Cl(1)	2.486(3)	W(1)–Cl(2)	2.482(3)
W(1)–P(1)	2.517(2)	W(1)–P(2)	2.530(3)
W(1)–N(1)	1.747(8)	W(1)–C(1)	2.171(9)
W(1)–C(2)	2.160(9)	W(1)–Cnt[a]	2.040
N(1)–C(16)	1.404(13)	C(1)–C(2)	1.452(12)
C(1)–C(3)	1.526(12)	C(2)–C(3)	1.518(13)
C(3)–C(4)	1.484(14)	C(3)–C(10)	1.531(13)
Bond Angles (deg)			
Cl(1)–W(1)–Cl(2)	83.9(1)	Cl(1)–W(1)–P(1)	84.3(1)
Cl(2)–W(1)–P(1)	89.3(1)	Cl(1)–W(1)–P(2)	84.2(1)
Cl(2)–W(1)–P(2)	86.1(1)	P(1)–W(1)–P(2)	168.0(1)
Cl(1)–W(1)–N(1)	90.8(2)	Cl(2)–W(1)–N(1)	174.6(2)
P(1)–W(1)–N(1)	91.5(2)	P(2)–W(1)–N(1)	92.1(2)
Cl(1)–W(1)–C(1)	156.3(2)	Cl(2)–W(1)–C(1)	82.9(2)
P(1)–W(1)–C(1)	76.0(2)	P(2)–W(1)–C(1)	114.3(2)
N(1)–W(1)–C(1)	102.5(3)	Cl(1)–W(1)–C(2)	156.7(3)
Cl(2)–W(1)–C(2)	83.6(2)	P(1)–W(1)–C(2)	115.1(3)
P(2)–W(1)–C(2)	75.3(3)	N(1)–W(1)–C(2)	101.0(3)
C(1)–W(1)–C(2)	39.2(3)	Cnt–W(1)–N(1)[a]	102.5
Cnt–W(1)–P(1)[a]	95.5	Cnt–W(1)–P(2)[a]	94.9
Cnt–W(1)–Cl(1)[a]	166.7	Cnt–W(1)–Cl(2)[a]	82.8
W(1)–N(1)–C(16)	170.8(6)	C(2)–C(1)–C(3)	61.3(6)
C(1)–C(2)–C(3)	61.8(6)	C(1)–C(3)–C(2)	57.0(6)
C(1)–C(3)–C(4)	123.7(8)	C(2)–C(3)–C(4)	124.3(8)
C(1)–C(3)–C(10)	112.4(7)	C(2)–C(3)–C(10)	113.2(8)
C(4)–C(3)–C(10)	114.3(8)		

[a] Cnt is the centroid of the C(1)–C(2) bond.

Diphenylvinyl Alkylidene Complexes. General Observations and Trends. In general, diphenylvinyl alkylidene formation was slower than η^2-diphenylcyclopropene coordination, and an increase in the steric bulk of the tungsten(IV) precursor favored the generation of the diphenylvinyl alkylidene complex over the η^2-diphenylcyclopropene complex. The W(=CHCH=CPh$_2$)Cl$_2$(NAr)(PX$_3$)$_2$ compounds were observed as bright orange solutions

(28) Throughout this paper, the term "syn" describes the rotamer or isomer of the π-acceptor complex (e.g., η^2-olefin or alkylidene complex) in which the substituent of the π-acceptor ligand lies on the same side of the equatorial plane as the imido ligand, while the term "anti" refers to the rotamer or isomer in which the π-acceptor ligand is rotated 180° relative to that of the syn rotamer and the π-acceptor substituent thus lies on the opposite side of the equatorial plane from the imido ligand. For a more detailed description of the bonding in these complexes, see: (a) Reference 11b and (b) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988; pp 33–36. For detailed studies of syn and anti rotamers of arylimido alkylidene complexes, see: (c) Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832–1843.

(29) Wiberg, K. B. In *The Chemistry of the Cyclopropyl Group*; Rappoport, A., Ed.; John Wiley & Sons: New York, 1987; Part 1, Chapter 1.

Table IV. Selected NMR Spectral Data for (2,6-Dimethyl- and (2,6-Diisopropylphenyl)imido Diphenylvinyl Alkylidene Complexes[a]

diphenylvinyl alkylidene complex	H_α				C_α			
	δ	J_{HH}	J_{HP}	H_β, δ	δ	J_{CH}	J_{CP}	J_{CW}
anti-W[*trans*-(=CHCH=CPh_2)]Cl_2[N-2,6-C_6H_3(*i*-Pr)$_2$][$P(OMe)_3$]$_2$ (**15**)	12.9[b]	12.8	6.37	10.2	277	130	18.2	123
anti-W[*trans*-(=CHCH=CPh_2)][N-2,6-C_6H_3(*i*-Pr)$_2$][$OCMe(CF_3)_2$]$_2$[$P(OMe)_3$] (**16**)	12.3	14.4	8.06	8.72	264	151	20.7	153
syn-W[*trans*-(=CHCH=CPh_2)][N-2,6-C_6H_3(*i*-Pr)$_2$][$OCMe(CF_3)_2$]$_2$[$P(OMe)_3$] (**16**)	11.6	11.0	5.13	8.72	256		21.7	
anti-W[*trans*-(=CHCH=CPh_2)][N-2,6-C_6H_3(*i*-Pr)$_2$][O-2,6-C_6H_3(*i*-Pr)$_2$]$_2$[$P(OMe)_3$] (**17**)	12.4	14.3	7.89	9.32	259	152	20.8	156
syn-W[*trans*-(=CHCH=CPh_2)][N-2,6-C_6H_3(*i*-Pr)$_2$][O-2,6-C_6H_3(*i*-Pr)$_2$]$_2$[$P(OMe)_3$] (**17**)	12.2	11.4	6.31	8.89	253	125	22.2	164
anti-W[*trans*-(=CHCH=CPh_2)]Cl_2(N-2,6-$C_6H_3Me_2$)(PEt_2Ph)$_2$ (**18**)	12.2	13.1	4.4	9.55	272	128	12.6	
syn-W[*trans*-(=CHCH=CPh_2)]Cl_2(N-2,6-$C_6H_3Me_2$)(PEt_2Ph)$_2$ (**18**)	11.9	13.1	4.4	8.72	278	130	12.6	
anti-W[*trans*-(=CHCH=CPh_2)]Cl_2(N-2,6-$C_6H_3Me_2$)[$P(OMe)_3$]$_2$ (**19**)	12.9	13.0	6.24	9.62	277	130	17.6	117
syn-W[*trans*-(=CHCH=CPh_2)]Cl_2(N-2,6-$C_6H_3Me_2$)[$P(OMe)_3$]$_2$ (**19**)	12.4	13.3	6.69	8.80	284	133	17.5	

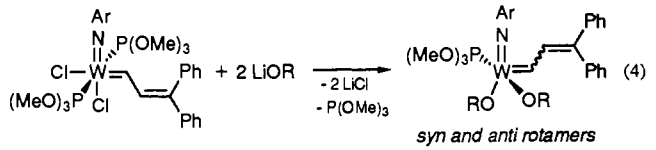
[a] All spectra were acquired in CD_2Cl_2 unless indicated otherwise. [b] Tol-d_8.

and isolated as orange or yellow-orange powders. Coordination of the diphenylvinyl alkylidene moiety to tungsten was indicated spectroscopically by the downfield shifts of H_α and C_α,[30] the splitting of these resonances by the phosphite/phosphine ligands, and the coupling of C_α to tungsten (Table IV). In addition, a downfield shift of H_β of the alkylidene moiety was also observed, and the large coupling between H_α and H_β was indicative of an s-trans arrangement of the double bonds of the diphenylvinyl alkylidene ligand.

(2,6-Diisopropylphenyl)imido Precursor. The synthesis of W(=CHCH=CPh_2)Cl_2[N-2,6-C_6H_3(*i*-Pr)$_2$][$P(OMe)_3$]$_2$ (**15**) was achieved when a concentrated benzene solution containing WCl_2[N-2,6-C_6H_3(*i*-Pr)$_2$][$P(OMe)_3$]$_3$ (**4**) and a slight excess of diphenylcyclopropene was stirred for 2 h at 80 °C (Scheme Ib). Small amounts of **4** that remained unreacted could be separated from **15** by recrystallization from diethyl ether or by washing the product mixture with pentane. The observation of characteristic H_α and H_β resonances coupled to the two mutually trans phosphite ligands provided confirmation of the preparation of **15**, and difference nOe and low-temperature ^{1}H NMR spectra lent further insight into its structure. For example, the observation of a 19.2% nOe enhancement of the alkylidene H_α resonance of **15** upon irradiation of the isopropyl methine resonance and a 12.4% nOe enhancement in the other direction was indicative of an anti arrangement of the alkylidene ligand relative to the imido group. In the 90 MHz ^{1}H NMR spectrum of **15** at room temperature, the isopropyl methyl and methine protons gave rise to one doublet and one septet, respectively, indicative of free rotation about the arylimido ligand. Upon cooling of the sample to −80 °C, restricted rotation resulted in two doublet resonances for the isopropyl methyl protons and two septet resonances for the methine protons, thus requiring that the arylimido ring lie in the Cl–W(N)–C_α plane, an arrangement that would minimize steric interactions between the isopropyl groups and the phosphite ligands.

High temperatures were necessary for the complete conversion of **4** and diphenylcyclopropene to the diphenylvinyl alkylidene **15**. For example, stirring a 1:1 mixture of diphenylcyclopropene and **4** in a concentrated diethyl ether or diethyl ether/methylene chloride solution for as long as 48 h at room temperature did not lead to complete vinyl alkylidene formation. Instead an orange mixture composed of **4**, **15**, and what are tentatively assigned as two η^2-cyclopropene species was isolated. An approximately 2:1 ratio of triplets at 5.31 (J_{HP} = 5.91 Hz) and 5.36 (J_{HP} = 5.36 Hz) ppm in the ^{1}H NMR spectrum in C_6D_6 was indicative of η^2-cyclopropene complex formation. These chemical shifts are slightly downfield of that observed for the analogous (dimethylphenyl)imido compound **11**, again consistent with weaker binding of the cyclopropene to the sterically more bulky imido precursor. For all other combinations of imido and phosphine/phosphite ancillary ligands that were studied, only one form of the η^2-cyclopropene complex was observed.

Reactions of **15** with 2 equiv of $LiOCMe(CF_3)_2$ or LiO-2,6-C_6H_3(*i*-Pr)$_2$ yielded the mono(phosphite) adducts of the corresponding tungsten alkoxide complexes W(=CHCH=CPh_2)[N-2,6-C_6H_3(*i*-Pr)$_2$][$OCMe(CF_3)_2$]$_2$[$P(OMe)_3$] (**16**) and W(=CHCH=CPh_2)[N-2,6-C_6H_3(*i*-Pr)$_2$][O-2,6-C_6H_3(*i*-Pr)$_2$]$_2$[$P(OMe)_3$] (**17**) (eq 4). Both complexes were isolated as a mixture



(4)

Ar = 2,6-C_6H_3-(*i*-Pr)$_2$; OR = $OCMe(CF_3)_2$ (**16**) or O-2,6-C_6H_3-(*i*-Pr)$_2$ (**17**)

of syn and anti rotamers. Difference nOe measurements for **16** are consistent with the synthesis of mainly the anti rotamer, and syn and anti designations for **17** are based on comparisons with analogous vinyl alkylidene complexes.[28c] These complexes are derivatives of the arylimido metathesis catalysts that were developed by Schrock,[31] and their metathesis activity will be reported separately.[32]

An X-ray diffraction study of **16** provided further confirmation of the ring-opening of diphenylcyclopropene to give the corresponding vinyl alkylidene ligand. An ORTEP diagram of the structure, which closely resembles that of *anti*-W[*trans*-(=CHCH=CHMe)][N-2,6-C_6H_3(*i*-Pr)$_2$][$OCMe(CF_3)_2$]$_2$-(quinuclidene),[28c] is shown in Figure 3 and selected bond lengths and angles are given in Table V. The geometry of **16** is a distorted trigonal bipyramid with the phosphite ligand and one alkoxide ligand [P(1) and O(2)] occupying the apical positions. The structure supports an s-trans resonance-stabilized diphenylvinyl alkylidene ligand, consistent with the large H_α–H_β coupling constant (14.4 Hz) of this complex.

(2,6-Dimethylphenyl)imido Precursors. The room-temperature reaction of diphenylcyclopropene with the phosphine precursor WCl_2(N-2,6-$C_6H_3Me_2$)(PEt_2Ph)$_3$ (**1**) in a mixture of diethyl ether and pentane produced the yellow-orange vinyl alkylidene complex W(=CHCH=CPh_2)Cl_2(N-2,6-$C_6H_3Me_2$)(PEt_2Ph)$_2$ (**18**) in good yield as an approximately two to one mixture of rotamers (Scheme Ib). Irradiation of the imido methyl groups of the major rotamer resulted in a 20% nOe enhancement of the alkylidene H_α resonance, indicative of an anti arrangement of the two ligands, and correspondingly, irradiation of the imido methyl groups of the minor rotamer caused a 14% enhancement of the alkylidene H_β resonance, indicative of a syn arrangement of the two ligands.

In contrast, stirring a mixture of diphenylcyclopropene with the analogous phosphite precursor WCl_2(N-2,6-$C_6H_3Me_2$)-[$P(OMe)_3$]$_3$ (**3**) in diethyl ether gave the yellow η^2-cyclopropene complex W(η^2-diphenylcyclopropene)Cl_2(N-2,6-$C_6H_3Me_2$)-[$P(OMe)_3$]$_2$ (**11**) (Scheme Ia). A room-temperature, concentrated CD_2Cl_2 solution of this compound was monitored over a 24-h period by ^{1}H, ^{13}C, and ^{31}P NMR spectroscopy, enabling the

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(31) (a) 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. (b) Schrock, R. R.; Feldman, J.; Cannizzo, L. F.; Grubbs, R. H. *Macromolecules* **1987**, *20*, 1169–1172.

(32) Claverie, J. P.; Lee, T. R.; Grubbs, R. H. Manuscript in preparation.

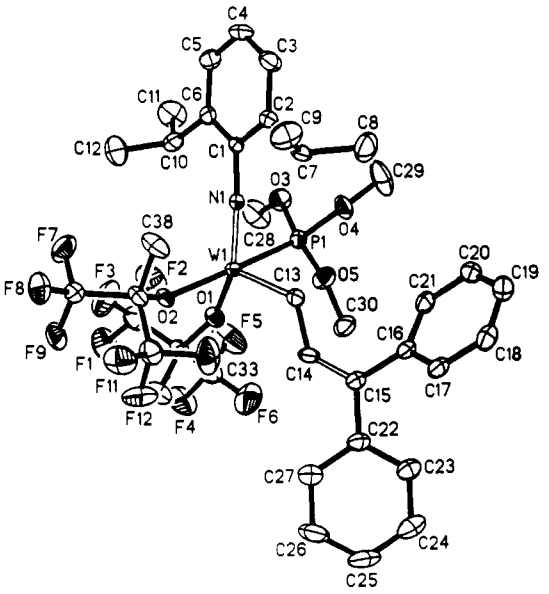

Figure 3. ORTEP plot of $W(=CHCH=CPh_2)[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]$-$[OCMe(CF_3)_2]_2[P(OMe)_3]$ (**16**). Thermal ellipsoids are drawn at the 50% probability level.

Table V. Selected Bond Lengths and Angles for **16**

Bond Lengths (Å)			
W(1)–P(1)	2.505(1)	W(1)–O(1)	1.975(4)
W(1)–O(2)	1.996(3)	W(1)–N(1)	1.753(4)
W(1)–C(13)	1.947(5)	C(13)–C(14)	1.450(9)
C(14)–C(15)	1.363(7)	C(15)–C(16)	1.479(7)
C(15)–C(22)	1.483(9)		
Bond Angles (deg)			
P(1)–W(1)–O(1)	81.8(1)	P(1)–W(1)–O(2)	163.7(1)
O(1)–W(1)–O(2)	84.6(1)	P(1)–W(1)–N(1)	83.6(1)
O(1)–W(1)–N(1)	146.9(2)	O(2)–W(1)–N(1)	103.3(2)
P(1)–W(1)–C(13)	86.7(1)	O(1)–W(1)–C(13)	109.8(2)
O(2)–W(1)–C(13)	106.4(2)	N(1)–W(1)–C(13)	98.8(2)
W(1)–O(1)–C(31)	150.4(3)	W(1)–O(2)–C(35)	137.5(3)
W(1)–N(1)–C(1)	168.0(3)	W(1)–C(13)–C(14)	122.2(4)
C(13)–C(14)–C(15)	127.5(5)	C(14)–C(15)–C(16)	123.1(5)
C(14)–C(15)–C(22)	118.7(5)		

observation of the clean and complete conversion of the η^2-diphenylcyclopropene species to the diphenylvinyl alkylidene complex $W(=CHCH=CPh_2)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]_2$ (**19**) (Scheme Ic). Addition of excess diphenylcyclopropene to a CD_2Cl_2 solution of **11** slowed the rate of conversion to vinyl alkylidene **19**. Conversion to the vinyl alkylidene product was also slowed by the addition of 1 equiv of ketalcyclopropene to **11**; a complex mixture of products containing both the diphenylvinyl alkylidene complex **19** and the ketalvinyl alkylidene complex **22-B** was obtained.

Phenylimido Precursors. The phenylimido precursors $WCl_2(NPh)(PMePh_2)_3$ and $WCl_2(NPh)[P(OMe)_3]_3$ (**1**) formed relatively stable η^2-cyclopropene complexes, and initial attempts to thermally convert these complexes gave low yields of vinyl alkylidenes. However, there are literature precedents for the ring-opening of cyclopropenes upon photolysis[33] or upon catalysis by $HgCl_2$,[34] and therefore, both of these methods were investigated. Catalytic amounts of $HgCl_2$ converted CD_2Cl_2 solutions of the η^2-olefin complexes **9** and **10** to the corresponding tungsten vinyl alkylidenes within several hours (Scheme Id). Conversion was complete within minutes upon addition of 1 equiv of $HgCl_2$; however, such large amounts of $HgCl_2$ also slowly catalyzed the decomposition of the vinyl alkylidene complex. Photolyzing dilute solutions of the η^2-cyclopropene complexes **9** and **10** at 0 °C also promoted rearrangement to the corresponding vinyl alkylidene compounds (Scheme Ie).

Ketalvinyl Alkylidene Complexes. Similar to vinyl alkylidene syntheses from diphenylcyclopropene, an increase in the steric bulk of the tungsten(IV) precursor favored formation of the ketalvinyl alkylidene complex over the corresponding η^2-ketalcyclopropene complex. Moreover, ring-opening of ketalcyclopropene occurred more readily than for 3,3-diphenylcyclopropene. However, the chemistry was also more complex, as several forms of the ketalvinyl alkylidene were noted. As shown in Scheme II, 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 and were the thermodynamic products of the reaction. In the remainder of this paper, the formulas for these ketalvinyl alkylidene compounds will be written as $W(CHR_Y)Cl_m(NAr)(PX_3)_n$, where Y = A–C and denotes the structure of the alkylidene.

Spectroscopic Data. The ketalvinyl alkylidenes **A**–**C** were distinguished by color and by spectroscopic data. Solutions of **A** and/or **B** were red, whereas solutions of **C** were green. The characteristic spectroscopic feature of **A** was the large coupling between H_α and H_β of the s-trans-ketalvinyl alkylidene ligand, which was similar to that of the diphenylvinyl alkylidene ligand. The H_α and C_α resonances of **A** appeared as triplets due to coupling with the two mutually trans PX_3 ligands.

For **B**, difference nOe measurements were consistent with an anti orientation of the alkylidene ligand relative to the imido group and an s-cis arrangement of the double bonds of the alkylidene moiety. The coupling constant between H_α and H_β was smaller than that of s-trans-vinyl alkylidene ligands and also indicative of s-cis double bonds. These observations implied chelation by the ketalvinyl alkylidene group to tungsten, and the incorporation of only one PX_3 ligand in **B**, as was indicated by the appearance of doublet resonances for H_α and C_α, further supported 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 in **B** (OC_xH, 5.08 ppm; OC_xH', 4.82 ppm) was consistent with coordination by the adjacent oxygen atom to tungsten.[35]

In order to maximize π-bonding in **B**, the alkylidene ligand must be cis to the imido ligand and the alkylidene substituents must lie in the N–W–C_α plane;[28b] this would place the chelating ketal functionality trans to the imido ligand. Given these restrictions, the PX_3 and chloride ligands must lie in the equatorial plane, with the PX_3 ligand situated either cis or trans to the alkylidene ligand. The inequivalent chemical shifts of the geminal protons of the two ketal methylene groups that lie closest to tungsten (e.g., C_xHH' and C_yHH') support the asymmetric structure in which the PX_3 ligand occupies a position cis to the alkylidene ligand. The slightly larger coupling of phosphorus to H_α and C_α in **B** than in **A** can then be explained by the weaker trans effect of chloride versus PX_3 ligands leading to tighter binding of PX_3 to tungsten in **B**.[36]

Difference nOe measurements and a small H_α–H_β coupling constant supported an anti arrangement of the imido and alkylidene ligands and also an s-cis double bond arrangement in **C**, again implying chelation by the ketalvinyl alkylidene ligand. However, in contrast to **B**, a marked upfield shift (~20 ppm) of

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(34) (a) Bishop, K. C., III. *Chem. Rev.* **1976**, *76*, 461–486. (b) Shirafuji, T.; Yamamoto, Y.; Nozaki, H. *Tetrahedron Lett.* **1971**, 4713–4714.

(35) Structurally similar, chelating *o*-methoxybenzylidene complexes have been reported: (a) Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384–5385. (b) Johnson, L. K.; Frey, M.; Ulibarri, T. A.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.*, in press.

(36) Huheey, J. E. *Inorganic Chemistry*, 3rd ed.; Harper & Row: New York, 1983; p 540.

Table VI. Selected NMR Spectral Data for (2,6-Dimethyl- and (2,6-Diisopropylphenyl)imido Ketalvinyl Alkylidene Complexes[a]

ketalvinyl alkylidene complex	H_α			C_α				C_γ, δ	OCH_2, δ	XCH_2, δ
	δ	J_{HH}	J_{HP}	δ	J_{CH}	J_{CP}	J_{CW}			
$W(CHR_B)Cl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]$ (**20-B**)	11.7	9.81	6.82	260	144	20.7	124	165	68.8	67.6[b]
$W(CHR_C)Cl[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_2$ (**20-C**)	12.6	8.26	2.30	257		10.2		177	62.3	41.1[c]
$W(CHR_A)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_2$ (**21-A**)[d]	12.7[e]	14.2	3.98	264		11.0				
$W(CHR_A)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_2$ (**21-A**)[d]	12.6[e]	13.6	3.79	270		10.8				
$W(CHR_B)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)$ (**21-B**)	11.5[e]	9.93	5.51							
$W(CHR_C)Cl(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_2$ (**21-C**)	12.2	8.07	2.13	262	134	7.2	119	174	61.9	41.6[c]
$W(CHR_B)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)Cl_2[P(OMe)_3]$ (**22-B**)	11.9	9.79	6.80	260	145	20.5	122	165	68.7	67.5[b]
$W(CHR_C)Cl(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]_2$ (**22-C**)	12.7			258	135	10.0	114	177	62.2	41.0[c]

[a] All spectra were acquired in CD_2Cl_2 unless indicated otherwise. [b] X = O. [c] X = Cl. [d] Syn or anti rotamer. [e] C_6D_6.

the ^{13}C NMR resonance of one of the ether methylene carbons was observed upon formation of **C**. An X-ray crystallographic study of **C** (*vide infra*) indicated that this upfield shift was due to substitution of oxygen by one of the chloride ligands of tungsten.[37] Another characteristic feature of **C** was an approximately 10 ppm downfield shift of C_γ, which resulted from the contribution of the enone resonance form to the structure of **C**.[37] Contribution by this resonance form also resulted in a lengthening of the W–C_α bond in **C** and, hence, in smaller phosphorus couplings to H_α and C_α in **C** than in **A** and **B** (Table VI).

(2,6-Diisopropylphenyl)imido Precursor. Ketalcyclopropene reacted with $WCl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_3$ (**4**) at room temperature to give the corresponding s-cis-vinyl alkylidene **20-B** (Scheme IIb). When the reaction was followed by ^1H NMR spectroscopy, the η^2-cyclopropene complex was not observed. The reaction yields were highest when a highly concentrated, heterogeneous mixture of the tris(phosphite) precursor **4** in diethyl ether was mixed with a slight excess of ketalcyclopropene, although even under these conditions, some of the tris(phosphite) precursor always remained after all of the ketalcyclopropene had reacted. The nature of the side reaction was not identified. The tris(phosphite) compound was separated from **20-B** by washing the reaction mixture with a diethyl ether solution containing 5 equiv of $P(OMe)_3$, and the product was then isolated as a golden bis(phosphite) adduct, which exhibited poor solubility in C_6D_6 and tol-d_8 but dissolved readily in THF-d_8 and CD_2Cl_2.

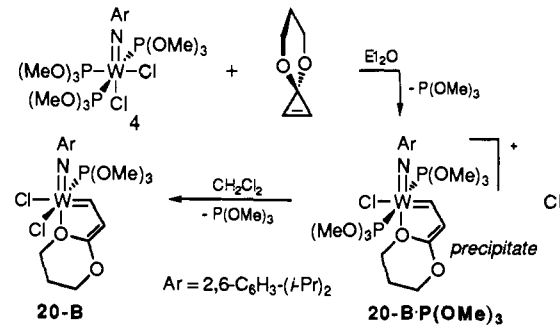
The ^1H NMR spectrum in CD_2Cl_2 showed only the red mono(phosphite) adduct of the s-cis-vinyl alkylidene **20-B** along with 1 equiv of free $P(OMe)_3$. In the NOSY spectrum, enhancements were observed between H_α and H_β and also between H_α and the isopropyl methine resonance. At both room temperature and at –80 °C, one isopropyl methine resonance and two isopropyl methyl resonances appeared in the ^1H NMR spectrum of **20-B**; given the proposed geometry of complexes **B**, this observation is consistent with free rotation about the imido ligand at both temperatures.

A reasonable explanation for the poor solubility of the isolated form of **20-B** in C_6D_6 and tol-d_8 and its existence as a bis(phosphite) adduct is that **20-B** precipitates from diethyl ether solution as a cationic species **20-B·P(OMe)$_3$** in which a phosphite ligand has displaced a chloride ligand (Scheme III). This would account for the difficulties encountered in redissolving **20-B·P(OMe)$_3$** in nonpolar solvents and is consistent with the observed rearrangement of complexes **B** to form **C** (*vide infra*). Upon dissolution in CH_2Cl_2, the cationic species must rapidly form the observed neutral complex **20-B** (Scheme III).

In CD_2Cl_2 solution and in the solid state, slow conversion of **20-B·P(OMe)$_3$** to **20-C** was observed. Specifically, less than 50% of **20-B·P(OMe)$_3$** converted to **20-C** during 12 h in a concentrated CD_2Cl_2 solution, and conversion of **20-B·P(OMe)$_3$** to **20-C** occurred over a period of months in the solid state at room temperature. Upon removal of 1 equiv of phosphite from the

(37) (a) Silverstein, R. M.; Bassler, G. C.; Morrill, T. C. *Spectrometric Identification of Organic Compounds*, 4th ed.; John Wiley & Sons: New York, 1981; Chapter 5.

Scheme III



complex, the rearrangement of neutral **20-B** to **20-C** was not observed after a few days in CD_2Cl_2 solution.

(2,6-Dimethylphenyl)imido Precursors. The room-temperature reaction of ketalcyclopropene with $WCl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_3$ (**1**) resulted in the isolation of a mixture of **21-A**, **21-B**, and **21-C** as a red powder in good yield (Scheme IIb). NMR spectra (^1H, ^{13}C, ^{31}P) of solutions of this powder were clean but complex, and only the H_α and C_α resonances were assigned. Large H_α–H_β coupling constants of two of the isomers, which composed 71% of the isomeric mixture, were indicative of syn and anti rotamers of **21-A**. The H_α resonances of these rotamers appeared at 12.70 (J_{HH} = 14.17 Hz, J_{HP} = 3.98 Hz) and 12.66 (J_{HH} = 13.60 Hz, J_{HP} = 3.79 Hz) ppm, and the C_α chemical shifts appeared at 270.4 and 263.9 ppm. Five percent of the product mixture was the mono(phosphite) adduct **21-B**. Consistent with its assigned structure, the H_α–H_β and H_α–P coupling constants of **21-B** (J_{HH} = 9.93 Hz, J_{HP} = 5.51 Hz) were smaller and larger, respectively, than the analogous couplings observed for H_α of **21-A**.

The red isomeric mixture turned green upon dissolution in CD_2Cl_2 for less than a day at room temperature, and only the fourth isomer, **21-C**, was then observed. Single crystals of **21-C** were grown from a saturated pentane solution that was slowly cooled to –20 °C, and the structure of this complex was then determined by an X-ray diffraction study. An ORTEP diagram of **21-C** is shown in Figure 4, and Table VII contains selected bond angles and lengths. The geometry of **21-C** is basically a distorted octahedron with all of the equatorial ligands lying on the opposite side of the plane from the apical imido ligand. The arylimido ring lies in the N(1)–W(1)–C(1) plane, thus further minimizing unfavorable steric interactions between the imido methyl groups and the equatorial phosphine ligands. The W(1)–C(1) bond length is longer than that of a normal tungsten alkylidene, and a substantial amount of π-delocalization of the chelating five-membered ring is indicated by its structure, which lies intermediate between that of a tungsten enolate and a chelating enone, although the bond lengths are slightly closer to those of the latter resonance form.

The NMR spectra of **21-C** are consistent with its structural determination. For example, the H_α and C_α resonances are coupled to the two mutually trans phosphine ligands and are shifted slightly upfield of the same resonances of **21-A**. The

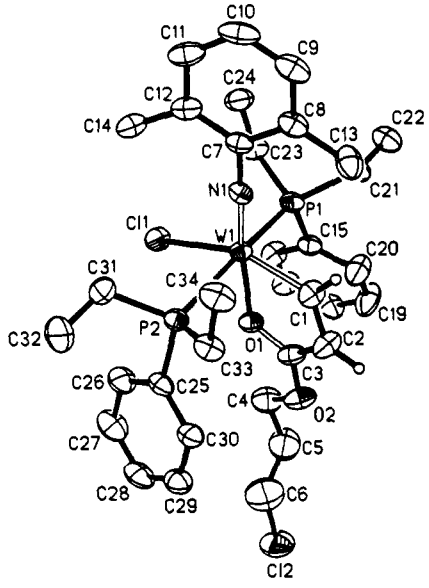


Figure 4. ORTEP plot of **21-C**. Thermal ellipsoids are drawn at the 50% probability level.

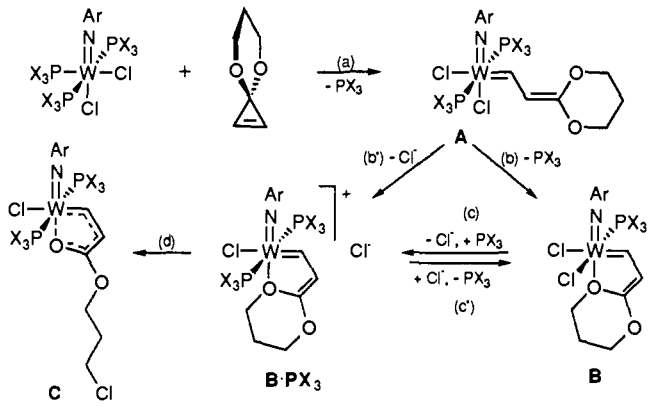
Table VII. Selected Bond Lengths and Angles for **21-C**

Bond Lengths (Å)			
W(1)–Cl(1)	2.495(1)	W(1)–P(1)	2.509(1)
W(1)–P(2)	2.512(1)	W(1)–O(1)	2.191(3)
W(1)–N(1)	1.766(3)	W(1)–C(1)	2.032(5)
Cl(2)–C(6)	1.819(8)	O(1)–C(3)	1.275(6)
O(2)–C(3)	1.350(5)	O(2)–C(4)	1.430(7)
N(1)–C(7)	1.393(5)	C(1)–C(2)	1.398(6)
C(2)–C(3)	1.388(7)	C(4)–C(5)	1.519(8)
C(5)–C(6)	1.430(10)		
Bond Angles (deg)			
Cl(1)–W(1)–P(1)	85.5(1)	Cl(1)–W(1)–P(2)	85.7(1)
P(1)–W(1)–P(2)	166.1(1)	Cl(1)–W(1)–O(1)	81.0(1)
P(1)–W(1)–O(1)	83.9(1)	P(2)–W(1)–O(1)	84.2(1)
Cl(1)–W(1)–N(1)	106.6(1)	P(1)–W(1)–N(1)	95.7(1)
P(2)–W(1)–N(1)	97.1(1)	O(1)–W(1)–N(1)	172.4(1)
Cl(1)–W(1)–C(1)	154.5(1)	P(1)–W(1)–C(1)	94.7(1)
P(2)–W(1)–C(1)	88.7(1)	O(1)–W(1)–C(1)	73.8(1)
N(1)–W(1)–C(1)	98.8(2)	C(3)–O(2)–C(4)	115.7(4)
W(1)–O(1)–C(3)	114.9(3)	W(1)–C(1)–C(2)	120.0(4)
W(1)–N(1)–C(7)	177.6(3)	O(1)–C(3)–O(2)	119.4(4)
C(1)–C(2)–C(3)	111.5(5)	O(2)–C(3)–C(2)	121.0(4)
O(1)–C(3)–C(2)	119.6(4)	C(4)–C(5)–C(6)	111.8(6)
O(2)–C(4)–C(5)	109.5(5)	Cl(2)–C(6)–C(5)	113.0(6)

coupling of these resonances to phosphorus and to tungsten is smaller than the analogous coupling observed in **21-A**, indicative of a lengthening of the W–C_α bond, and the coupling between H_α and H_β is relatively small (7.96 Hz) 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 at 61.9 ppm, the methylene carbon adjacent to chlorine appeared 20 ppm upfield at 41.6 ppm, and C_γ was shifted downfield to 174 ppm.

Stirring an extremely concentrated diethyl ether mixture of WCl_2(N-2,6-$C_6H_3Me_2$)[$P(OMe)_3$]$_3$ (**3**) and ketalcyclopropene for several hours yielded the tan η^2-cyclopropene complex **14** (Scheme IIa). Clean and complete conversion of W(η^2-ketalcyclopropene)Cl_2(N-2,6-$C_6H_3Me_2$)[$P(OMe)_3$]$_2$ (**14**) to **22-B** (25%) and **22-C** (75%) was observed after **14** was dissolved in a concentrated CD_2Cl_2 solution at room temperature for 1 day (Scheme IIc). Addition of 1 equiv of diphenylcyclopropene to **14** slowed its conversion to the vinyl alkylidene product and resulted in the production of a complex mixture of products containing both the diphenylvinyl alkylidene complex **19** and the ketalvinyl alkylidene complex **22-B**, although the latter complex constituted a larger percentage of the product mixture.

Scheme IV



When the same starting materials, **3** and ketalcyclopropene, were stirred together in a more dilute diethyl ether solution (Scheme IIb), the red vinyl alkylidene **22-B** was isolated as a mono(phosphite) adduct, which did not undergo a rearrangement when dissolved in CD_2Cl_2 for 12 h or when stored in the solid state for months at room temperature, again indicating that a second equivalent of phosphite is needed to promote the conversion of **B** to **C**. An anti arrangement of the alkylidene and imido ligands of **22-B** was determined by difference nOe measurements, and the methyl groups of the imido ligand were equivalent at both room temperature and at −80 °C, consistent with free rotation of the arylimido ring.

Phenylimido Precursors. As with the η^2-diphenylcyclopropene complexes, clean thermal conversion of the η^2-ketalcyclopropene phenylimido complexes to the corresponding vinyl alkylidene species was not observed. In fact, the cleanest thermal conversion observed thus far for the phenylimido compounds was the decomposition of W(η^2-ketalcyclopropene)Cl_2(NPh)[$P(OMe)_3$]$_2$ (**13**) in the solid state over a period of several months, which resulted in the formation of the ketalvinyl alkylidene complex along with WCl_2(NPh)[$P(OMe)_3$]$_3$ (**1**) and other products. Although the phenylimido η^2-ketalcyclopropene complexes **12** and **13** decomposed upon addition of $HgCl_2$, photochemical conversion to the ketalvinyl alkylidene was observed (Scheme IId).

Mechanism for the Formation of C. A mechanism for the formation of isomer **C** is proposed in Scheme IV and is based upon the following observations: (1) The s-trans-vinyl alkylidene **A** was only observed in the reaction with the phosphine precursor WCl_2(N-2,6-$C_6H_3Me_2$)(PEt_2Ph)$_3$ (**2**). (2) For the same precursor, only a small percentage of **B** was observed and overall conversion to **C** was more rapid than for the phosphite precursors. (3) For the phosphite precursors **2**–**4**, isomer **B** was formed more rapidly than for the phosphine complex **1** and slower overall conversion to **C** was then observed in CH_2Cl_2. (4) In the absence of a second equivalent of phosphite/phosphine, **B** was stable and did not undergo rearrangement to **C**. (5) All of the experimental data pointed toward the isolation of **20-B·P(OMe)$_3$** as a cationic complex, in which a phosphite ligand had displaced one of the chloride ligands.

These observations are consistent with the initial formation of the s-trans-vinyl alkylidene complex **A** upon ring-opening of ketalcyclopropene. Loss of a phosphite/phosphine ligand from **A** and rotation to an s-cis-vinyl alkylidene ligand would result in the formation of **B** (path b). Alternatively, loss of a chloride ligand from **A** and rotation of the alkylidene ligand would enable trapping of a cationic intermediate **B·PX$_3$** (path b'), such as was proposed in the isolation of **20-B**. One or both pathways (b and b') may be operating, perhaps depending on the nature of the donating ligand. For example, strong donation by phosphine

ligands would stabilize the cationic intermediate **B**·PX_3 and thus promote rapid rearrangement to **C** via nucleophilic attack by the chloride counterion on the ether methylene carbon (path d). Poor binding by phosphite ligands would favor path b and thus account for the rapid production of **B** by phosphite precursors. The presence of a second equivalent of phosphite would enable the production of the cationic species **B**·PX_3 and, hence, the formation of **C**.

Conclusion. To summarize, $WCl_2(NAr)(PX_3)_3$ precursors react with diphenyl- and ketalcyclopropene to give η^2-cyclopropene complexes and/or vinyl alkylidene complexes. The stability of the η^2-cyclopropene complexes decreases as the steric bulk of the ancillary ligands increases, and some of the larger precursors do not form observable η^2-cyclopropene complexes. The cyclopropene to vinyl alkylidene rearrangement is promoted thermally, chemically, and photochemically and is observed thermally for the sterically more bulky tungsten(IV) precursors. Although additional studies are needed in order to determine the mechanism of conversion, a tungsten-catalyzed rearrangement is indicated, as uncatalyzed thermal ring-openings of cyclopropenes normally require higher temperatures than those reported here.[38]

In general, the results of this work and those of other studies[2] indicate that the rearrangement of cyclopropenes is a very promising method for the synthesis of transition-metal alkylidene complexes. Not only is it useful for synthesizing alkylidenes of early transition metals, such as titanium,[2a] zirconium,[2a] and tungsten, but it can also be used to synthesize functional group tolerant, vinyl alkylidene metathesis catalysts of late metals, such as ruthenium[2b,c] and rhenium.[39]

Experimental Section

General Considerations. All manipulations of air- and/or water-sensitive compounds were performed using standard high-vacuum or Schlenk techniques. Argon was purified by passage through columns of BASF R3-11 catalyst (Chemalog) and 4-Å molecular sieves (Linde). Solid organometallic compounds were transferred and stored in a nitrogen-filled Vacuum Atmospheres drybox. All photolyses were Pyrex-filtered and conducted with a 450-W high-pressure mercury Hanovia lamp. Temperatures were maintained with a clear Pyrex dewar filled with ice water. NMR spectra were recorded with either a JEOL FX-90Q (89.60 MHz ^{1}H; 22.53 MHz ^{13}C; 36.20 MHz ^{31}P), a JEOL GX-400 (399.65 MHz ^{1}H; 100.40 MHz ^{13}C), or a QE-300 Plus (300.10 MHz ^{1}H; 75.49 MHz ^{13}C) spectrometer. All coupling constants are reported in Hz. For the ^{1}H and ^{13}C NMR virtual triplet resonances of the trans phosphine/phosphite ligands, the coupling constant $N = |^2J_{HP} + {}^4J_{HP}|$ is given, where N is the separation of the outer lines of the triplet.[40]

Materials. Toluene, benzene, diethyl ether, and tetrahydrofuran were distilled or vacuum-transferred from sodium benzophenone ketyl. *p*-Xylene was dried over CaH_2 and distilled under argon. Methylene chloride was dried over CaH_2, vacuum-transferred, and then degassed by repeated freeze–pump–thaw cycles. Pentane and hexane were stirred over concentrated H_2SO_4, dried over $MgSO_4$ and CaH_2, transferred onto sodium benzophenone ketyl solubilized with tetraglyme, and then vacuum-transferred and distilled, respectively. Benzene-d_6, toluene-d_8, and THF-d_8 were dried over sodium benzophenone ketyl and then vacuum-transferred. Chloroform-*d* and methylene chloride-d_2 were dried over P_2O_5, vacuum-transferred, and then degassed by repeated freeze–pump–thaw cycles. Isocyanates were purchased from Trans World Chemicals or Aldrich and purified by fractional distillation under argon. Diphenylcyclopropene,[25] ketalcyclopropene,[26] PEt_2Ph,[41] $WCl_4(O)$,[42] $WCl_4(NPh)$,[10] and $WCl_2(NPh)(PMePh_2)_3$[10] were synthesized according to literature methods. PEt_2Ph was purified by vacuum distillation (20 Torr), and $P(OMe)_3$ was vacuum-transferred off Na and then subjected to several freeze–pump–thaw cycles. $(CF_3)_2CH_3COH$ was purchased from PCR, dissolved in Et_2O, and deprotonated with 1 equiv of freshly titrated BuLi.[43] White crystals of $(CF_3)_2CH_3COLi$ were obtained by recrystallization at low temperature from a filtered Et_2O/pentane solution. HO-2,6-$C_6H_3(i\text{-}Pr)_2$ was purchased from Aldrich, purified by fractional distillation under vacuum (8 Torr), and dissolved in Et_2O. White Li–O-2,6-$C_6H_3(i\text{-}Pr)_2$ precipitated upon addition of 1 equiv of freshly titrated BuLi.

WCl_4(N-2,6-$C_6H_3Me_2$)(Et_2O). 2,6-Dimethylphenyl isocyanate (11.2 mL, 80.4 mmol) was added via syringe to a suspension of $WCl_4(O)$ (25.02 g, 73.24 mmol) in 115 mL of toluene. After the mixture was refluxed for 48 h, the toluene was removed in vacuo, and the resulting brick-red powder was dissolved in 400 mL of Et_2O. The solution was filtered and then slowly cooled to −50 °C to give 37.2 g of brown crystals in three crops (97.8%): ^{1}H NMR (C_6D_6) δ 6.75 (d, 2, J = 7.6, H_m), 5.89 (t, 1, J = 7.6, H_p), 4.34 (q, 4, J = 6.9, Et_2O), 3.29 (s, 6, Me), 1.07 (t, 6, J = 6.9, Et_2O); ^{13}C NMR (C_6D_6) δ 148.3 (C_{ipso}), 145.4 (C_o), 133.9 (C_p), 126.1 (C_m), 65.9 (Et_2O), 17.6 (Me), 13.0 (Et_2O). Alternatively, recrystallization from a 50:50 mixture of Et_2O and THF gave WCl_4(N-2,6-$C_6H_3Me_2$)(THF). After removal of the Et_2O in vacuo (several days under vacuum), an elemental analysis was obtained for orange-brown WCl_4(N-2,6-$C_6H_3Me_2$). Anal. Calcd for ($C_8H_9Cl_4NW$): C, 21.60; H, 2.04; N, 3.15. Found: C, 21.96; H, 2.15; N, 3.08.

WCl_4[N-2,6-$C_6H_3(i\text{-}Pr)_2$].[13] 2,6-Diisopropylphenyl isocyanate (11.59 g, 57.00 mmol) was added via cannula to a suspension of $WCl_4(O)$ (19.47 g, 57.00 mmol) in 100 mL of *p*-xylene. After being refluxed for 12 h, the hot solution was added via cannula to 400 mL of pentane, inducing the precipitation of a red-brown powder. After cooling of the solution to −50 °C, brick-red crystals (25.9 g, 90.5%) were isolated: ^{1}H NMR (THF-d_8) δ 7.63 (d, 2, J = 8.06, H_m), 6.74 (t, 1, J = 7.69, H_p), 4.62 (septet, 2, J = 6.59, C*H*Me$_2$), 1.37 (d, 12, J = 6.59, CH*Me*$_2$); ^{13}C NMR (THF-d_8) δ 156.3 (C_o), 146.1 (C_{ipso}), 135.0 (C_p), 122.7 (C_m), 28.2 (*C*H(CH$_3$)$_2$), 26.4 (CH(*C*H$_3$)$_2$).

WCl_4[N-2,6-$C_6H_3(i\text{-}Pr)_2$](THF). Brick-red W[N-2,6-$C_6H_3(i\text{-}Pr)_2$]Cl_4 (3.02 g, 6.03 mmol) was dissolved in 10 mL of THF and 90 mL of Et_2O. After the solution was filtered, recrystallization at −50 °C gave feathery green crystals (2.58 g, 74.7%): ^{1}H NMR (CD_2Cl_2) δ 7.59 (d, 2, J = 7.81, H_m), 6.71 (t, 1, J = 7.81, H_p), 4.74 (m, 4, THF), 4.58 (septet, 2, J = 6.59, C*H*Me$_2$), 2.17 (m, 4, THF), 1.40 (d, 12, J = 6.59, CH*Me*$_2$); ^{13}C NMR (CD_2Cl_2) δ 156.3 (C_o), 145.7 (C_{ipso}), 134.7 (C_p), 122.1 (C_m), 74.1 (THF), 27.8 (*C*H(CH$_3$)$_2$), 26.3 (CH(*C*H$_3$)$_2$), 26.1 (THF). Anal. Calcd for ($C_{16}H_{25}Cl_4NOW$): C, 33.54; H, 4.40; N, 2.44. Found: C, 33.72; H, 4.35; N, 2.57.

WCl_2(N-2,6-$C_6H_3Me_2$)(PEt_2Ph)$_3$ (1). Diethylphenylphosphine (14.4 mL, ~3.5 equiv) was added via syringe to a green solution of WCl_4(N-2,6-$C_6H_3Me_2$)(Et_2O) (12.25 g, 24.02 mmol) in 140 mL of benzene. The resulting brown solution was transferred via cannula onto a 1% sodium amalgam (1.99 g of Na, 86.6 mmol) and stirred for 11.5 h. The spent amalgam was allowed to settle, and the solution was transferred via cannula into a septum-covered centrifuge tube that had been previously evacuated and back-filled with argon. After being centrifuged, the solution was transferred via cannula into another flask. The spent amalgam was washed twice with a total of 165 mL of benzene, and the resulting solution was also centrifuged. The combined solvent was then removed in vacuo, and the product was washed 3 times with a total of 240 mL of pentane. A tan powder (11.31 g, 53%) was obtained: ^{1}H NMR (C_6D_6) δ 7.4–6.5 (m, 18, H_{aryl}), 3.21 (m, 2, P(CH_2CH$_3$)$_2$Ph), 2.59 (m, 2, P(CH_2CH$_3$)$_2$Ph), 2.22 (br s, 6, Ar: Me), 2.17–1.84 (m, 8, P(CH_2CH$_3$)$_2$Ph), 1.39 (m, 6, P(CH$_2$CH_3)$_2$Ph), 0.74 (m, 12, P(CH$_2$CH_3)$_2$Ph); ^{13}C NMR (C_6D_6) δ 156.5 (Ar: C_{ipso}), 141.5 (t, J_{CP} = 15.4, C_{ipso} of mutually trans PEt$_2$*Ph*'s), 138.0 (d, J_{CP} = 29.4, C_{ipso} of PEt$_2$*Ph* trans to Cl), 135.2 (br s, Ar: C_o), 133.3 (d, J_{CP} = 7.0, C_o of PEt$_2$*Ph* trans to Cl), 131.6 (t, J_{CP} = 3.8, C_o of mutually trans PEt$_2$*Ph*'s), 129.1 and 128.4 (Ar: C_m and C_p of mutually trans PEt$_2$*Ph*'s), 128.6 (C_p of PEt$_2$*Ph* trans to Cl), 128.0 (t, J_{CP} = 3.5, C_m of mutually trans PEt$_2$*Ph*'s), 127.8 (d, J_{CP} = 7.5, C_m of PEt$_2$*Ph* trans to Cl), 123.8 (Ar: C_p), 27.5 (d, J_{CP} = 25.6, P(*C*H$_2$CH$_3$)$_2$Ph trans to Cl), 21.4 (Ar: Me), 18.1 (t, N = 22.0, mutually trans P(*C*H$_2$CH$_3$)$_2$Ph's), 15.8 (t, N = 23.8, mutually trans P(*C*H$_2$CH$_3$)$_2$Ph's), 11.4 (d, J_{CP} = 7.7, P(CH$_2$C*H*$_3$)$_2$Ph trans to Cl), 8.3 and 8.0 (mutually trans P(CH$_2$C*H*$_3$)$_2$Ph's); ^{31}P NMR (C_6D_6) δ −6.9 (s, J_{PW} = 356, PEt$_2$Ph trans to Cl), −9.2 (s, J_{PW} = 295, mutually trans PEt$_2$Ph's). Anal. Calcd for

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(42) $WOCl_4$ may be purchased commercially or synthesized from: (a) WO_3 and $SOCl_2$ (Nielson, A. J. In *Inorg Syntheses*; Kirschner, S., Ed.; John Wiley & Sons: New York, 1985; pp 195–199), (b) WCl_6 and $MeOSiMe_3$ (ref 23), or (c) WCl_6 and $(Me_3Si)_2O$ (Gibson, V. C.; Kee, T. P.; Shaw, A. *Polyhedron* **1988**, *7*, 579–580).

(43) Lipton, M. F.; Sorensen, C. M.; Sadler, A. C.; Shapiro, R. H. *J. Organomet. Chem.* **1980**, *186*, 155–158.

($C_{38}H_{54}Cl_2NP_3W$): C, 52.31; H, 6.24; N, 1.61. Found: C, 51.09; H, 5.99; N, 1.47. The high lability of the PEt_2Ph ligands of **1** prevented a more satisfactory analysis from being obtained.

$WCl_2(NPh)[P(OMe)_3]_3$ (2). Benzene (210 mL) was added to olive-green $WCl_4(NPh)$ (20.85 g, 50.02 mmol). Subsequent addition of 24 mL of $P(OMe)_3$ to the $WCl_4(NPh)$ suspension resulted in the formation of a green solution, which was then transferred via cannula onto a 1% sodium amalgam (4.15 g Na). After being stirred for 27 min, the solution turned purple, and the mixture was then allowed to settle. The purple solution was transferred via cannula into another Schlenk flask. After the spent amalgam was washed with 90 mL of benzene, benzene and excess $P(OMe)_3$ were removed in vacuo. The resulting residue was dissolved in 200 mL of THF, the solution was filtered, and THF was then removed in vacuo. The remaining purple powder was washed with 100 mL of pentane and dried in vacuo (28.60 g, 79.6%): ^{1}H NMR (CD_2Cl_2) δ 7.25–7.17 (m, 5, H_{aryl}), 3.75 (t, 18, N = 10.8, mutually trans $P(OMe)_3$'s), 3.63 (d, 9, J_{HP} = 10.5, $P(OMe)_3$ trans to Cl); ^{13}C NMR (CD_2Cl_2) δ 156.6 (C_{ipso}), 128.6 (Ar: C_m), 126.1 (Ar: C_o), 125.7 (Ar: C_p), 53.3 (d, J_{CP} = 6.6, $P(OMe)_3$ trans to Cl), 52.9 (t, N = 5.2, mutually trans $P(OMe)_3$'s); ^{31}P NMR (C_6D_6) δ 141.1 (t, J_{PP} = 22, J_{PW} = 564, $P(OMe)_3$ trans to Cl), 129.3 (d, J_{PP} = 22, J_{PW} = 454, mutually trans $P(OMe)_3$'s). Anal. Calcd for ($C_{15}H_{32}Cl_2NO_9P_3W$): C, 25.09; H, 4.49; N, 1.95. Found: C, 24.82; H, 4.37; N, 1.99.

$WCl_2(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]_3$ (3). Trimethyl phosphite (25.5 mL) was added to a benzene (210 mL) solution of $WCl_4(N\text{-}2,6\text{-}C_6H_3Me_2)(THF)$ (25.86 g, 50.0 mmol). The resulting green solution was transferred via cannula onto a 1% sodium amalgam (4.20 g Na), and the mixture was stirred until it turned purple (1 h). After the mixture settled, the solution was transferred via cannula into another Schlenk flask, and then the spent amalgam was washed with a total of 120 mL of benzene. After benzene and excess $P(OMe)_3$ were removed in vacuo, the remaining solid was dissolved in 180 mL of THF, and the solution was filtered. Next, THF was removed in vacuo, and the product was washed with 100 mL of pentane and dried in vacuo to give 29.86 g (80.0%) of gray powder: ^{1}H NMR (CD_2Cl_2) δ 6.99 (t, 1, J = 7.6, Ar: H_p), 6.87 (d, 2, J = 7.6, Ar: H_m), 3.71 (t, 18, N = 10.4, mutually trans $P(OMe)_3$'s), 3.68 (d, 9, J_{HP} = 10.5, $P(OMe)_3$ trans to Cl), 2.46 (s, 6, Ar: Me); ^{13}C NMR (CD_2Cl_2) δ 154.0 (Ar: C_{ipso}), 137.9 (Ar: C_o), 127.9 (Ar: C_m), 125.8 (Ar: C_p), 53.2 (d, J_{CP} = 7.3, $P(OMe)_3$ trans to Cl), 52.8 (t, N = 5.2, mutually trans $P(OMe)_3$'s), 19.2 (Ar: CH_3); ^{31}P NMR (C_6D_6) δ 144.8 (t, J_{PP} = 19.5, J_{PW} = 568, $P(OMe)_3$ trans to Cl), 127.8 (d, J_{PP} = 19.5, J_{PW} = 456, mutually trans $P(OMe)_3$'s). Anal. Calcd for ($C_{17}H_{36}Cl_2NO_9P_3W$): C, 27.37; H, 4.86; N, 1.88. Found: C, 27.48; H, 4.68; N, 1.87.

$WCl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_3$ (4). Brick-red $WCl_4[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2]$ (25.04 g, 49.99 mmol) was suspended in 210 mL of benzene. Upon addition of 24.8 mL of $P(OMe)_3$ to the suspension, a green solution was formed. The solution was transferred via cannula onto a 1% sodium amalgam (4.15 g Na), and the mixture was stirred until it turned purple (45 min). After the mixture was allowed to settle, the solution was transferred via cannula into another Schlenk flask, and the spent amalgam was washed with 70 mL of THF. The combined solvents and excess $P(OMe)_3$ were removed in vacuo, and the solid residue was dissolved in 250 mL of THF and filtered twice. After removal of THF in vacuo, the purple-gray powder was washed with 100 mL of pentane and dried in vacuo to give 31.17 g (77.7%) of product: ^{1}H NMR (CD_2Cl_2) δ 7.19 (t, 1, J = 7.59, Ar: H_p), 7.01 (d, 2, J = 7.59, Ar: H_m), 4.15 (septet, 2, J = 6.59, $CHMe_2$), 3.72 (d, 9, J_{HP} = 10.25, $P(OMe)_3$ trans to Cl), 3.71 (t, 18, N = 10.76, mutually trans $P(OMe)_3$'s), 1.11 (d, 12, J = 6.59, $CHMe_2$); ^{13}C NMR (CD_2Cl_2) δ 150.9 (Ar: C_{ipso}), 147.9 (Ar: C_o), 126.5 (Ar: C_p), 123.5 (Ar: C_m), 53.5 (d, J_{CP} = 7.3, $P(OMe)_3$ trans to Cl), 52.9 (t, N = 4.4, mutually trans $P(OMe)_3$'s), 27.3 ($CH(CH_3)_2$), 25.1 ($CH(CH_3)_2$); ^{31}P NMR (C_6D_6) δ 143.4 (t, J_{PP} = 20, J_{PW} = 566, $P(OMe)_3$ trans to Cl), 128.0 (d, J_{PP} = 20, J_{PW} = 456, mutually trans $P(OMe)_3$'s). Anal. Calcd for ($C_{21}H_{44}Cl_2NO_9P_3W$): C, 31.44; H, 5.53; N, 1.75. Found: C, 31.54; H, 5.52; N, 1.68.

$W(PhC{\equiv}CPh)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_2$ (5). A 7-mL Et_2O solution of $PhC{\equiv}CPh$ (314 mg, 1.76 mmol) was added to 1.54 g (1.76 mmol) of $WCl_2(N\text{-}2,6\text{-}C_6H_3Me_2)(PEt_2Ph)_3$ (**1**). After the solution was stirred for 17.5 h, 30 mL of pentane was added in order to precipitate the product. The suspension was filtered, and the light tan powder was washed with an additional 15 mL of pentane and then dried in vacuo to yield 674 mg (43.2%) of **5**: ^{1}H NMR (C_6D_6) δ 7.74–6.64 (m, 23, H_{aryl}), 3.44 (m, 2, $P(CH_2CH_3)_2Ph$), 2.99 (s, 3, NAr: *Me*), 2.62 (m, 2, $P(CH_2CH_3)_2Ph$), 2.22 (m, 2, $P(CH_2CH_3)_2Ph$), 2.08 (s, 3, NAr: *Me*), 1.99 (m, 2, $P(CH_2CH_3)_2Ph$), 1.38 (quintet, 6, J = 7.52, $P(CH_2CH_3)(CH_2CH_3)'Ph$), 0.52 (quintet, 6, J = 7.18, $P(CH_2CH_3)(CH_2CH_3)'Ph$); ^{13}C NMR (CD_2Cl_2) δ 157.3 (t, J_{CP} = 11.57, $PhC{\equiv}CPh$), 153.6 (t, J_{CP} = 2.33, NAr: C_{ipso}), 144.2 ($PhC{\equiv}CPh$: C_{ipso}), 143.0 and 139.7 (NAr: C_o, C_o'), 133.3 (t, J_{CP} = 20.11, PEt_2Ph: C_{ipso}), 130.6 (t, J_{CP} = 3.81, PEt_2Ph: C_o), 128.5 (PEt_2Ph: C_p), 129.1, 128.1, and 127.9 (NAr: C_m, $C_{m'}$, C_p), 127.5 ($PhC{\equiv}CPh$: C_m), 127.4 (t, J_{CP} = 4.28, PEt_2Ph: C_m), 126.0 ($PhC{\equiv}CPh$: C_o), 125.2 ($PhC{\equiv}CPh$: C_p), 21.5 (NAr: Me), 19.9 (NAr: Me'), 16.6 (t, N = 25.38, $P(CH_2CH_3)(CH_2CH_3)'Ph$), 14.9 (t, N = 24.20, $P(CH_2CH_3)(CH_2CH_3)'Ph$), 8.0 ($P(CH_2CH_3)(CH_2CH_3)'Ph$), 7.3 (t, J_{CP} = 3.10, $P(CH_2CH_3)(CH_2CH_3)'Ph$); ^{31}P NMR (C_6D_6) δ 6.80 (J_{PW} = 203). The high lability of the PEt_2Ph ligands of **5** prevented a satisfactory analysis from being obtained.

$W(H_2C{=}CH_2)Cl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_2$ (6). Purple $WCl_2[N\text{-}2,6\text{-}C_6H_3(i\text{-}Pr)_2][P(OMe)_3]_3$ (**4**) (1.56 g, 1.79 mmol) was dissolved in 20 mL of toluene, and the resulting solution was stirred under 1 atm of ethylene for 0.5 h at room temperature. Orange crystals precipitated from the toluene solution at −50 °C, and subsequent addition of the supernatant to 60 mL of rapidly stirring pentane yielded a golden yellow powder. A total of 0.80 g (64%) was isolated: ^{1}H NMR (C_6D_6) δ 6.89–6.87 (s, 3, H_{aryl}), 3.95 (br m, 2, $CH(CH_3)_2$), 3.55 (t, 18, N = 10.38, $P(OMe)_3$), 3.25 (m, 2, $HH'C{=}CHH'$, protons anti to the imido ligand), 2.85 (m, 2, $HH'C{=}CHH'$, protons syn to the imido ligand), 1.23 (d, 12, J = 6.75, $CH(CH_3)_2$); ^{13}C NMR (CD_2Cl_2) δ 150.0 (t, J_{CP} = 2.9, J_{CW} = 33, Ar: C_{ipso}), 149.8 (Ar: C_o), 127.5 (Ar: C_p), 123.5 (Ar: C_m), 53.65 (t, N = 6.0, $P(OMe)_3$), 42.3 (t, J_{CH} = 160.6, J_{CP} = 5.62, J_{CW} = 29, $H_2C{=}CH_2$), 26.9 ($CH(CH_3)_2$), 24.4 ($CH(CH_3)_2$); ^{31}P NMR (CD_2Cl_2) δ 120.48 (J_{PW} = 385.7); NOEDS (C_6D_6) irradiation at 3.95 ppm, δ 2.85 (8.1% NOE); irradiation at 3.25 ppm, δ 2.85 (20.2% NOE); irradiation at 2.85 ppm, δ 3.95 (8.0% NOE), 3.25 (20.6% NOE). Anal. Calcd for ($C_{20}H_{39}Cl_2NO_6P_2W$): C, 34.01; H, 5.57; N, 1.98. Found: C, 34.33; H, 5.65; N, 1.91.

$W(PhC{\equiv}CH)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]_2$ (7). A 15-mL benzene solution of phenylacetylene (1.09 g, 10.7 mmol) was transferred via cannula onto a 40-mL purple benzene solution of $WCl_2(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]_3$ (7.74 g, 10.4 mmol). The solution turned golden brown after stirring for 1 **h** at 25 °C and then for 1 h at 44 °C. The solvent and free $P(OMe)_3$ were removed in vacuo to yield a yellow powder, which was moderately soluble in Et_2O and toluene. Recrystallization from these solvents yielded 6.45 g (85.8%) of yellow product: ^{1}H NMR (C_6D_6) δ 10.43 (dd, 1, J_{HP} = 16.85, 5.62, $PhC{\equiv}CH$), 7.74 (d, 2, J = 7.57, $PhC{\equiv}CH$: C_o), 7.26 (t, 2, J = 7.81, $PhC{\equiv}CH$: C_m), 7.05 (t, 1, J = 7.57, $PhC{\equiv}CH$: C_p), 6.68 (d, 2, J = 7.81, NAr: C_m), 6.63 (t, 1, J = 7.57, NAr: C_p), 3.58 (dd, 9, J = 9.3, 0.98, $P(OMe)_3$), 3.42 (dd, 9, J = 9.3, 0.98, $P(OMe)_3$), 2.6 (br s, 6, NAr: Me_2); ^{13}C NMR (CD_2Cl_2) δ 153.1 (t, J_{CP} = 2.9, NAr: C_{ipso}), 148.6 (dd, J_{CP} = 21.3, 6.6, $PhC{\equiv}CH$), 142.6 (t, $PhC{\equiv}CH$: C_{ipso}), 140.8 (br s, NAr: C_o), 135.6 (m, J_{CH} = 217.6, J_{CP} = 28.2, 7.7, $PhC{\equiv}CH$), 128.5, 127.9, 127.8, 127.5, and 126.7 (NAr: C_m, C_p and $PhC{\equiv}CH$: C_o, C_m, C_p), 54.4 (d, J_{CP} = 6, $P(OMe)_3$), 52.9 (d, J_{CP} = 6, $P(OMe)_3$), 20.0 (NAr: Me_2); ^{31}P NMR (CD_2Cl_2) δ 118.8 (J_{PW} = 354), 117.6 (J_{PW} = 366); NOEDS (C_6D_6) irradiation at 10.43 ppm, δ 3.58 (1.2% NOE), 2.6 (2.2% NOE); irradiation at 3.58 ppm, δ 10.43 (7.3% NOE); irradiation at 3.42 ppm, no NOE's; irradiation at 2.6 ppm, δ 10.43 (6.9% NOE), 7.74 (5.8% NOE), 6.68 (12.2% NOE), 3.58 (0.5% NOE), 3.42 (0.6% NOE). Anal. Calcd for ($C_{22}H_{33}Cl_2NO_6P_2W$): C, 36.49; H, 4.59; N, 1.93. Found: C, 36.78; H, 4.51; N, 1.95.

Observation of $W(PhC{\equiv}CH)Cl_2(N\text{-}2,6\text{-}C_6H_3Me_2)[P(OMe)_3]$ (8). Even in concentrated solutions (tol-d_8, C_6D_6, THF-d_8, CD_2Cl_2), **7** was observed to be in equilibrium with the monophosphite adduct **8**. After equimolar amounts of CuCl and **7** were dissolved in CD_2Cl_2 for 24 h, only **8** was observed: ^{1}H NMR (CD_2Cl_2) δ 10.72 (d, 1, J_{HP} = 20.03, J_{HW} = 9.71, $PhC{\equiv}CH$), 7.81–6.75 (m, 8, H_{aryl}), 3.85 (d, 9, J_{HP} = 10.71, $W(P(OMe)_3)$), 3.67 (d, 9, J_{HP} = 12.59, $Cu(P(OMe)_3)$), 2.32 (s, 6, NAr: Me_2); ^{13}C NMR (CD_2Cl_2, selected C_{aryl} only) δ 161.3 (d, J_{CP} = 7.55, $PhC{\equiv}CH$), 153.1 (d, J_{CP} = 3.49, NAr: C_{ipso}), 139.9 (d, J_{CP} = 2.14, NAr: C_o), 138.4 (m, $PhC{\equiv}CH$), 136.6 (J_{CP} = 3.78, $PhC{\equiv}CH$: C_{ipso}), 54.0 (d, J_{CP} = 6.58, $W(P(OMe)_3)$), 51.2 ($Cu(P(OMe)_3)$), 19.14 (NAr: Me_2); ^{31}P NMR (CD_2Cl_2) δ 130.44 (J_{PW} = 405).

$W(HC{=}CHCPh_2)Cl_2(NPh)(PMePh_2)_2$ (9). 3,3-Diphenylcyclopropene (420 mg, 2.19 mmol) was dissolved in 15 mL of toluene, and then the solution was added via cannula to a 90-mL toluene solution of $WCl_2(NPh)(PMePh_2)_3$ (2.01 g, 2.13 mmol). After the reaction mixture was stirred for 9 h, all but ~10 mL of the toluene was removed in vacuo. Addition of 30 mL of pentane and filtration yielded 1.45 g (76.5%) of yellow powder, which was dried under vacuum: ^{1}H NMR (CD_2Cl_2) δ

7.68–6.59 (m, 33, H_{aryl}), 5.51 (d, 2, NPh: H_o), 3.75 (t, 2, J_{HP} = 5.63, HC=CH), 2.47 (t, 6, N = 9.18, P*Me*Ph_2); ^{13}C NMR (CD_2Cl_2; only select C_{aryl} chemical shifts are listed) δ 153.2 and 153.1 (NAr: C_{ipso} and C*Ph*Ph′: C_{ipso}), 144.6 (CPh*Ph*′: C′$_{ipso}$), 134.1 (PMe*Ph*Ph′: C_{ipso}), 130.5 (PMePh*Ph*′: C′$_{ipso}$), 72.4 (t, J_{CH} = 195, J_{CP} = 9, J_{CW} = 45, HC=CH), 69.7 (*C*Ph_2), 12.1 (t, N = 32, P*Me*Ph_2); ^{31}P NMR (CD_2Cl_2) δ 4.7 (J_{PW} = 208).

Stability: Complex **9** was stable in the solid state for months at room temperature and stable for at least 12 h in CD_2Cl_2 solution at room temperature.

W(HC=CHCPh$_2$)Cl$_2$(NPh)[P(OMe)$_3$]$_2$ (10). A 6-mL Et_2O solution of 3,3-diphenylcyclopropene (154 mg, 0.803 mmol) was added to a purple suspension of $WCl_2(NPh)[P(OMe)_3]_3$ (538 mg, 0.749 mmol) in 6 mL of Et_2O. A yellow precipitate formed as the reaction mixture was stirred for 23 h. Pentane (10 mL) was added to the suspension, the reaction mixture was filtered, and the pale yellow powder (477 mg, 80.9%) was dried in vacuo: ^1H NMR (CD_2Cl_2) δ 7.22–6.67 (m, 13, H_{aryl}), 6.31 (d, 2, J = 6.74, NPh: H_m), 4.50 (t, 2, J_{HP} = 6.01, HC=CH), 3.92 (t, 18, N = 10.48, $P(OMe)_3$); ^{13}C NMR (CD_2Cl_2) δ 152.9 (C*Ph*Ph′: C_{ipso}), 152.8 (t, J_{CP} = 3.3, NPh: C_{ipso}), 143.1 (CPh*Ph*′: C′$_{ipso}$), 131.7, 128.1, 127.5, 127.2 and 127.0 (NPh: C_m and CPhPh′: C_o, C′$_o$, C_m, C′$_m$), 126.1, 125.9 and 125.4 (NPh: C_p and CPhPh′: C_p, C′$_p$), 125.8 (t, J_{CP} = 3.3, NPh: C_o), 64.8 (t, J_{CH} = 193, J_{CP} = 16, J_{CW} = 37, HC=CH), 64.3 (*C*Ph_2), 54.4 (t, N = 6.6, $P(OMe)_3$); ^{31}P NMR (CD_2Cl_2) δ 118.1 (J_{PW} = 364); ^{31}P NMR (tol-d_8) δ 117.6 (J_{PW} = 361).

Stability: Complex **10** was stable in the solid state for months at room temperature; after **10** was dissolved for ~12 h in CD_2Cl_2 solution at room temperature, partial decomposition and conversion to the vinyl alkylidene was observed.

W(HC=CHCPh$_2$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe)$_3$]$_2$ (11). A 30-mL Et_2O solution of 3,3-diphenylcyclopropene (392 mg, 2.04 mmol) was added via cannula to a 1.52 g (2.04 mmol) suspension of WCl_2(N-2,6-$C_6H_3Me_2$)$[P(OMe)_3]_3$ in 120 mL of Et_2O. After being stirred for several hours, the reaction mixture was filtered, and the yellow powder (668 mg, 40.2%) was dried in vacuo and stored at –30 °C: ^1H NMR (CD_2Cl_2) δ 7.35–6.49 (m, 13, H_{aryl}), 4.74 (t, 2, J_{HP} = 5.79, HC=CH), 3.99 (t, 18, N = 9.08, $P(OMe)_3$), 2.22 (s, 6, NAr: Me); ^{13}C NMR (CD_2Cl_2) δ 153.2 (J_{CW} = 5.4, C*Ph*Ph′: C_{ipso}), 151.2 (t, J_{CP} = 5.4, NAr: C_{ipso}), 142.1 (CPh*Ph*′: C′$_{ipso}$), 136.1 (NAr: C_o), 132.3, 127.7, 127.5, 127.0, and 126.6 (NAr: C_m and CPhPh′: C_o, C′$_o$, C_m, C′$_m$), 125.6, 125.5 and 125.4 (NAr: C_p and CPhPh′: C_p, C′$_p$), 66.7 (J_{CW} = 2.9, *C*Ph_2), 66.2 (t, J_{CH} = 194, J_{CP} = 15, J_{CW} = 40, HC=CH), 55.3 (t, N = 8, $P(OMe)_3$), 19.7 (NAr: Me_2); ^{31}P NMR (CD_2Cl_2) δ 109.8 (J_{PW} = 379, $P(OMe)_3$). Anal. Calcd for ($C_{29}H_{39}Cl_2NO_6P_2W$): C, 42.77; H, 4.83; N, 1.72. Found: C, 42.63; H, 4.73; N, 1.48.

Stability: After ~12 h in CD_2Cl_2 solution at room temperature, conversion of **11** to the corresponding vinyl alkylidene **19** was observed.

W(HC=CHCOCH$_2$CH$_2$CH$_2$O)Cl$_2$(NPh)[P(OMe)$_2$]$_2$ (12). A 20-mL Et_2O solution of ketalcyclopropene (247 mg, 2.20 mmol) was added via cannula to a suspension of $WCl_2(NPh)(PMePh_2)_3$ (2.01 g, 2.13 mmol) in a mixture of 130 mL of Et_2O and 50 mL of toluene. After being stirred for 12 h, the reaction mixture was filtered to yield 643 mg (35.2%) of yellow powder, which was dried under vacuum: ^1H NMR (CD_2Cl_2) δ 7.67–6.86 (m, 25, H_{aryl}), 3.74 (t, 2, J = 5.07, OCH_2), 3.66 (t, 2, J = 5.15, OCH_2), 3.30 (t, 2, J_{HP} = 5.71, HC=CH), 2.35 (t, 6, N = 8.79, P*Me*Ph_2), 1.69 (quintet, 2, J = 5.22, $CH_2CH_2CH_2$); ^{13}C NMR (CD_2Cl_2) δ 154.1 (NPh: C_{ipso}), 134.2 (t, J_{CP} = 23.1, PMe*Ph*Ph′: C_{ipso}), 133.8 (t, J_{CP} = 4.4, PMe*Ph*Ph′: C_o), 132.9 (t, J_{CP} = 4.4, PMePh*Ph*′: C′$_o$), 131.4 (t, J_{CP} = 21.6, PMePh*Ph*′: C_{ipso}), 130.1 (2, PMe*Ph*Ph′: C_p, C′$_p$), 128.1 (t, J_{CP} = 4.8, PMe*Ph*Ph′: C_m) 128.0 (t, J_{CP} = 4.4, PMePh*Ph*′: C′$_m$), 127.8 and 127.5 (NPh: C_o, C_m), 127.2 (NPh: C_p), 106.4 (HC=*C*HCO_2), 67.5 (t, J_{CH} = 188, J_{CP} = 9.2, J_{CW} = 41.6, HC=CH), 67.0 (OCH_2), 66.4 (OCH_2), 26.3 ($CH_2CH_2CH_2$), 12.0 (t, N = 31.6, P*Me*Ph_2); ^{31}P NMR (CD_2Cl_2) δ 5.1 (J_{PW} = 212). Anal. Calcd for ($C_{38}H_{39}Cl_2NO_2P_2W$): C, 53.17; H, 4.58; N, 1.63. Found: C, 52.78; H, 4.38; N, 1.22.

Stability: Complex **12** was stable for months in the solid state at room temperature and also stable for at least 12 h in CD_2Cl_2 solution at room temperature.

W(HC=CHCOCH$_2$CH$_2$CH$_2$O)Cl$_2$(NPh)[P(OMe)$_3$]$_2$ (13). An 8-mL Et_2O solution of ketalcyclopropene (220 mg, 1.96 mmol) was added to 1.10 g (1.53 mmol) of purple $WCl_2(NPh)[P(OMe)_3]_3$. The suspension was stirred for 23 h, washed with 75 mL of pentane, and then filtered. The pale yellow powder (985 mg, 91.5%) was dried in vacuo and stored at –30 °C in the drybox freezer: ^1H NMR (CD_2Cl_2) δ 7.25–7.09 (m, 5, H_{aryl}), 4.14 (t, 2, J_{HP} = 5.98, HC=CH), 4.03 (t, 2, J = 5.39, OCH_2), 3.86 (t, 18, N = 10.62, $P(OMe)_3$), 3.65 (t, 2, J = 5.22, OCH_2), 1.70 (quintet, 2, J = 5.23, $CH_2CH_2CH_2$); ^{13}C NMR (CD_2Cl_2) δ 153.0 (t, J_{CP} = 3.1, NPh: C_{ipso}), 127.5 (NPh: C_m), 126.7 (NPh: C_p), 126.4 (t, J_{CP} = 2.8, NPh: C_o), 103.5 (HC=CH-*C*O_2), 66.5 (OCH_2), 65.2 (OCH_2), 59.9 (t, J_{CH} = 209.9, J_{CP} = 15.3, J_{CW} = 36.6, HC=CH), 52.3 (t, N = 4.0, $P(OMe)_3$), 25.7 ($CH_2CH_2CH_2$); ^{31}P NMR (CD_2Cl_2) δ 120 (J_{PW} = 361, $P(OMe)_3$); ^1H NMR (C_6D_6) δ 7.47 (d, 2, J = 7.58, NPh: H_o), 6.98 (t, 2, J = 7.83, NPh: H_m), 6.81 (t, 1, J = 7.51, NPh: H_p), 4.81 (t, 2, J_{HP} = 5.77, J_{HW} = 1.74, HC=CH), 3.96 (t, 2, J = 5.42, OCH_2 anti to tungsten), 3.72 (t, 2, J = 5.52, OCH_2 syn to tungsten), 3.60 (t, 18, N = 10.62, $P(OMe)_3$), 1.46 (quintet, 2, J = 5.39, $CH_2CH_2CH_2$); NOEDS (C_6D_6) irradiation at 4.81 ppm, no NOEs; irradiation at 3.96 ppm, δ 4.81 (5.2% NOE); irradiation at 3.72 ppm, δ 7.47 (4.5% NOE). Anal. Calcd for ($C_{18}H_{31}Cl_2NO_8P_2W$): C, 30.62; H, 4.42; N, 1.98. Found: C, 29.86; H, 4.26; N, 1.91.

Stability: Solid **13** decomposed to a black, sticky oil when stored at room temperature for 5 months. Partial decomposition and conversion of **13** to the vinyl alkylidene was observed after ~12 h in CD_2Cl_2 solution at room temperature.

W(HC=CHCOCH$_2$CH$_2$CH$_2$O)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe$_3$]$_2$ (14). A 10-mL Et_2O solution of ketalcyclopropene (458 mg, 4.08 mmol) was added to 3.00 g (4.02 mmol) of WCl_2(N-2,6-$C_6H_3Me_2$)$[P(OMe)_3]_3$, and the resulting suspension was stirred for 13 h. Removal of the solvent and free $P(OMe)_3$ in vacuo yielded a pale yellow powder, which was washed with one 30-mL portion and one 150-mL portion of pentane. The tan product (2.58 g, 87.4%) was dried under vacuum and stored at –30 °C in the drybox freezer: ^1H NMR (CD_2Cl_2) δ 7.02–6.78 (m, 3, H_{aryl}), 4.27 (t, 2, J_{HP} = 5.91, HC=CH), 3.98 (t, 2, J = 5.32, OCH_2), 3.89 (t, 18, N = 10.30, $P(OMe)_3$), 3.34 (t, 2, J = 5.43, OCH_2), 2.50 (s, 6, NAr: Me_2), 1.60 (quintet, 2, J = 5.31, $CH_2CH_2CH_2$); ^{13}C NMR (CD_2Cl_2) δ 150.9 (t, J_{CP} = 2, J_{CW} = 16, NAr: C_{ipso}), 138.3 (NAr: C_o), 126.9 (NAr: C_m), 126.1 (NAr: C_p), 104.0 (HC=CH-*C*O_2), 66.7 (OCH_2), 64.9 (OCH_2), 61.5 (t, J_{CH} = 193.7, J_{CP} = 14.9, J_{CW} = 31.2, HC=CH), 54.5 (t, N = 6.90, $P(OMe)_3$), 25.8 ($CH_2CH_2CH_2$), 18.8 (NAr: Me_2); ^{31}P NMR (CD_2Cl_2) δ 113 (J_{PW} = 376, $P(OMe)_3$). Anal. Calcd for ($C_{20}H_{35}Cl_2NP_2O_8W$): C, 32.72; H, 4.81; N, 1.91. Found: C, 33.01; H, 4.71; N, 1.59.

Stability: Conversion of **14** to the vinyl alkylidenes **22-B** and **22-C** was observed after ~12 h in CD_2Cl_2 solution at room temperature.

W(=CHCH=CPh$_2$)Cl$_2$[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][P(OMe)$_3$]$_2$ (15). A 30-mL benzene solution of 3,3-diphenylcyclopropene (1.84 g, 9.55 mmol) was added via cannula to a 60-mL benzene solution of WCl_2[N-2,6-C_6H_3(*i*-Pr)$_2$][$P(OMe)_3]_3$ (7.12 g, 8.88 mmol), and the reaction mixture was then stirred for 2 h at 80 °C. The solvent was removed in vacuo, and the resulting orange oil was left under dynamic vacuum for an additional 12 h. The product was then dissolved in 95 mL of THF, and the resulting orange solution was filtered. After all but 10 mL of THF was removed in vacuo, addition of 150 mL of pentane yielded 5.50 g (72.1%) of orange powder: ^1H NMR [tol-d_8, room temperature, 90 MHz (broad multiplets were observed for the CH*Me*$_2$ protons at higher fields due to slow rotation about the arylimido ligand)] δ 12.85 (d of t, 1, J_{HH} = 12.75, J_{HP} = 6.37, H_α), 10.23 (d of t, 1, J_{HH} = 12.75, J_{HP} = 2.45, H_β), 7.6–7.0 (m, 13, H_{aryl}), 4.56 (br m, 2, C*H*Me_2), 3.58 (t, 18, N = 10.90, $P(OMe)_3$), 1.15 (d, 12, J = 6.37, CH*Me*$_2$); ^1H NMR (CD_2Cl_2, 300 MHz, –80 °C) δ 12.6 (d of t, 1, H_α), 9.36 (d, 1, J_{HH} = 12.02, H_β), 7.44–7.00 (m, 13, H_{aryl}), 4.30 (m, 1, C*H*Me_2), 3.91 (m, 1, C*H*′Me_2), 3.65 (t, 18, $P(OMe)_3$), 1.09 (d, 6, J = 5.82, CH*Me*$_2$), 0.65 (d, 6, J = 5.35, CH*Me*′$_2$); ^{13}C NMR (CD_2Cl_2) δ 276.8 (t, J_{CH} = 129.9, J_{CP} = 18.2, J_{CW} = 122.9, C_α), 150.5 (br s, NAr: C_o), 149.0 (t, J_{CP} = 3.0, NAr: C_{ipso}), 142.8 (t, J_{CP} = 5.9, C_γ), 141.1 (t, J_{CP} = 2.3, C*Ph*Ph′: C_{ipso}), 139.5 (CPh*Ph*′: C_{ipso}), 139.0 (t, J_{CH} = 158.7, J_{CP} = 5.8, C_β), 131.6 (C*Ph*Ph′: C_o), 129.7 (CPh*Ph*′: C_o), 128.5 (C*Ph*Ph′: C_p), 128.3 (C*Ph*Ph′: C_m), 128.2 (NAr: C_m), 128.1 (CPh*Ph*′: C_p), 128.0 (CPh*Ph*′: C_m), 123.1 (NAr: C_p), 53.3 (t, N = 4.6, $P(OMe)_3$), 27.4 (C*H*Me_2), 24.5 (CH*Me*$_2$); ^{31}P NMR (tol-d_8) δ 130.4 (J_{PW} = 439, $P(OMe)_3$); NOEDS (C_6D_6) irradiation at 12.85 ppm, δ 10.23 (5.9% NOE), 4.56 (12.4% NOE), 1.15 (2.8% NOE); irradiation at 10.23, δ 12.85 (3.3% NOE), 1.15 (1.9% NOE); irradiation at 4.56 ppm, δ 12.85 (19.2% NOE), 1.15 (3.3% NOE); irradiation at 1.15, δ 12.85 (6.6% NOE), 4.56 (21.6% NOE). Anal. Calcd for ($C_{33}H_{47}Cl_2NO_6P_2W$): C, 45.54; H, 5.44; N, 1.61. Found: C, 44.96; H, 5.34; N, 1.58.

W(=CHCH=CPh$_2$)[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][OCMe(CF$_3$)$_2$]$_2$[P(OMe)$_3$] (16). A 30-mL THF solution of $(CF_3)_2$MeCOLi (878 mg, 4.67 mmol) was cooled to –78 °C and added via cannula over a period of 15 min to

a 30-mL THF solution of W[=CHCH=CPh$_2$]Cl$_2$[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][P(OMe)$_3$] (2.02 g, 2.35 mmol) also cooled to −78 °C. After the addition was complete, the orange solution was allowed to warm to room temperature as it was stirred for a total of 7.5 h. After the solvent and free P(OMe)$_3$ were removed in vacuo, the yellow powder was dissolved in Et$_2$O and the resulting solution was filtered and cooled to −50 °C to give yellow crystals (1.56 g, 64.0%): ^{1}H NMR (CD$_2$Cl$_2$) anti rotamer, δ 12.25 (dd, J_{HH} = 14.41, J_{HP} = 8.06, H$_\alpha$), 8.72 (d, J = 14.16, H$_\beta$), 7.51–7.02 (m, 13, H$_{aryl}$), 3.74 (septet, 1, J = 6.59, C*H*Me$_2$), 3.60 (d, 9, J_{HP} = 10.25, P(OMe)$_3$), 3.53 (m, 1, C′*H*Me$_2$, overlaps with syn: P(OMe)$_3$), 1.88 (s, 3, OC*Me*(CF$_3$)$_2$), 1.35 (s, 3, OC′*Me*(CF$_3$)$_2$), 1.27 (d, 3, J = 6.84, CH*Me*Me′), 1.23 (d, 3, J = 6.34, CHMe*Me*′), 1.09 (d, 3, J = 6.83, C′H*Me*Me′), 1.00 (d, 3, J = 6.83, C′HMe*Me*′); syn rotamer, δ 11.62 (dd, 1, J_{HH} = 11.00, J_{HP} = 5.13, H$_\alpha$), 8.72 (d, 1, H$_\beta$, overlaps with anti: H$_\beta$), 3.53 (d, 9, J_{HP} = 10.25, P(OMe)$_3$), 1.73 (s, 3, OC*Me*(CF$_3$)$_2$), 1.48 (s, 3, OC′*Me*(CF$_3$)$_2$), 1.3–1.2 (m, 12, CH*Me*$_2$, overlaps with anti: CH*Me*$_2$); ^{13}C NMR (CD$_2$Cl$_2$) anti rotamer, δ 264.3 (d, J_{CH} = 150.6, J_{CP} = 20.7, J_{CW} = 153.4, C$_\alpha$), 151.0 (d, J_{CP} = 3.0, NAr: C$_{ipso}$), 147.6 (d, J_{CP} = 2.5, NAr: C$_o$), 146.0 (d, J_{CP} = 2.5, NAr: C′$_o$), 140.3 (d, J_{CP} = 3.0, C*Ph*Ph′: C$_{ipso}$), 138.9 (d, J_{CP} = 2.0, CPh*Ph*′: C$_{ipso}$), 136.0 (d, J_{CP} = 7.1, C$_\gamma$), 131.3 (C*Ph*Ph′: C$_o$), 129.2 (CPh*Ph*′: C$_o$), 128.7 (C*Ph*Ph′: C$_m$), 128.6 (d, NAr: C$_m$), 128.6 (C*Ph*Ph′: C$_p$), 128.5 (CPh*Ph*′: C$_m$), 128.4 (d, J = 2.5, NAr: C′$_m$), 128.1 (CPh*Ph*′: C$_p$), 127.1 (NAr: C$_p$), 125.2 (q, J_{CF} = 287, OCMe(*C*F$_3$)(CF$_3$)′), 124.94 (q, J_{CF} = 290, OCMe(CF$_3$)(*C*F$_3$)′), 124.87 (q, J_{CF} = 290, OC′Me(*C*F$_3$)(CF$_3$)′), 124.8 (q, J_{CF} = 188, OC′Me(CF$_3$)(*C*F$_3$)′), 122.9 (d, J_{CH} = 157.6, J_{CP} = 6.6, C$_\beta$), 82.1 (septet, J_{CF} = 29.0, O*C*Me(CF$_3$)$_2$), 80.8 (septet, J_{CF} = 28.3, OC′Me(CF$_3$)$_2$), 53.4 (d, J_{CP} = 7.1, P(OMe)$_3$), 29.9 (*C*HMe$_2$), 28.3 (*C*′HMe$_2$), 24.0 (CH*Me*$_2$), 23.54 (C′H*Me*Me′), 23.50 (C′HMe*Me*′), 19.4 (OC*Me*(CF$_3$)$_2$), 17.8 (OC*Me*′(CF$_3$)$_2$); syn rotamer, 256.3 (d, J_{CP} = 21.7, C$_\alpha$); ^{31}P NMR (CD$_2$Cl$_2$) anti rotamer, δ 147.6 (J_{CW} = 476); syn rotamer, δ 147.9 (J_{CW} = 481). Anal. Calcd for (C$_{38}$H$_{44}$F$_{12}$NO$_5$PW): C, 43.99; H, 4.27; N, 1.35. Found: C, 44.22; H, 4.14; N, 1.32.

W(=CHCH=CPh$_2$)[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][O-2,6-C$_6$H$_3$(*i*-Pr)$_2$]$_2$-[P(OMe)$_3$]$_2$ (17). A mixture of W(=CHCH=CPh$_2$)Cl$_2$[N-2,6-C$_6$H$_3$-(*i*-Pr)$_2$][P(OMe)$_3$]$_2$ (3.53 g, 4.11 mmol) and LiO-2,6-C$_6$H$_3$(*i*-Pr$_2$)$_2$ (1.51 g, 8.17 mmol) was suspended in 40 mL of cold (−78 °C) Et$_2$O. The solution was allowed to warm to room temperature as it was stirred for a total of 1.5 h. The solvent and free P(OMe)$_3$ were removed in vacuo, and then the product was dissolved in 120 mL of hexane. The solution was filtered, concentrated to ∼90 mL, and then cooled to yield 2.96 g (70.0%) of a deep yellow powder. Two isomers were observed in a 61:39 ratio, and the diagnostic NMR signals are as follows: ^{1}H NMR (CD$_2$Cl$_2$) major isomer, δ 12.24 (dd, 1, J_{HH} = 11.37, J_{HP} = 6.31, H$_\alpha$), 8.89 (d, 1, J = 11.30, H$_\beta$); 3.68 (d, 9, J_{HP} = 10.39, P(OMe)$_3$); minor isomer, δ 12.38 (dd, 1, J_{HH} = 14.28, J_{HP} = 7.89, H$_\alpha$), 9.32 (d, 1, J_{HH} = 14.55, H$_\beta$), 3.70 (d, 9, J_{HP} = 10.33, P(OMe)$_3$); ^{13}C NMR (CD$_2$Cl$_2$) major isomer δ 252.9 (d, J_{CH} = 125.4, J_{CP} = 22.2, J_{CW} = 163.8, C$_\alpha$), 150.8 (J_{CW} = 31.1, NAr: C$_{ipso}$), 53.3 (J_{CP} = 7.0, P(OMe)$_3$); minor isomer, δ 258.9 (d, J_{CH} = 152.2, J_{CP} = 20.8, J_{CW} = 156.1, C$_\alpha$), 151.6 (J_{CW} = 35.3, NAr: C$_{ipso}$), 53.2 (J_{CP} = 6.5, P(OMe)$_3$); ^{31}P NMR (CD$_2$Cl$_2$) major isomer, δ 145.3 (J_{PW} = 459); minor isomer δ 146.6 (J_{PW} = 435). Anal. Calcd for (C$_{54}$-H$_{72}$NO$_5$PW): C, 62.97; H, 7.09; N, 1.36. Found: C, 61.95; H, 7.17; N, 1.37.

W(=CHCH=CPh$_2$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)(PEt$_2$Ph)$_2$ (18). A 6-mL Et$_2$O solution of 3,3-diphenylcyclopropene (469 mg, 2.44 mmol) was added to a Schlenk flask containing 2.02 g (2.31 mmol) of tan WCl$_2$(N-2,6-C$_6$H$_3$Me$_2$)(PEt$_2$Ph)$_3$. The solution was stirred for 0.5 h before 10 mL of pentane was added. After the yellow-orange suspension was stirred for an additional 16.5 h, the solvent was removed in vacuo. Next, the product was washed with one 25-mL portion and one 50-mL portion of pentane in order to remove free PEt$_2$Ph, and then the remaining orange-yellow powder (1.66 g, 79.9%) was dried in vacuo. Anti and syn rotamers of **18** were obtained in a 65:35 ratio: ^{1}H NMR (CD$_2$Cl$_2$) anti rotamer, δ 12.15 (d of t, 1, J_{HH} = 13.1, J_{HP} = 4.4, H$_\alpha$), 9.55 (d, 1, J = 13.1, H$_\beta$), 7.6–6.6 (m, H$_{aryl}$), 2.5–2.3 (m, P(C*H*$_2$CH$_3$)$_2$Ph), 2.42 (s, 3, NAr: *Me*Me′), 1.63 (s, 3, NAr: Me*Me*′), 1.2–1.0 (m, P(CH$_2$C*H*$_3$)$_2$Ph); syn rotamer, δ 11.89 (d of t, 1, J_{HH} = 13.1, J_{HP} = 4.4, H$_\alpha$), 8.72 (d, 1, J = 13.3, H$_\beta$), 2.33 (br s, NAr: Me$_2$); ^{13}C NMR (CD$_2$Cl$_2$, only selected C$_{aryl}$ resonances listed) anti rotamer, δ 271.7 (t, J_{CH} = 128, J_{CP} = 12.6, C$_\alpha$), 151.6 (NAr: C$_{ipso}$), 140.5 (t, J_{CP} = 4.7, C$_\gamma$), 138.2 (t, J_{CH} = 155.6, J_{CP} = 4.4, C$_\beta$), 21.0, 20.5 and 19.4 (NAr*Me*Me′ and syn: NAr*Me*Me′), 17.0 (t, N = 26.8, P(*C*H$_2$CH$_3$)(CH$_2$CH$_3$)′Ph), 15.6 (t, N = 26.0, P(CH$_2$CH$_3$)-(*C*H$_2$CH$_3$)′Ph), 7.9 (NAr: Me*Me*′), 7.5 (P(CH$_2$CH$_3$)$_2$Ph and syn: P(CH$_2$CH$_3$)$_2$Ph); syn rotamer, δ 277.9 (t, J_{CH} = 130, J_{CP} = 12.6, C$_\alpha$), 150.6 (NAr: C$_{ipso}$), 141.2 (br m, J_{CH} = 157.0, C$_\beta$), 139.3 (t, J_{CP} = 4.2, C$_\gamma$), 18.1 (t, N = 27.2, P(*C*H$_2$CH$_3$)(CH$_2$CH$_3$)′Ph), 16.9 (t, N = 31.0, P(CH$_2$CH$_3$)(*C*H$_2$CH$_3$)′Ph); ^{31}P NMR (CD$_2$Cl$_2$) anti rotamer, δ 15.3 (J_{PW} = 266); syn rotamer, δ 16.2 (J_{PW} = 273); NOEDS (CD$_2$Cl$_2$) anti rotamer, irradiation at 12.15 ppm, δ 9.55 (3.6% NOE), 1.63 (5.1% NOE); irradiation at 9.55 ppm, δ 12.15 (1.0% NOE); irradiation at 1.63 ppm, δ 12.15 (19.7% NOE); syn rotamer, irradiation at 8.72 ppm, δ 2.33 (0.3% NOE); irradiation at 2.33 ppm, δ 8.72 (13.9% NOE). Anal. Calcd for (C$_{43}$H$_{51}$Cl$_2$NP$_2$W): C, 57.48; H, 5.72; N, 1.56. Found: C, 56.36; H, 5.71; N, 1.57.

Observation of W(=CHCH=CPh$_2$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe)$_3$]$_2$ (19). The cyclopropene complex W(CH=CHCPh$_2$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)-[P(OMe)$_3$]$_2$ (205.3 mg) was dissolved in 450 μL of CD$_2$Cl$_2$. In less than 24 h, complete conversion to the corresponding vinylcarbene complex (an 87:13 mixture of rotamers) was observed by NMR spectroscopy. No other products were observed: ^{1}H NMR (CD$_2$Cl$_2$) major rotamer, δ 12.88 (d of t, 1, J_{HH} = 12.99, J_{HP} = 6.24, H$_\alpha$), 9.62 (d, 1, J = 12.93, H$_\beta$), 7.5–6.8 (m, 13, H$_{aryl}$), 3.73 (t, 18, N = 10.96, P(OMe)$_3$), 2.55 (s, 6, NAr: Me$_2$); minor rotamer, δ 12.41 (d of t, 1, J_{HH} = 13.28, J_{HP} = 6.69, H$_\alpha$), 8.80 (d, 1, J = 14.54, H$_\beta$), 2.75 (s, 6, NAr: Me$_2$); ^{13}C NMR (CD$_2$Cl$_2$) major rotamer, δ 276.6 (t, J_{CH} = 129.6, J_{CP} = 17.6, J_{CW} = 116.8, C$_\alpha$), 151.9 (t, J_{CP} = 3.0, J_{CW} = 35.6, NAr: C$_{ipso}$), 142.8 (t, J_{CP} = 5.6, C$_\gamma$), 140.3 (br s, NAr: C$_o$), 140.1 (C*Ph*Ph′: C$_{ipso}$), 139.3 (CPh*Ph*′: C′$_{ipso}$), 138.2 (t, J_{CH} = 159.2, J_{CP} = 5.7, C$_\beta$), 131.0 (C*Ph*Ph′: C$_o$), 129.5 (CPh*Ph*′: C′$_o$), 128.5, 128.1, 127.9, 127.7, 127.6, 127.2 (NAr: C$_m$, C$_p$ and C*Ph*Ph′: C$_m$, C′$_m$, C$_p$, C′$_p$), 53.1 (t, N = 4.4, P(OMe)$_3$), 19.5 (NAr: Me$_2$); minor rotamer, δ 283.7 (t, J_{CH} = 132.7, J_{CP} = 17.5, C$_\alpha$); ^{31}P NMR (CD$_2$Cl$_2$) major rotamer, δ 132.4 (J_{PW} = 442).

W(=CHR$_B$)Cl$_2$[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][P(OMe)$_3$]·P(OMe)$_3$ [(20-B)·P-(OMe)$_3$]. A 10-mL Et$_2$O solution of ketalcyclopropene (0.99 g, 8.85 mmol) was added via cannula to a purple suspension of WCl$_2$[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][P(OMe)$_3$]$_3$·THF[44] (6.12 g, 7.00 mmol) in 20 mL of Et$_2$O. After a few minutes of stirring, the solution turned deep red. As the stirring was continued for a total of 19.5 h, a large amount of tan precipitate formed. Pentane (120 mL) was added to the reaction mixture, which was then filtered to yield 4.48 g of tan powder and a pale green-yellow filtrate. At this point, a ^{1}H NMR spectrum of the tan powder in CD$_2$Cl$_2$ indicated an 86:14 mixture of **20-B·P(OMe)$_3$** and the tris(phosphite) precursor **4**. The tan powder was then washed first with 30 mL of Et$_2$O containing 5 equiv of P(OMe)$_3$ and next with 30 mL of pentane to yield 2.84 g (51.3%) of pure **20-B·P(OMe)$_3$** as a tan powder. This powder was sparingly soluble in nonpolar NMR solvents, such as C$_6$D$_6$ and tol-*d*$_8$. A ^{1}H NMR spectrum of **20-B·P(OMe)$_3$** in CD$_2$Cl$_2$ indicated the presence of **20-B** and 1 equiv of free P(OMe)$_3$. Spectroscopic data for **20-B** are reported below. Anal. Calcd for (C$_{24}$H$_{43}$Cl$_2$NO$_8$P$_2$W): C, 36.47; H, 5.48; N, 1.77. Found: C, 36.82; H, 5.34, N 1.42.

W(=CHR$_B$)Cl$_2$[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][P(OMe)$_3$] (20-B). Removal of the second equivalent of phosphite from **20-B·P(OMe)$_3$** was achieved after washing the compound several times with ∼100 mL portions of pentane and leaving the compound under dynamic vacuum for at least 1 day after each washing. In the absence of the second equivalent of phosphite, **20-B** was stable in solution and in the solid state: ^{1}H NMR (CD$_2$Cl$_2$) δ 11.73 (dd, 1, J_{HH} = 9.81, J_{HP} = 6.82, H$_\alpha$), 7.15 (s, 3, H$_{aryl}$), 6.00 (dd, 1, J_{HH} = 9.81, J_{HP} = 1.84, H$_\beta$), 5.08 (m, 1, OC*H*H′), 4.82 (m, 1, OCH*H*′), 4.32 (m, 2, OCH$_2$), 4.16 (septet, 2, J = 6.83, C*H*Me$_2$), 3.65 (d, 9, J = 10.89, P(OMe)$_3$), 2.55 (m, 1, CH$_2$C*H*H′CH$_2$), 2.09 (m, 1, CH$_2$CH*H*′CH$_2$), 1.28 (d, 6, J = 6.89, CH*Me*Me′), 1.25 (d, 6, J = 6.82, CHMe*Me*′); ^{13}C NMR (CD$_2$Cl$_2$) δ 259.5 (d, J_{CH} = 143.8, J_{CP} = 20.7, J_{CW} = 124.2, C$_\alpha$), 165.4 (d, J_{CP} = 5.1, C$_\gamma$), 151.7 (d, J_{CP} = 3.0, J_{CW} = 38.9, NAr: C$_{ipso}$), 147.5 (d, J_{CP} = 2.4, NAr: C$_o$), 127.7 (NAr: C$_p$), 123.2 (NAr: C$_m$), 93.0 (d, J_{CP} = 6.1, C$_\beta$), 68.8 (OCH$_2$), 67.6 (OCH$_2$′), 53.4 (d, J_{CP} = 5.8, P(OMe)$_3$), 28.0 (*C*HMe$_2$), 24.5 (CH$_2$*C*H$_2$CH$_2$), 24.2 (CH*Me*Me′), 23.9 (CHMe*Me*′); ^{31}P NMR (CD$_2$Cl$_2$) δ 147.1 (J_{PW} = 520). ^{1}H–^{1}H and ^{1}H–^{13}C COSY spectra and a NOSY spectrum of **20-B** are included in the supplementary material.

Observation of W(=CHR$_C$)Cl[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][P(OMe)$_3$]$_2$ (20-C). At room temperature, **20-B·P(OMe)$_3$** converted to **20-C** in solution (<50% conversion after 12 h in concentrated CD$_2$Cl$_2$ solution) and in the solid state (∼15% conversion after 2 months): ^{1}H NMR (CD$_2$Cl$_2$) δ 12.64 (d of t, J_{HH} = 8.26, J_{HP} = 2.30, H$_\alpha$); ^{13}C NMR (CD$_2$Cl$_2$) δ 257.0 (t, J_{CP} = 10.2, C$_\alpha$), 176.7 (C$_\gamma$), 98.8 (C$_\beta$), 62.3 (OCH$_2$), 41.1 (CH$_2$Cl); ^{31}P NMR (CD$_2$Cl$_2$) δ 144.1 (J_{PW} = 459).

A very concentrated CD$_2$Cl$_2$ solution was used to follow the rearrangement of **20-B·P(OMe)$_3$** to **20-C**, and under these conditions, a third

(44) WCl$_2$[N-2,6-C$_6$H$_3$(*i*-Pr)$_2$][P(OMe)$_3$]$_3$·THF was obtained by recrystallizing **3** from THF. Complex **3** is easier to handle and very pure without recrystallization from THF, and thus, recrystallization is not recommended.

alkylidene resonance was observed. This same resonance was also observed when 6 equiv of $P(OMe)_3$ was added to a more dilute sample of **20-B·P(OMe)$_3$**: ^{1}H NMR (CD_2Cl_2) δ 12.89 (d of t, J_{HH} = 13.97, J_{HP} = 5.04, H_α); ^{13}C NMR (CD_2Cl_2) δ 264.0 (t, J_{CP} = 14.4, C_α), 101.4 (C_β).

W(CHR$_A$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)(PEt$_2$Ph)$_2$ (Syn and Anti) (21-A), W(CHR$_B$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)(PEt$_2$Ph) (21-B), and W(CHR$_C$)Cl(N-2,6-C$_6$H$_3$Me$_2$)(PEt$_2$Ph)$_2$ (21-C). A 6-mL solution of ketalcyclopropene (274 mg, 2.45 mmol) was added to a Schlenk flask containing 2.01 g (2.30 mmol) of tan WCl_2(N-2,6-C_6H_3-Me_2)(PEt_2Ph)$_3$. The solution was stirred for 0.5 h before adding 10 mL of pentane. After the red suspension was stirred for an additional 16.5 h, the solvent was removed in vacuo. Next, free PEt_2Ph was removed by washing the product with one 25-mL portion and one 50-mL portion of pentane, and the brick-red powder (1.39 g, 73.6%) was then dried in vacuo. ^{1}H, ^{13}C, and ^{31}P NMR spectra acquired immediately after the complex was dissolved in C_6D_6, tol-d_8, or CD_2Cl_2 indicated the presence of four alkylidene species: three bis(phosphine) adducts [**21-A** (syn and anti rotamers) and **21-C**] and one monophosphine adduct (**21-B**). An equivalent amount of free PEt_2Ph relative to the mono(phosphine) adduct **21-B** was observed by ^{31}P NMR spectroscopy: ^{1}H NMR (C_6D_6) **21-A** (syn and anti), δ 12.70 (d of t, J_{HH} = 14.17, J_{HP} = 3.98, H_α, 11%), 12.66 (d of t, J_{HH} = 13.60, J_{HP} = 3.79, H_α, 60%); **21-C**, δ 12.42 (d of t, J_{HH} = 7.96, J_{HP} = 2.03, H_α, 24%); **21-B**, δ 11.54 (d of d, J_{HH} = 9.93, J_{HP} = 5.51, H_α, 5%); ^{13}C NMR (CD_2Cl_2) **21-A** (syn and anti) δ 270.4 (t, J_{CP} = 10.8, C_α), 263.9 (t, J_{CP} = 11.0, C_α), **21-C**, δ 262.1 (t, J_{CP} = 7.14, C_α); ^{31}P NMR (tol-d_8) 33.0, 17.8 (J_{PW} = 283), 15.3 (J_{PW} = 278), 13.4 (J_{PW} = 276).

W(=CHR$_C$)Cl(N-2,6-C$_6$H$_3$Me$_2$)(PEt$_2$Ph)$_2$ (21-C). The red isomeric mixture of **21-A**, **21-B**, and **21-C** (812 mg, 1.00 mmol) was dissolved in 25 mL of CH_2Cl_2 and stirred for 19.5 h before removing the solvent in vacuo. The green powder (512 mg, 63.1%) was washed with 50 mL of pentane and dried in vacuo: ^{1}H NMR (CD_2Cl_2) δ 12.23 (d of t, 1, J_{HH} = 8.07, J_{HP} = 2.13, H_α), 7.7–6.8 (m, 13, H_{aryl}), 5.18 (d, 1, J = 8.04, H_β), 3.53 (t, 2, J = 6.58, CH_2Cl or OCH_2), 3.52 (t, 2, J = 5.99, CH_2Cl or OCH_2), 2.3–2.0 (m, 8, $P(CH_2CH_3)_2Ph$), 2.15 (s, 6, NAr: Me_2), 1.84 (quintet, 2, J = 6.27, $CH_2CH_2CH_2$), 1.08–0.87 (m, 12, $P(CH_2CH_3)_2Ph$); ^{13}C NMR (CD_2Cl_2) δ 261.6 (t, J_{CH} = 134.2, J_{CP} = 7.2, J_{CW} = 118.6, C_α), 174.3 (C_γ), 155.4 (J_{CW} = 38.0, NAr: C_{ipso}), 136 (br s, NAr: C_o), 132.6 (t, J_{CP} = 19.5, PEt_2Ph: C_{ipso}), 130.3 (t, J_{CP} = 3.8, PEt_2Ph: C_o), 128.3 and 128.0 (NAr: C_m and PEt_2Ph: C_p), 127.2 (t, J_{CP} = 3.8, PEt_2Ph: C_m), 123.0 (NAr: C_p), 94.8 (J_{CH} = 164.6, C_β), 61.9 (OCH_2), 41.6 (CH_2Cl), 32.0 ($CH_2CH_2CH_2$), 19.7 (br s, NAr: Me_2), 16.2 (t, N = 24.2, $P(CH_2CH_3)(CH_2CH_3)'Ph$), 14.4 (t, N = 24.0, $P(CH_2CH_3)$-$(CH_2CH_3)'Ph$), 6.9 ($PCH_2CH_3)_2Ph$); ^{31}P NMR (CD_2Cl_2) δ 18.6 (J_{PW} = 283); NOEDS (CD_2Cl_2) irradiation at 12.23 ppm, δ 5.18 (11.6% NOE), 2.15 (2.2% NOE); irradiation at 5.18 ppm, δ 12.23 (8.2% NOE); irradiation at 2.15 ppm, δ 12.23 (18.5% NOE). Anal. Calcd for ($C_{34}H_{47}NO_2P_2W$): C, 49.90; H, 5.79; N, 1.71. Found: C, 50.23; H, 5.78; N, 1.70.

W(=CHR$_B$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe)$_3$] (22-B). A 30-mL Et_2O solution of ketalcyclopropene (319 mg, 2.84 mmol) was transferred via cannula onto a 30-mL Et_2O suspension of purple WCl_2(N-2,6-$C_6H_3Me_2$)[$P(OMe)_3$]$_3$ (2.06 g, 2.76 mmol), and the reaction mixture was stirred for 14.25 h. Almost immediately, a yellow precipitate formed; later in the reaction, a red precipitate was observed. Pentane (60 mL) was added to the reaction mixture, which was then filtered, and the resulting red powder (758 mg, 45.0%) was dried in vacuo: ^{1}H NMR (CD_2Cl_2) δ 11.88 (dd, 1, J_{HH} = 9.79, J_{HP} = 6.80, H_α), 7.05–6.95 (m, 3, H_{aryl}), 6.00 (dd, 1, J_{HH} = 9.78, J_{HP} = 1.83, H_β), 5.08 (m, 1, $OCHH'$), 4.82 (m, 1, $OCHH'$), 4.32 (m, 2, OCH_2), 3.65 (d, 9, J = 10.95, $P(OMe)_3$), 2.64 (s, 6, NAr: Me_2), 2.35 (m, 1, $CH_2CHH'CH_2$), 2.20 (m, 1, $CH_2CHH'CH_2$); ^{13}C NMR (CD_2Cl_2) δ 259.7 (d, J_{CH} = 144.7, J_{CP} = 20.5, J_{CW} = 122, C_α), 165.3 (C_γ), 154.2 (J_{CW} = 38.9, NAr: C_{ipso}), 137.5 (NAr: C_o), 127.7 (NAr: C_p), 126.8 (NAr: C_m), 92.7 (J_{CH} = 168.0, C_β), 68.7 (OCH_2), 67.5 (OCH_2), 53.1 (d, J_{CP} = 5.7, $P(OMe)_3$), 24.3 ($CH_2CH_2CH_2$), 19.1 (NAr: Me_2); ^{31}P NMR (CD_2Cl_2) δ 147.5 (J_{PW} = 522); NOEDS (CD_2Cl_2) irradiation at 11.88 ppm, δ 6.00 (10.7% NOE), 2.64 (2.0% NOE); irradiation at 6.00 ppm, δ 11.88 (6.6% NOE); irradiation at 2.64 ppm, δ 11.88 (12.9% NOE). Anal. Calcd for ($C_{17}H_{26}Cl_2NO_5PW$): C, 33.47; H, 4.30; N, 2.30. Found: C, 33.35; H, 4.32; N, 2.57.

Observation of W(=CHR$_B$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe)$_3$] (22-B) and W(=CHR$_C$)Cl(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe)$_3$]$_2$ (22-C). The cyclopropene complex **14** (289 mg) was dissolved in 300 μL of CD_2Cl_2. In less than 24 h, complete conversion to a mono(phosphite) (**22-B**, 25%) and a bis(phosphite) (**22-C**, 75%) vinyl alkylidene complex was observed by NMR spectroscopy. The ^{1}H, ^{13}C, and ^{31}P NMR spectra of the mono(phosphite) vinyl alkylidene complex are identical with those of isolated **22-B**, and the spectral assignments for **22-C** follow: ^{1}H NMR (CD_2Cl_2) δ 12.74 (m, 1, H_α); ^{13}C NMR (CD_2Cl_2) 257.5 (t, J_{CH} = 135.0, J_{CP} = 10.0, J_{CW} = 113.6, C_α), 176.5 (C_γ), 155.2 (J_{CW} = 38.8, NAr: C_{ipso}), 135.7 (NAr: C_o), 127.6 (NAr: C_m), 124.1 (NAr: C_p), 98.9 (J_{CH} = 166.7, C_β), 62.2 (OCH_2), 51.6 ($P(OMe)_3$), 41.0 (CH_2Cl), 31.6 ($CH_2CH_2CH_2$), 18.9 (NAr: Me_2); ^{31}P NMR (CD_2Cl_2) δ 144.5 (J_{PW} = 457).

Table VIII. Conversion of **11** to **19** in the Presence of Excess Diphenylcyclopropene

n	time, h	% **11**	% diphenyl-cyclopropene	% **19** anti	% **19** syn	% **19** + diphenyl-cyclopropene
0	3	38	0	28	14	0
2.2	3	52	141	8	5	8
0	22	0	0	65	17	0
2.2	22	26	131	10	10	40

Table IX. Reaction of **11** with Ketalcyclopropene and of **14** with Diphenylcyclopropene

reacn	% **11**	% **14**	% **19**	% **22-B**	% ketal-cyclopropene	% diphenyl-cyclopropene
11 + ketal-cyclopropene	55	0	7	4	39	2
14 + diphenyl-cyclopropene	0	?[a]	<5	25	0	63

[a] Two overlapping triplets (84% together) were observed at 4.3 ppm.

Conversion of 11 to 19 in the Presence of Excess Diphenylcyclopropene (Table VIII). Complex **11** (34.2 mg, 0.0420 mmol) was dissolved in 600 μL of CD_2Cl_2 (0.0036 M in mesitylene internal standard) together with n equivalents (n = 0 or 2.2) of diphenylcyclopropene. The solution was transferred to an NMR tube, the NMR tube was capped with a rubber septum, and the septum was wrapped with Parafilm. The tube was mechanically rotated for 3 h before a ^{1}H NMR spectrum was acquired; after rotation of the tube for an additional 19 h, another ^{1}H NMR spectrum was acquired. The percentages of compounds were determined by integration relative to the mesitylene internal standard and are reported in Table VIII. The insertion product W(=CHC(Ph)$_2$-CH=CHCH=CPh$_2$)Cl$_2$(N-2,6-C$_6$H$_3$Me$_2$)[P(OMe)$_3$] derived from the reaction of diphenylcyclopropene with **19** (first product of ring-opening metathesis polymerization of diphenylcyclopropene by **19**) is tentatively proposed on the basis of the following chemical shifts: δ 11.39 (d, J_{HP} = 4.79, H_α), 6.08 (d, J = 11.17, $C(Ph)_2CH$= or CH=CPh_2), 5.73 (dd, J = 15.69, 11.13, $CHCH$=CPh_2).

Reaction of 11 with Ketalcyclopropene and of 14 with Diphenylcyclopropene (Table IX). The η^2-cyclopropene complex (0.086 mmol) and 1 equiv of 3,3-disubstituted cyclopropene were dissolved together in 600 μL of CD_2Cl_2 (0.0036 M in mesitylene internal standard). The NMR tube was capped with a rubber septum, the septum was wrapped with Parafilm, and the solution was then left at room temperature for 5.6 h without any external mixing. A ^{1}H NMR spectrum was then acquired, and the percentages of species present were determined by integration versus the mesitylene internal standard. The reactions were quite complex, and only the readily identifiable η^2-cyclopropene and vinyl alkylidene complexes are reported in Table IX.

Observation of HgCl$_2$-Catalyzed Rearrangements of 9 and 10. Procedure A. The η^2-cyclopropene complex (40 mg) was dissolved in 600 μL of CD_2Cl_2 (0.0036 M in mesitylene internal standard), and a ^{1}H NMR spectrum was acquired. Solid $HgCl_2$ was then added to the solution, and the mixture was shaken or mechanically rotated before acquiring a second ^{1}H NMR spectrum.

Procedure B. The η^2-cyclopropene complex (21 mg, 0.023 mmol) and $HgCl_2$ (6 mg, 0.02 mmol) were combined in a mixture of C_6D_6 and THF-d_8, and the reaction mixture was shaken briefly before acquiring a ^{1}H NMR spectrum. Experimental and spectral data for the conversions of the diphenylcyclopropene complexes **9** and **10** are given below. Attempted conversions of the η^2-ketalcyclopropene complexes **12** and **13** resulted only in decomposition.

9. Compound **9** was mixed with 0.088 equiv of $HgCl_2$ for 2.7 h (procedure A), and complete conversion to the vinyl alkylidene was observed: ^{1}H NMR (CD_2Cl_2) major rotamer (85%), δ 12.39 (d of t, J_{HH} = 13.09, J_{HP} = 5.71, H_α), 9.00 (d of t, J_{HH} = 13.13, J_{HP} = 1.87, H_β); minor rotamer (15%), δ 12.55 (d of t, J_{HP} = 6.24, H_α), 9.44 (d of t, J_{HH}

= 12.70, H_β). Complete conversion (procedure A) to the vinyl alkylidene (>95% rotamer with 12.39 ppm H_α resonance) was also observed when **9** was mixed for several minutes with 1 equiv of $HgCl_2$. After mixing with 1 equiv of $HgCl_2$ was continued overnight, only 28% of the vinyl alkylidene product remained.

10. A 6.3:1 ratio of **10** to the vinyl alkylidene was observed prior to the addition of $HgCl_2$; following the addition of 0.079 equiv of $HgCl_2$ (procedure A) and 2.7 h of mixing, a 1.3:1 ratio was observed: ^{1}H NMR (CD_2Cl_2) δ 11.96 (d of t, J_{HH} = 13.28, J_{HP} = 4.23, H_α), 8.82 (d of t, J_{HH} = 13.16, J_{HP} = 1.29, H_β). Complete conversion to the vinyl alkylidene product was observed when **10** was mixed for several minutes with 1 equiv of $HgCl_2$ (procedure B): ^{1}H NMR (C_6D_6/THF-d_8) δ 12.39 (d of t, J_{HH} = 13.24, J_{HP} = 4.17, H_α), 9.16 (d of t, J_{HH} = 13.24, H_β), 2.38 (t, N = 8.82, P*Me*Ph_2).

Observation of Rearrangements of 9, 10, 12, and 13 Induced by Photolysis. The η^2-cyclopropene complex (10.5 mg) was dissolved in 600 μL of toluene-d_8 (0.0035 M in mesitylene internal standard), the solution was immediately cooled to 0 °C, and a ^{1}H NMR spectrum was acquired. The complex was photolyzed for 7 h at 0 °C before acquiring another ^{1}H NMR spectrum. Complexes **10** and **13** were not completely soluble in tol-d_8 at these concentrations, possibly explaining their incomplete conversion.

9. Before photolysis, a 10.4:1 mixture of **9**:vinyl alkylidene was observed; only the vinyl alkylidene was observed after photolysis: ^{1}H NMR (tol-d_8) 75% major rotamer, δ 12.32 (d of t, 1, J_{HH} = 13.35, J_{HP} = 4.27, H_α), 9.13 (d of t, 1, J_{HH} = 13.41, J_{HP} = 1.341, H_β), 2.36 (t, 6, N = 8.98, P*Me*Ph_2); 25% minor rotamer, δ 12.35 (m, H_α), 9.35 (m, J_{HH} = 13, H_β), 2.38 (t, N = 8.46, PMePh_2).

10. After photolysis, a 1:3.4 ratio of **10** to vinyl alkylidene was observed: ^{1}H NMR (tol-d_8) δ 12.84 (d of t, 1, J_{HH} = 13.22, J_{HP} = 6.57, H_α), 9.36 (d of t, 1, J_{HH} = 13.06, J_{HP} = 2.05, H_β), 3.61 (t, 18, N = 10.82, P(OMe)$_3$).

12. After photolysis, only the vinyl alkylidene product was observed: ^{1}H NMR (tol-d_8) major isomer (form **A**), δ 12.48 (d of t, 1, J_{HH} = 13.58, J_{HP} = 3.74, H_α), 3.49 (t, 2, J = 6.13, OCH_2), 3.44 (t, 2, J = 6.19, OCH_2), 2.47 (t, 6, N = 8.74, P*Me*Ph_2).

13. After photolysis, a 1:3.3 ratio of **13** to the vinyl alkylidene product was observed: ^{1}H NMR (tol-d_8) 53% major isomer (form **A**), δ 13.14 (d of t, J_{HH} = 13.98, J_{HP} = 4.69, H_α); 47% minor isomer (form **B**), δ 11.72 (d of d, J_{HH} = 9.54, J_{HP} = 7.02, H_α), 6.10 (d of d, J_{HH} = 9.33, J_{HP} = 1.58, H_β).

X-ray Data Collection, Structure Determination, and Refinement for WCl_2[N-2,6-C_6H_3(*i*-Pr)$_2$][P(OMe)$_3$]$_3$ (4). A purple crystal of approximate dimensions 0.28 × 0.40 × 0.43 mm was oil-mounted on a glass fiber and transferred to the Siemens P3 diffractometer which is equipped with a modified LT-2 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill.[45] Low-temperature (158 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation.

All 7579 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) <0 was assigned the value $|F_o| = 0$. The systematic extinctions observed were $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is thus uniquely defined.

All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package[47] or the SHELXTL PLUS program set.[48] The analytical scattering factors for neutral atoms were used throughout the analysis;[49a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[49b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0003(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.06 Å^2. Refinement of positional and anisotropic thermal parameters led to convergence with R_F = 2.8%, R_{wF} = 3.2%, and GOF = 1.26 for 334 variables refined against those 6690 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max) = 0.94 e Å^{-3}.

X-ray Data Collection, Structure Determination, and Refinement for W(HC═CHCPh$_2$)Cl$_2$(NPh)[P(OMe)$_3$]$_2$ (10). A yellow/gold crystal of approximate dimensions 0.20 × 0.30 × 0.30 mm was oil-mounted on a glass fiber and transferred to the Syntex P2$_1$ diffractometer which is equipped with a modified LT-1 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill.[45] Low-temperature (183 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation.

All 4899 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. The systematic extinctions observed were $0k0$ for $k = 2n + 1$ and $h0l$ for $l = 2n + 1$; the diffraction symmetry was $2/m$. The centrosymmetric monoclinic space group $P2_1/c$ [C_{2h}^5; No. 14] is thus uniquely defined.

All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package[47] or the SHELXTL PLUS program set.[48] The analytical scattering factors for neutral atoms were used throughout the analysis;[49a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[49b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0010(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with d(C–H) = 0.96 Å and U(iso) = 0.08 Å^2. There is a benzene molecule located about an inversion center ($^1/_2$, $^1/_2$, $^1/_2$). Refinement of positional and anisotropic thermal parameters (isotropic for the three unique benzene carbon atoms) led to convergence with R_F = 4.5%, R_{wF} = 6.0%, and GOF = 1.45 for 364 variables refined against those 3721 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max) = 1.38 e Å^{-3}.

X-ray Data Collection, Structure Determination, and Refinement for W(═CHCHCPh$_2$)[N-2,6-C_6H_3(i-Pr)$_2$][OCMe(CF$_3$)$_2$]$_2$[P(OMe)$_3$] (16). A yellow crystal of approximate dimensions 0.20 × 0.30 × 0.37 mm was oil-mounted on a glass fiber and transferred to the Siemens P3 diffractometer which is equipped with a modified LT-2 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill.[45] Low-temperature (158 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation.

All 6801 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with I(net) < 0 was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C_1^1; No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. With Z = 2 and no expectation of a resolved chiral molecule, the latter centrosymmetric space group is far more probable[46] and was later shown to be the correct choice.

All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package[47] or the SHELXTL PLUS program set.[48] The analytical scattering factors for neutral atoms were used throughout the analysis;[49a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[49b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0002(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were located from difference-Fourier maps and included with isotropic temperature factors. Refinement of the model led to convergence with R_F = 3.4%, R_{wF} = 3.7%, and GOF = 1.64 for 699 variables refined against those 6200 data with $|F_o| > 2.0\sigma(|F_o|)$. A final difference-Fourier map yielded ρ(max) = 2.2 e Å^{-3} at a distance of 0.85 Å from tungsten.

X-ray Data Collection, Structure Determination, and Refinement for W(═CHR$_C$)Cl(N-2,6-C_6H_3Me$_2$)(PEt$_2$Ph)$_2$ (21-C). A green crystal of approximate dimensions 0.23 × 0.33 × 0.37 mm was oil-mounted on a glass fiber and transferred to the Siemens P3 diffractometer which is equipped with a modified LT-2 low-temperature system. Determination of Laue symmetry, crystal class, unit cell parameters, and the crystal's orientation matrix were carried out by previously described techniques similar to those of Churchill.[45] Low-temperature (158 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation.

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All 6596 data were corrected for absorption and for Lorentz and polarization effects and placed on an approximately absolute scale. Any reflection with $I(\text{net}) < 0$ was assigned the value $|F_o| = 0$. There were no systematic extinctions nor any diffraction symmetry other than the Friedel condition. The two possible triclinic space groups are the noncentrosymmetric $P1$ [C_1^1; No. 1] or the centrosymmetric $P\bar{1}$ [C_i^1; No. 2]. With $Z = 2$ and no expectation of a resolved chiral molecule, the latter centrosymmetric space group is far more probable[46] and was later shown to be the correct choice.

All crystallographic calculations were carried out using either the UCI modified version of the UCLA Crystallographic Computing Package[47] or the SHELXTL PLUS program set.[48] The analytical scattering factors for neutral atoms were used throughout the analysis;[49a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[49b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0004(|F_o|)^2$.

The structure was solved by direct methods (SHELXTL PLUS) and refined by full-matrix least-squares techniques. Hydrogen atoms were included using a riding model with $d(\text{C–H}) = 0.96$ Å and $U(\text{iso}) = 0.08$ Å^2. At convergence, $R_F = 3.0\%$, $R_{wF} = 3.7\%$, and GOF = 1.37 for 379 variables refined against those 5920 data with $|F_o| > 2.0\sigma(|F_o|)$. A final difference-Fourier map yielded $\rho(\text{max}) = 1.5$ e Å^{-3} at a distance of 1.36 Å from Cl(2).

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Supplementary Material Available: Figures showing ^{1}H–^{1}H COSY, NOSY, and ^{1}H–^{13}C COSY spectra for **20-B** and tables of experimental data, atomic coordinates, bond lengths, and bond angles for the X-ray diffraction studies of **4**, **10**, **16**, and **21-C** (47 pages); tables of observed and calculated structure factors for the X-ray diffraction studies of **4**, **10**, **16**, and **21-C** (56 pages). Ordering information is given on any current masthead page.