Alkylidene Transfer from Phosphoranes to Tungsten(IV) Imido Complexes

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Abstract: The reactions of $WCl_2(NPh)(PMePh_2)_3$ with a number of triphenylphosphoranes were surveyed, and alkylidene transfer to give $W(=CHR)Cl_2(NPh)(PMePh_2)_2$ was observed for variously substituted aryl ylides $Ph_3P{=}CHAr'$, where Ar' = C_6H_5, C_6H_4-*p*-Me, C_6H_4-*m*-Me, C_6H_4-*o*-Me, C_6H_4-*p*-OEt, C_6H_4-*o*-OMe, C_6H_4-*p*-CF_3, C_6F_5, *o*-Np, and *m*-Np, for the vinyl ylide $Ph_3P{=}CH{-}CH{=}CMe_2$, and also for the bis(ylide) $Ph_3P{=}CH{-}C_6H_4{-}C_6H_4{-}CH{=}PPh_3$. A mechanism is proposed for the transfer reaction. A crystal structure of $W(=CHC_6H_4$-*p*-Me$)Cl_2(NPh)(PMePh_2)_2$ indicated an octahedral geometry in which the two mutually trans phosphines and the alkylidene are cis to the apical imido ligand and the alkylidene substituent lies syn to the imido ligand. Reduction of $WCl_2(N{-}2,6\text{-}C_6H_3{-}Me_2)[OCMe(CF_3)_2]_2(THF)$ in the presence of a number of aryl ylides yielded the corresponding benzylidene complexes $W(=CHAr')(N{-}2,6\text{-}C_6H_3{-}Me_2)[OCMe(CF_3)_2]_2(PPh_3)$, which were stable in solution but only isolable upon addition of a stronger donor ligand than PPh_3 (e.g., PMe_3). Transfer of *o*-methoxybenzylidene from phosphorus to reduced $WCl_2(NAr)[OCMe(CF_3)_2]_2(THF)$ complexes was especially favorable, as chelation by the *o*-methoxy group aided the transfer reaction, stabilized the resulting product, and, hence, enabled the synthesis of several arylimido derivatives $W(=CHC_6H_4$-*o*-OMe$)(NAr)[OCMe(CF_3)_2]_2(THF)$, where Ar = Ph, 2,6-$C_6H_3{-}Me_2$, and 2,6-$C_6H_3{-}(i\text{-}Pr)_2$. Crystal structures of the *o*-methoxybenzylidene complexes, with and without THF coordinated to tungsten, were obtained and supported donation by the *o*-methoxy group to tungsten. The *o*-methoxybenzylidene complexes rapidly polymerized norbornene but only slowly metathesized acyclic olefins.

Introduction

Phosphorus ylides (phosphoranes) are easily synthesized and readily isolated, making them attractive precursors to metal alkylidenes. However, although a myriad of transition-metal compounds with ylide donor ligands have been synthesized,[1] loss of phosphine to yield an alkylidene complex has rarely been observed. Three known examples are shown in Figure 1 and include the first synthesis of a terminal ethylidene complex.[2-4] In these examples, nucleophilic alkylidene ligands were formed, thus favoring loss of phosphine from the proposed intermediate ylide adducts.[2] The crowded coordination spheres of these intermediates may also have aided phosphine loss, as well as prevented alkylidene deprotonation by excess phosphorane.[2]

The further extension of the alkylidene-transfer reaction would be desirable, as it provides an alternative to traditional α-hydrogen abstraction pathways for forming nucleophilic alkylidene complexes.[5] In addition, upon development of suitable transition-metal precursors, the wide variety of known phosphorus ylides could potentially enable the synthesis of alkylidene ligands incorporating a number of different substituents. This would allow control of the polymer end-group in ring-opening metathesis polymerization (ROMP)[6,7] and the selection of the products

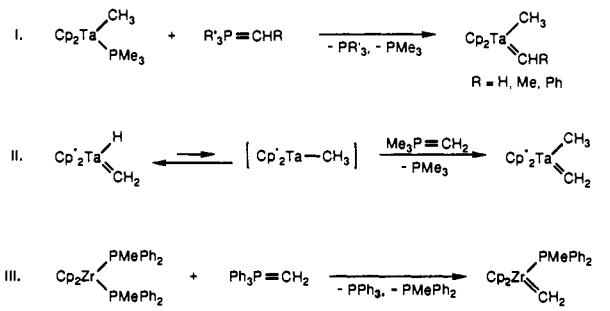

Figure 1. Three examples of alkylidene transfer from phosphoranes to transition-metal centers.[2-4]

obtained from the Wittig-type olefinations of carbonyl compounds, including esters and amides.[8] Finally, the synthesis of di-initiators for ROMP can easily be envisioned via the use of bis(ylide) precursors. A bis(titanacyclobutane) initiator A has already been

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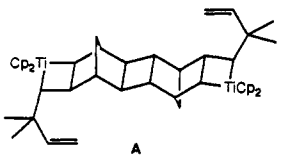
reported, and its efficacy in the synthesis of block copolymers was demonstrated.[9] The isolable chain-carrying species of ROMP catalysts of later metals, for example, groups VI and VII, are alkylidenes,[10] and routes to di-initiators of these catalysts have not been reported.[41]

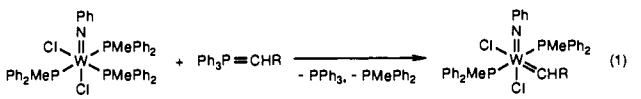


A

The promise of phosphorus ylides as precursors to metal alkylidenes prompted the following research, which involved an investigation of the reactivity of reduced tungsten imido complexes with phosphorus ylides. Initial studies involved the use of $WCl_2(NPh)(PMePh_2)_3$,[11] since this compound is known to react with a number of π-acceptors (L), including carbon monoxide, isonitriles, aldehydes, olefins, and acetylenes, to give $WCl_2(L)(NPh)(PMePh_2)_2$ and free $PMePh_2$.[12] It was hoped that similar substitution reactions with phosphorus ylides to give $W(=CHR)Cl_2(NPh)(PMePh_2)_2$ might be possible, especially since analogs of the expected alkylidene-transfer products, for example, $W(=CH\text{-}t\text{-}Bu)Cl_2(NPh)(PR_3)_2$ (R = Me, Et), are known, stable compounds.[13]

Results and Discussion

Reactions of Phosphoranes with $WCl_2(NAr)(PX_3)_3$ Complexes. Synthesis of $W(=CHR)Cl_2(NPh)(PMePh_2)_2$ Complexes. The reactions of $WCl_2(NPh)(PMePh_2)_3$ with a number of triphenylphosphoranes were surveyed, and alkylidene transfer was observed for variously substituted aryl ylides $Ph_3P{=}CHAr'$, where Ar' = C_6H_5, C_6H_4-*p*-Me, C_6H_4-*m*-Me, C_6H_4-*o*-Me, C_6H_4-*p*-OEt, C_6H_4-*o*-OMe, C_6H_4-*p*-CF_3, C_6F_5, *o*-Np, and *m*-Np, and also for the vinyl ylide $Ph_3P{=}CH{-}CH{=}CMe_2$ (eq 1). Several



R = Ar and CH=CMe2

of these derivatives were synthesized on a preparatory scale, and selected NMR data for these complexes is listed in Table I. In addition, alkylidene transfer from the bis(ylide) $Ph_3P{=}CH{-}C_6H_4{-}C_6H_4{-}CH{=}PPh_3$ to $WCl_2(NPh)(PMePh_2)_3$ was observed and the resulting bimetallic compound **7** (H_α, 12.14 ppm; C_α, 288.8 ppm) was isolated as a single isomer in high yield. For all of the reactions, transfer of the alkylidene moiety from phosphorus to tungsten was clearly indicated by the downfield shifts of the alkylidene H_α and C_α resonances,[14] by the appearance of both of these resonances as triplets due to coupling with the mutually trans phosphine ligands, and also by the coupling of the alkylidene C_α resonance to tungsten.

Table I. Selected NMR Data for $W(=CHR)Cl_2(NPh)(PMePh_2)_2$ Complexes[a]

cmpd	R	H_α	J_{HP}	C_α	J_{CH}	J_{CP}	J_{CW}
1	Ph	12.52[b]	4.77	290.9	126.5	12.0	132.8
2	C_6H_4-*p*-Me	12.21	4.64	290.7	126.7		
3	C_6H_4-*p*-CF_3	12.13	4.63	288.3	128.6	12.2	131.6
4	2-Np	12.31	4.72	290.4	125.3	12.1	132.3
5	C_6F_5	11.71	4.12	261.5	133.9	12.0	146
6[e]	$CH{=}CMe_2$[e]	12.22[c]	4.14	284.0	134.4	11.6	129.3
6[e]	$CH{=}CMe_2$[e]	12.45[d]	4.35	274.2	126.3	11.9	

[a] Spectra were acquired in CD_2Cl_2 unless indicated otherwise. [b] In C_6D_6. [c] δ 8.00 (H_β, $J_{H_\alpha H_\beta}$ = 12.77 Hz). [d] δ 7.9 (H_β, $J_{H_\alpha H_\beta}$ = 13.11 Hz). [e] Syn or anti rotamer.

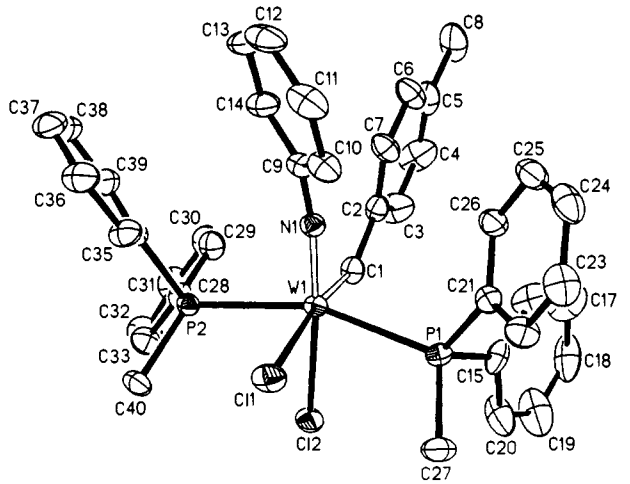
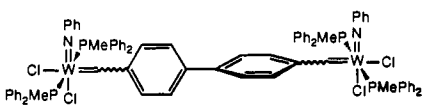


Figure 2. ORTEP plot of $W(=CHC_6H_4\text{-}p\text{-}Me)Cl_2(NPh)(PMePh_2)_2$ (**2**). Thermal ellipsoids are drawn at the 50% probability level.



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X-ray Diffraction Study of $W(=CHC_6H_4\text{-}p\text{-}Me)Cl_2(NPh)(PMePh_2)_2$ (2). The structure of the alkylidene-transfer products was further confirmed by an X-ray diffraction study of the *p*-methylbenzylidene complex **2**. An ORTEP diagram is shown in Figure 2, and selected bond lengths and angles are given in Table II.[15] The geometry of the complex is a distorted octahedron in which the C_α of the alkylidene moiety and the two phosphorus atoms all lie beneath the equatorial plane, on the side opposite to the imido ligand. The *p*-methylbenzylidene ring is syn to the imido ligand, and the steric interactions between these two ligands are lessened by the widening of the W(1)–C(1)–C(2) angle to 138.1(3)° and the bending of the imido ligand away from the alkylidene moiety at an angle of 168.8(2)° (W(1)–N(1)–C(9) angle).

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(14) Schrock, R. R. In *Reactions of Coordinated Ligands*; Braterman, P. S., Ed.; Plenum: New York, 1986; Vol. 1, pp 221–283.

(15) This structure may be compared with that of $W(=CH\text{-}t\text{-}Bu)Cl_2(O)(PMe_3)_2$. In this molecule, the alkylidene substituent lies syn to the oxo ligand, the W=C distance is 1.986(21) Å, and the W(1)–C(1)–C(2) angle is 142.4(19)°. See: Churchill, M. R.; Rheingold, A. R. *Inorg. Chem.* **1982**, *21*, 1357–1359.

Table II. Selected Bond Lengths and Angles for **2**

Bond Lengths (Å)			
W(1)–Cl(1)	2.556(1)	W(1)–Cl(2)	2.490(1)
W(1)–P(1)	2.546(1)	W(1)–P(2)	2.538(1)
W(1)–N(1)	1.752(3)	W(1)–C(1)	1.975(3)
Bond Angles (deg)			
Cl(1)–W(1)–Cl(2)	84.7(1)	Cl(1)–W(1)–P(1)	83.4(1)
Cl(2)–W(1)–P(1)	81.4(1)	Cl(1)–W(1)–P(2)	85.8(1)
Cl(2)–W(1)–P(2)	80.7(1)	P(1)–W(1)–P(2)	159.8(1)
Cl(1)–W(1)–N(1)	89.5(1)	Cl(2)–W(1)–N(1)	173.5(1)
P(1)–W(1)–N(1)	100.9(1)	P(2)–W(1)–N(1)	96.1(1)
Cl(1)–W(1)–C(1)	170.8(1)	Cl(2)–W(1)–C(1)	86.9(1)
P(1)–W(1)–C(1)	91.8(1)	P(2)–W(1)–C(1)	96.3(1)
N(1)–W(1)–C(1)	99.1(1)	W(1)–N(1)–C(9)	168.8(2)
W(1)–C(1)–C(2)	138.1(3)		

Synthetic and Mechanistic Observations. The alkylidene-transfer reaction proceeded slowly at room temperature in C_6D_6 or toluene-d_8, and the reactions could therefore be monitored by ^1H NMR spectroscopy. With the exception of the *o*-naphthyl- and (pentafluoroaryl)alkylidenes, two alkylidene H_α resonances, consistent with the formation of both the syn and anti rotamers of the alkylidene ligand,[16] were initially observed in the ^1H NMR spectra for the aryl- and vinylalkylidenes. With time and heating, gradual conversion to one rotamer was observed. For the arylalkylidenes, the downfield H_α resonance corresponded to the thermodynamic rotamer, whereas, for the vinylalkylidene complex **6**, the rotamer with the upfield H_α resonance was the thermodynamic product. On the basis of the X-ray diffraction study of **2**, the thermodynamic arylalkylidene product is the syn rotamer.

NMR studies indicated that the transfer of arylalkylidenes was hindered by the incorporation of ortho substituents (e.g., *o*-methyl, *o*-methoxy, and *o*-naphthyl) on the benzylidene ring and also by the incorporation of electronegative substituents, as in the case of pentafluorobenzylidene. As the reaction progressed, the rate of alkylidene transfer was slowed by the buildup of free phosphine, and high temperatures (~60–80 °C for several hours) were required to drive the reactions to completion.

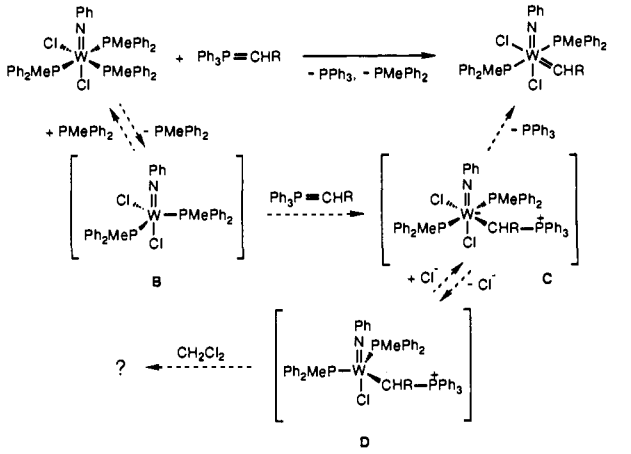
Observation of the alkylidene-transfer product depended markedly on the choice of solvent. Transfer was most favorable when the reaction was conducted in benzene and, to a slightly lesser extent, toluene. Formation of the tungsten alkylidene also occurred in THF-d_8, but at a much slower rate. In CD_2Cl_2, alkylidene transfer to tungsten was not observed, although the ylide did react relatively rapidly with the tungsten precursor. Identification of the products of the CD_2Cl_2 reaction was not pursued.

The aryl- and vinylphosphoranes, $Ph_3P{=}CHAr'$ and $Ph_3P{=}CH{-}CH{=}CMe_2$, are both partially resonance-stabilized ylides with moderate steric requirements. The larger, more nucleophilic ylides, $Ph_3P{=}CH{-}t\text{-}Bu$ and $Ph_3P{=}CHSiMe_3$, did not react with $WCl_2(NPh)(PMePh_2)_3$. Similar to $WCl_2(NPh)(PMePh_2)_3$, the (2,6-dimethylphenyl)imido complex $WCl_2(N{-}2,6\text{-}C_6H_3{-}Me_2)(PEt_2Ph)_3$ readily forms π-acceptor complexes upon displacement of a PEt_2Ph ligand at room temperature.[17] However, alkylidene transfer was not observed from $Ph_3P{=}CHAr'$ and $Ph_3P{=}CH{-}CH{=}CMe_2$ to this complex. According to ^1H NMR spectroscopy, the reactions of $Ph_3P{=}CH_2$ and $Ph_3P{=}CHMe$ with $WCl_2(NPh)(PMePh_2)_3$ and $WCl_2(N{-}2,6\text{-}C_6H_3{-}Me_2)(PEt_2Ph)_3$ resulted in a complex mixture of products; alkylidene-transfer products formed in low yields, if at all.

(16) In order to maximize π-bonding, the alkylidene substituent must lie in the N–W–C_α plane. Two isomers are then possible: (1) a syn rotamer, in which the alkylidene substituent points toward the imido ligand, and (2) an anti rotamer, in which the alkylidene substituent points away from the imido ligand. Detailed studies of syn and anti rotamers of (arylimido)alkylidene complexes have been reported: Schrock, R. R.; Crowe, W. E.; Bazan, G. C.; DiMare, M.; O'Regan, M. B.; Schofield, M. H. *Organometallics* **1991**, *10*, 1832–1843.

(17) Johnson, L. K.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.*, in press.

Scheme I



The above observations are consistent with a mechanism in which loss of phosphine from the metal precursor precedes nucleophilic attack by the ylide carbon on the metal center of the 16-electron pentacoordinate intermediate B (Scheme I). Addition of the ylide is thus slowed by excess phosphine, an increase in the steric bulk of the alkylidene or imido substituents, or a decrease in the nucleophilicity of the ylide carbon. In contrast to the metal precursors involved in previous examples of alkylidene transfer (Figure 1), $WCl_2(NPh)(PMePh_2)_3$ has readily substituted anionic ligands, and therefore, two possible reactions, loss of triphenylphosphine or loss of a chloride ligand, would relieve the steric crowding in this molecule and in the zwitterionic ylide adduct **C**. In nonpolar solvents such as C_6D_6 and toluene-d_8, loss of phosphine to generate $W(=CHR)Cl_2(NPh)(PMePh_2)_2$ should be favored. However, chloride loss in polar solvents such as THF-d_8 is probable and may account for the slower rate of formation of the alkylidene-transfer product in these solvents. In addition, loss of a chloride ligand to generate the pentacoordinate cationic complex **D**, which would be stabilized by strong donation by the phosphine and imido ligands, is highly probable in CD_2Cl_2 and may be the reason that alkylidene transfer was not observed in this solvent.[18]

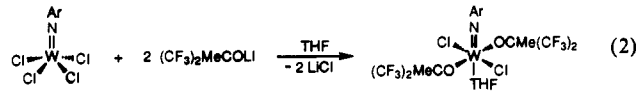
In Situ Trapping of Reduced Tungsten Complexes by Phosphoranes. The above examples of alkylidene transfer to $WCl_2(NPh)(PMePh_2)_3$ and the examples shown in Figure 1 all involved transfer to reduced metal complexes that were stabilized by donor ligands. Prior loss of a donor ligand was required for alkylidene transfer to occur, and therefore transfer was often slow and normally required high temperatures. An attractive method of alkylidene synthesis would involve the in situ trapping of reduced metal species by phosphoranes, thereby eliminating the synthesis and isolation of reduced intermediates. In order to determine the viability of this method, the following study was undertaken.

$WCl_4(NAr)$ Precursors. Initial investigations involving $WCl_4(NAr)$ precursors were not promising. Benzylidenetriphenylphosphorane reacted with these complexes in C_6D_6 to give an intractable precipitate. A green powder was formed when the reaction was carried out in CH_2Cl_2 and the solvent was removed in vacuo. Although the NMR of the product was broad and uninterpretable, initial displacement of a chloride ligand by the ylide is likely.[19]

$WCl_2(NAr)[OCMe(CF_3)_2]_2(THF)$ Precursors. Bis(alkoxide) precursors of the form $WCl_2(NAr)[OCMe(CF_3)_2]_2(THF)$ [Ar = Ph (**8**), 2,6-C_6H_3–Me_2 (**9**), and 2,6-C_6H_3–(*i*-Pr)$_2$ (**10**)] were synthesized by the addition of 2 equiv of $LiOCMe(CF_3)_3$ to $WCl_4(NAr)$ (eq 2). According to ^{19}F and ^{13}C NMR spectroscopy, the trifluoromethyl groups in these complexes are equivalent, suggesting a mutually trans arrangement of the two alkoxide ligands.

(18) There is evidence for loss of a chloride ligand in structurally related complexes: Reference 17.

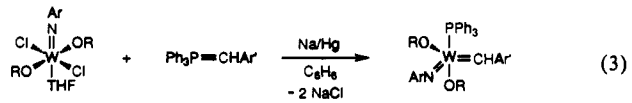
(19) See ref 1 for examples. Also, see: Finch, W. Ph.D. Thesis, California Institute of Technology, 1986.



(2)

Ar = Ph; 2,6-C_6H_3-Me_2, 2,6-C_6H_3-(*i*-Pr)$_2$

The increased steric stabilization of the $WCl_2(NAr)[OCMe(CF_3)_2]_2(THF)$ complexes prevented their reaction with aryl ylides in the absence of a reducing agent and enabled the reduction of these complexes in the presence of a number of phosphoranes to be investigated. When the (2,6-dimethylphenyl)imido precursor **9** was reduced by an excess of 1% sodium amalgam in the presence of phosphoranes, alkylidene transfer (yields of 60–85% by ^1H NMR spectroscopy) from phosphorus to tungsten was observed for several aryl ylides $Ph_3P{=}CHAr'$ (eq 3), where Ar' = Ph, C_6H_4-*p*-Me, C_6H_4-*m*-Me, C_6H_4-*o*-Me, and C_6H_4-*p*-OEt (**11a–e**), but not where Ar' = C_6F_5, 1-Np, and 2-Np. Alkylidene transfer from $Ph_3P{=}CH{-}CH{=}CMe_2$ and $Ph_3P{=}CH_2$ was also not observed, and $Ph_3P{=}CHC_6H_4$-*p*-CF_3 reacted with **9** prior to reduction.[20]



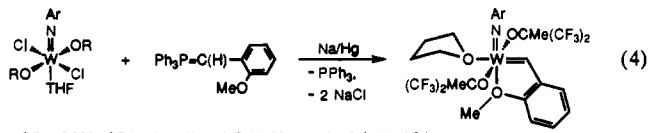
(3)

OR = $OCMe(CF_3)_2$; Ar = 2,6-C_6H_3-Me_2

Yields of the tungsten alkylidene complexes were low for the reactions of $Ph_3P{=}CHPh$ with the analogous phenyl- and (2,6-diisopropyl)phenylimido precursors **8** and **10**. Also, reduction and alkylidene transfer were less favorable when alkoxide ligands other than hexafluoro-*tert*-butoxide were used. For example, the bis(*tert*-butoxide) complex $WCl_2(N{-}2,6{-}C_6H_3{-}Me_2)(O{-}t{-}Bu)_2$ was not measurably reduced by sodium amalgam under the standard conditions used for the alkylidene-transfer reaction. Tungsten decomposition products and unreacted aryl ylides were observed when either two trifluoro-*tert*-butoxide or substituted phenoxide [e.g., O–2,6-C_6H_4–Me_2 and O–2,6-C_6H_4–$(i\text{-}Pr)_2$] ligands were incorporated on the tungsten precursor. Apparently, the very electron-withdrawing hexafluoro-*tert*-butoxide ligands enabled reduction of the tungsten(VI) precursor, and the combined steric bulk of the alkoxide and the (2,6-dimethylphenyl)imido substituents was sufficient to stabilize the reduced intermediates but not so great as to prevent alkylidene transfer.

Transfer of the benzylidenes to tungsten was indicated by the large downfield shifts of the H_α resonances (12.26–12.65 ppm) for complexes **11a–e**[14] and the coupling of these resonances to tungsten-coordinated PPh_3 (J_{HP} = 6.37–6.87 Hz). The imido methyl groups and the alkoxide ligands are inequivalent in these complexes, and comparisons with crystal structures of similar complexes suggest that the geometry shown in eq 3 is likely.[16,17] Triphenylphosphine was coordinated reversibly to these alkylidene complexes, as was indicated by its removal from the metal center by the addition of 1 equiv of CuCl.[13] The alkylidene complexes were stable in solution in the presence of PPh_3 but not in its absence, and the isolation of these complexes required the addition of a stronger donor ligand than PPh_3 in order to prevent decomposition upon solvent removal. For example, addition of PMe_3 to the final reaction mixture enabled the isolation of the benzylidene complex $W(=CHPh)(N{-}2,6{-}C_6H_3{-}Me_2)[OCMe(CF_3)_2]_2(PMe_3)$ (**12**) as an 18:1 mixture of rotamers.

Chelation by *o*-Methoxybenzylidene.[21] THF Adducts of *o*-Methoxybenzylidene Complexes. In contrast to the reactivity of the other aryl ylides, alkylidene transfer from $Ph_3P{=}CHC_6H_4$-*o*-OMe to tungsten was observed in high yields for the phenyl- and (2,6-diisopropylphenyl)imido precursors **8** and **10**, as well as for the (2,6-dimethylphenyl)imido precursor **9**, and stable alkylidene complexes that did not bind PPh_3 were isolated (eq 4). Recrystallization of the complexes from Et_2O or pentane in the presence of THF yielded the yellow, crystalline THF adducts $W(=CHC_6H_4$-*o*-OMe$)(NAr)[OCMe(CF_3)_2]_2(THF)$ [Ar = Ph (**13**), 2,6-C_6H_3–Me_2 (**14**), and 2,6-C_6H_3–$(i\text{-}Pr)_2$ (**15**)] in good yields.



(4)

OR = $OCMe(CF_3)_2$; Ar = Ph, 2,6-C_6H_3-Me_2, and 2,6-C_6H_3-(*i*-Pr)$_2$

Transfer of the *o*-methoxybenzylidene ligand from phosphorus to tungsten was confirmed by the downfield shifts of the H_α and C_α resonances of the alkylidene ligand. In addition, shifts to lower fields occurred for the methoxy protons upon transfer, indicative of chelation by the methoxy group to electron-deficient tungsten (Table III). In order to maximize π-bonding, the imido and alkylidene ligands must lie cis to each other,[22] and thus, the chelating *o*-methoxy moiety must coordinate trans to the imido group. The two alkoxide ligands in these complexes are equivalent with each ligand possessing two diastereotopic trifluoromethyl groups, consistent with the geometry shown in eq 4.

Supporting the proposed geometry, strong NOE enhancements, indicative of an anti orientation of the alkylidene substituents relative to the imido ligand, were observed between the methyl groups of the imido ligand and the alkylidene H_α resonance for the (2,6-dimethylphenyl)imido complex **14**. In addition, irradiation of the THF ether protons enhanced the *o*-methoxy resonance and the imido methyl resonance and vice versa. However, NOE enhancements were not observed in either direction between the methoxy group and the alkylidene α-proton, again consistent with binding of the *o*-methoxy group to tungsten. At room temperature, the arylimido ligand of **14** rotated freely; however, at –70 °C, two imido methyl groups were observed in the ^1H NMR spectrum, requiring that the aryl ring not lie in the RO–W(N)–OR plane.

The structure of **14** was confirmed by an X-ray diffraction study. An ORTEP diagram is included in Figure 3, and selected bond lengths and angles are given in Table IV. In complex **14**, the geometry about the metal center is a distorted octahedron with the imido and alkylidene ligands lying in the expected cis orientation.[22] The methoxy group of the benzylidene ligand is coordinated to tungsten and occupies an axial site of the octahedron; the 2.346(3)-Å W(1)–O(1) (OMe) bond distance is comparable to the 2.294(3)-Å W(1)–O(4) (THF) bond distance.[23] As a result of chelation by the methoxy group, the W(1)–C(1)–C(2) bond angle is approximately 16° and 23° smaller, respectively, than the analogous angles in $W(=CHC_6H_4{-}p\text{-}Me)Cl_2(NPh)(PMePh_2)_2$ (**2**) and $W(=CHPh)(NAr)[OCMe(CF_3)_2]_2$.[10a] The angle size is reflected in the respective C_α–H_α coupling constants of these three complexes: J_{CH_α} = 151 Hz for **14**, 127 Hz for **2**, and 121 Hz for $W(=CHPh)(NAr)[OCMe(CF_3)_2]_2$.[10a]

THF Lability. The reversible coordination of THF to complexes **13–15** was demonstrated by the rapid exchange of deuterio-THF with coordinated protio-THF and the production of yellow $W(=CHC_6H_4$-*o*-OMe$)(N{-}2,6{-}C_6H_3{-}Me_2)[OCMe(CF_3)_2]_2(PMe_3)$ (**16**) upon treatment of **14** with PMe_3 (eq 5a). In contrast

(20) A bright magenta solution formed upon reaction of **9** with $Ph_3P{=}CHC_6H_4$-*p*-CF_3, and very tentatively, the ^1H NMR spectrum appeared consistent with the displacement of a chloride ligand and formation of an ylide adduct: ^1H NMR (C_6D_6) δ 5.15 (d, J_{HP} = 16 Hz, C(*H*)(Ar)(PPh_3)), 3.29 (s, NAr Me_2), 2.13 (s, $OCMe(CF_3)_2$).

(21) A preliminary account of this research has been published: Johnson, L. K.; Virgil, S. C.; Grubbs, R. H.; Ziller, J. W. *J. Am. Chem. Soc.* **1990**, *112*, 5384–5385.

(22) Nugent, W. A.; Mayer, J. M. *Metal-Ligand Multiple Bonds*; John Wiley & Sons: New York, 1988; pp 35–36 and references therein.

(23) (a) According to an X-ray diffraction study, the methoxy group coordinates to chromium in $(OC)_4Cr[=C(OMe)(o\text{-}C_6H_4{-}OMe)]$. See: Dotz, K. H.; Sturm, W.; Popall, M.; Riede, J. *J. Organomet. Chem.* **1984**, *277*, 267–275. (b) For information on analogous tungsten complexes, see: Dotz, K. H.; Erben, H.-G.; Staudacher, W.; Harms, K.; Muller, G.; Riede, J. *J. Organomet. Chem.* **1988**, *355*, 177–191.

Table III. Selected NMR Data for Alkylidene Complexes Prepared by the in Situ Trapping of Reduced Tungsten Species by Phosphoranes

cmpd	formula	H_α	C_α	J_{CH}	J_{CW}	OMe[d]
12	W(=CHPh)(N—2,6-C_6H_3—Me_2)[OCMe$(CF_3)_2]_2$(PMe_3)	12.16[a]	266.5[a]	144	154	
13	W(=CHC_6H_4-*o*-OMe)(NPh)[OCMe$(CF_3)_2]_2$(THF)	10.46[b]	246.4[b]	149	161	4.09[b]
14	W(=CHC_6H_4-*o*-OMe)(N—2,6-C_6H_3—Me_2)[OCMe$(CF_3)_2]_2$(THF)	10.81[a]	240.2[a]	151	160	3.59[a]
15	W(=CHC_6H_4-*o*-OMe)[N—2,6-C_6H_3—(*i*-Pr)$_2$][OCMe$(CF_3)_2]_2$(THF)	10.60[b]	248.1[b]	148	167	4.03[b]
16	W(=CHC_6H_4-*o*-OMe)(N—2,6-C_6H_3—Me_2)[OCMe$(CF_3)_2]_2$(PMe_3)	12.48[c]	259.5[c]	147	148	4.05[c]
17a	W(=CHC_6H_4-*o*-OMe)(N—2,6-C_6H_3—Me_2)[OCMe$(CF_3)_2]_2$	10.94[a]	228.1[a]	155	172	3.75[a]
17b	W(=CHC_6H_4-*o*-OMe)[N—2,6-C_6H_3—(*i*-Pr)$_2$][OCMe$(CF_3)_2]_2$	10.79[c]	229.4[c]	155	176	4.22[c]

[a] In C_6D_6. [b] In THF-d_8. [c] In CD_2Cl_2. [d] Ph_3P=CHC_6H_4-*o*-OMe: ^1H NMR (C_6D_6) δ 3.21 (OMe); ^1H NMR (CD_2Cl_2) δ 3.49 (OMe).

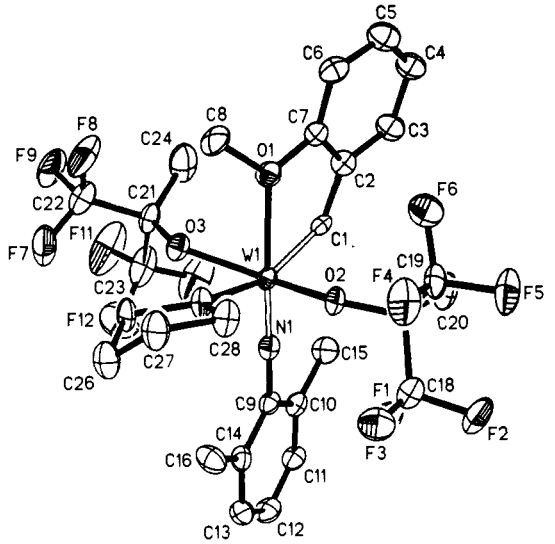
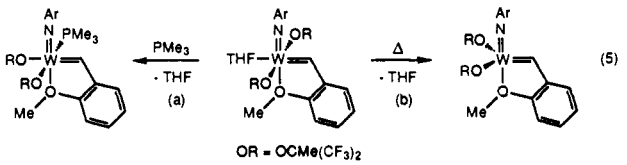


Figure 3. ORTEP plot of W(=CHC_6H_4-*o*-OMe)(N—2,6-C_6H_3—Me_2)-[OCMe$(CF_3)_2]_2$(THF) (**14**). Thermal ellipsoids are drawn at the 50% probability level.

Table IV. Selected Bond Lengths and Angles for **14**

Bond Lengths (Å)			
W(1)–C(1)	1.943(5)	W(1)–N(1)	1.737(4)
W(1)–O(1)	2.346(3)	W(1)–O(2)	1.995(4)
W(1)–O(3)	1.995(3)	W(1)–O(4)	2.294(3)
Bond Angles (deg)			
C(1)–W(1)–N(1)	99.2(2)	C(1)–W(1)–O(1)	74.2(2)
N(1)–W(1)–O(1)	173.0(2)	C(1)–W(1)–O(2)	97.6(2)
N(1)–W(1)–O(2)	101.2(2)	O(1)–W(1)–O(2)	82.0(1)
C(1)–W(1)–O(3)	103.0(2)	N(1)–W(1)–O(3)	100.2(2)
O(1)–W(1)–O(3)	79.7(1)	O(2)–W(1)–O(3)	147.3(1)
C(1)–W(1)–O(4)	153.7(2)	N(1)–W(1)–O(4)	107.0(2)
O(1)–W(1)–O(4)	79.8(1)	O(2)–W(1)–O(4)	75.2(1)
O(3)–W(1)–O(4)	75.1(1)	W(1)–N(1)–C(9)	174.6(4)
W(1)–O(1)–C(7)	112.1(3)	W(1)–O(1)–C(8)	128.4(3)
W(1)–O(2)–C(17)	138.8(3)	W(1)–O(3)–C(21)	138.4(3)
W(1)–O(4)–C(25)	123.5(3)	W(1)–O(4)–C(28)	126.9(3)
W(1)–C(1)–C(2)	121.9(4)	C(1)–C(2)–C(7)	117.4(5)
C(2)–C(7)–O(1)	112.8(4)		

to the THF adducts of the *o*-methoxybenzylidene complexes **13**–**15**, the alkoxide ligands in the case of the PMe_3 adduct **16** are



not equivalent, although a substantial downfield shift of the *o*-methoxy resonance indicates that this group is still bound to tungsten (Table III). These observations and the magnitudes of the coupling constants for phosphorus coupling to H_α and C_α (J_{HP} = 7.08 Hz, J_{CP} = 15 Hz) are consistent with a cis orientation

Table V. Selected Bond Lengths and Angles for **17b**

Bond Lengths (Å)			
W(1)–O(1)	2.352(3)	W(1)–O(2)	1.952(3)
W(1)–O(3)	1.923(3)	W(1)–N(1)	1.741(4)
W(1)–C(1)	1.939(5)		
Bond Angles (deg)			
O(1)–W(1)–O(2)	74.2(1)	O(1)–W(1)–O(3)	82.4(1)
O(2)–W(1)–O(3)	121.1(1)	O(1)–W(1)–N(1)	170.2(1)
O(2)–W(1)–N(1)	106.4(2)	O(3)–W(1)–N(1)	105.1(2)
O(1)–W(1)–C(1)	74.1(2)	O(2)–W(1)–C(1)	111.7(2)
O(3)–W(1)–C(1)	112.4(2)	N(1)–W(1)–C(1)	96.9(2)
W(1)–O(1)–C(7)	112.9(3)	W(1)–O(1)–C(8)	125.5(3)
W(1)–O(2)–C(21)	134.3(3)	W(1)–O(3)–C(25)	143.6(3)
W(1)–N(1)–C(9)	177.4(3)	W(1)–C(1)–C(2)	122.0(3)
C(1)–C(2)–C(7)	117.8(4)		

of the alkylidene and PMe_3 ligands in **16**, as shown in eq 5a.[24] Given the proposed geometry, the observation of only one resonance for the arylimido methyl protons of **16** at room temperature indicates that the arylimido ring is freely rotating.

Red, pentacoordinate, THF-free W(=CHC_6H_4-*o*-OMe)-(N—2,6-C_6H_3—Me_2)[OCMe$(CF_3)_2]_2$ (**17a**) and W(=CHC_6H_4-*o*-OMe)[N—2,6-C_6H_3—(*i*-Pr)$_2$][OCMe$(CF_3)_2]_2$ (**17b**) were formed upon heating toluene solutions of **14** and **15** under vacuum (eq 5b). Loss of THF occurred more readily from **14** than from **15**, and an increase in solubility was noted for both complexes upon loss of THF. The downfield chemical shifts of the α-protons of the *o*-methoxybenzylidene ligands of **17a** and **17b** can be compared with the downfield shifts reported for alkylidene complexes coordinated by Lewis bases.[25] This observation and the appearance of the *o*-methoxy proton resonances at lower fields (Table III) suggest that in solution the methoxy groups of **17a** and **17b** coordinate to tungsten. The continuum of the alkylidene C_α chemical shifts of **15** in THF-d_8 (248.1 ppm, sharp singlet, J_{CW} = 167 Hz) and CD_2Cl_2 (239.6 ppm, broad multiplet) and of **17b** in CD_2Cl_2 (229.4 ppm, sharp singlet, J_{CW} = 176 Hz) further demonstrates the reversible coordination of THF to **15**, and the increase in the C_α–W coupling constant is indicative of a shortening of the C_α–W bond upon loss of THF.

The synthesis of the THF-free complexes **17a–b** was confirmed by an X-ray diffraction study of **17b**. Selected bond distances and angles are given in Table V, and an ORTEP diagram is shown in Figure 4. The complex is best described as a distorted trigonal bipyramid with the imido and *o*-methoxy groups occupying the axial positions. All of the equatorial ligands lie on the opposite side of the plane from the arylimido ligand, thus relieving unfavorable steric interactions with the isopropyl groups, and a comparison with the structure of **14** indicates that the major adjustment upon loss of THF is a widening of the angles between the alkoxide and alkylidene ligands. A slight decrease in the W–C_α bond length is observed upon loss of THF, consistent with the trends noted previously for the W–C_α coupling constants.

Reactivity Studies. The *o*-methoxybenzylidene complexes are analogs of the arylimido metathesis catalysts W(=CH-*t*-Bu)-[N—2,6-C_6H_3—(*i*-Pr)$_2$](OR)$_2$,[10a] and their metathesis activity was determined by studying the reactions of the (2,6-dimeth-

(24) A similar geometry was proposed for structurally related chelating *s-cis*-(ketalvinyl)alkylidene complexes: Reference 17.

(25) For examples, see: References 11a, 14, 17, and 18.

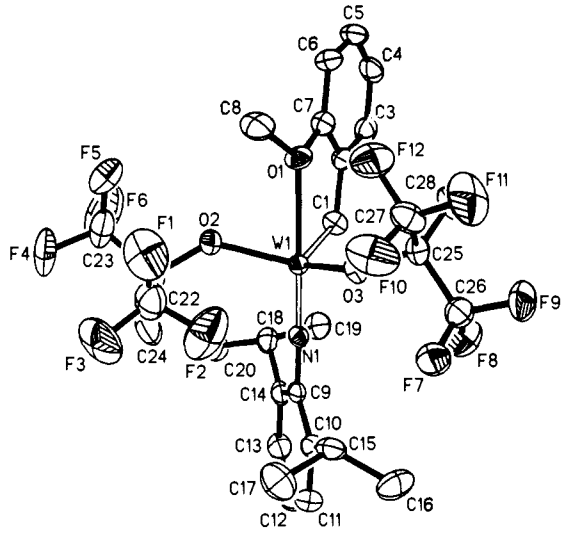


Figure 4. ORTEP plot of W(=CHC_6H_4-*o*-OMe)[N—2,6-C_6H_3—(*i*-Pr)$_2$][$OCMe(CF_3)_2$]$_2$ (**17b**). Thermal ellipsoids are drawn at the 50% probability level.

ylphenyl)imido THF adduct **14** and its THF-free derivative **17a**. For [W] = 0.012 M and [norbornene] = 0.63 M, the THF adduct **14** polymerized norbornene at a rate of 18 equiv/h at −40 °C [polydispersity index (PDI) = 1.5], and THF-free **17a** polymerized norbornene at a rate of 17 equiv/h at −60 °C (PDI = 1.6). The latter rate is the same as that of the analogous neopentylidene complex;[10b] however, **17a** metathesized *cis*-2-pentene at a much slower rate (lower limit = 1.4 equiv/min) than the neopentylidene derivative (lower limit = 1000 equiv/min).[10a] The molecular weights were obtained by GPC analysis vs polystyrene standards, and the relatively broad polydispersities are typical of polymerizations initiated by hexafluoro-*tert*-butoxide arylimido alkylidene catalysts.[10b] Analysis by ^{13}C NMR spectroscopy indicated that *cis*-polynorbornene was formed by the ROMP of norbornene initiated by both **14** and **17a**,[26] again typical of hexafluoro-*tert*-butoxide catalysts.[10b] Finally, complex **14** reacted in a Wittig-type fashion with carbonyl compounds, including esters and amides, in yields of 82–100% as measured by NMR spectroscopy.[8,27]

For practical applications, it is important to note again that the in situ alkylidene-transfer reaction required the use of the hexafluoro-*tert*-butoxide ligand. Arylimido metathesis catalysts incorporating this ligand are very active but are not living,[10b] and therefore these catalysts are best utilized in the polymerization of relatively unstrained monomers, such as cyclooctatetraene.[28,29] For the living polymerization of strained monomers and corresponding control over molecular weights and polydispersities, the *tert*-butoxide derivatives are needed.[10b] Clean substitution of the hexafluoro-*tert*-butoxide ligands by 2 equiv of the more donating *tert*-butoxide moiety was observed. However, the addition of PMe_2Ph was necessary in order to separate the product from free hexafluoro-*tert*-butoxide, and therefore, the living *tert*-butoxide catalysts are best prepared by other methods.[10a,c]

Conclusions

In this investigation, several examples of successful alkylidene transfer from phosphorus to reduced (arylimido)tungsten complexes were observed. These transfer reactions resulted in the synthesis of a number of new aryl- and vinylalkylidene complexes of tungsten, including a bis(alkylidene) complex. The transfer of the alkylidene from phosphorus to tungsten was sensitive to the steric congestion around the metal center and the nature of the ylide. Transfer of partially resonance-stabilized alkylidenes (e.g., transfer from $Ph_3P{=}CHPh$ and $Ph_3P{=}CH{-}CH{=}CMe_2$) was especially favorable, most likely for several reasons: (1) Stable alkylidene complexes were formed, as the substituents on the alkylidene ligand also stabilized the $M^+{-}C^-$ resonance structure of the resulting nucleophilic tungsten alkylidene. (2) The moderate steric requirements of these alkylidenes enabled the ylide carbon to approach the metal center. (3) The nucleophilicity of the ylide carbon was sufficient to enable transfer to the metal but not so great as to result in further side reactions, such as deprotonation of the metal alkylidene.

This study demonstrated that alkylidene transfer to complexes containing labile anionic ligands was possible with the proper choice of solvent and/or the incorporation of sufficient steric bulk around the metal center. For example, for the $WCl_2(NPh)(PMePh_2)_3$ precursor, alkylidene transfer was observed in nonpolar solvents, such as benzene and toluene, that disfavored formation of ionic intermediates, such as those resulting from displacement of a chloride ligand by the ylide. For the in situ reduction and trapping of reduced tungsten complexes by phosphoranes, the incorporation of bulky alkoxides on the metal precursors $WCl_2(NAr)[OCMe(CF_3)_2]_2(THF)$ prevented displacement of their chloride ligands by the phosphorane prior to reduction.

Although the in situ reduction and trapping of the tungsten complex by the phosphorane provided a very efficient method for the synthesis of alkylidenes, the appropriate tuning of the steric and electronic properties of the metal precursor and the phosphorane was critical, since if the reduced metal species was not trapped immediately by the phosphorane, there were no stabilizing donor ligands to prevent it from undergoing detrimental side reactions. Therefore, the use of the chelating *o*-methoxybenzylidene was especially effective in this case, as coordination by the *o*-methoxy group greatly aided the transfer reaction and, in addition, stabilized the resulting product.

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. NMR spectra were recorded with either a JEOL FX-90Q (89.60 MHz ^1H; 22.53 MHz ^{13}C; 36.20 MHz ^{31}P), a JEOL GX-400 (399.65 MHz ^1H; 100.40 MHz ^{13}C), or a QE-300 Plus (300.10 MHz ^1H; 75.49 MHz ^{13}C) spectrometer. All coupling constants are reported in Hz. For the ^1H and ^{13}C NMR virtual triplet resonances of the trans phosphine ligands, the coupling constant $N = |^2J_{HP} + {}^4J_{HP}|$ is given, where N is the separation of the outer lines of the triplet.[30] Gel permeation chromatography was performed on a Waters GPC-120C, and molecular weights are reported relative to narrow molecular weight polystyrene standards.

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. Pentane was 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. 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. PMe_3 was degassed by repeated freeze–pump–thaw cycles and vacuum-transferred immediately prior to use. Carbonyl compounds were dried and degassed; *cis*-2-pentene was dried over CaH_2, vacuum-transferred, and degassed by repeated freeze–pump–thaw cycles; and norbornene was dried over Na, distilled, and stored under nitrogen. Organic halides, which were used as precursors to the ylides, were purchased commercially

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(27) More detailed studies of the olefinations of carbonyl compounds by the alkylidene complexes reported in this paper have been undertaken: France, M. B.; Fu, G. C.; Ulibarri, T. A.; Grubbs, R. H. Unpublished results.

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Table VI. Alkylidene Transfer from *ortho*-, *meta*-, and *para*-Substituted Aryl Ylides

	yield of $W(=CHAr')Cl_2(NPh)(PMePh_2)_2$ (%); Ar' =			
time/temp	C_6H_4-*p*-Me	C_6H_4-*m*-Me	C_6H_4-*o*-Me	C_6H_4-*o*-OMe
0.33 h/rt	6	4	0	0
3.33 h/rt	15	10	0	0
6.33 h/rt	19	20	0	0
24.33 h/rt	35[a]	34[b]	0	0
+8 h/70 °C	41[c]	42[d]	25[e]	19[f]

[a] δ 12.38 (t, J_{HP} = 4.95, H_α, 21%); δ 12.42 (t, J_{HP} = 4.58, H_α, 15%). [b] δ 12.39 (t, J_{HP} = 4.55, H_α, 21%); δ 12.46 (t, J_{HP} = 4.64, H_α, 13%). [c] 12.42 H_α resonance only. [d] 12.46 H_α resonance only. [e] δ 12.71 (t, J_{HP} = 4.79, H_α, 25%). [f] δ 12.63 (t, J_{HP} = 2.72, H_α, 10%); δ 13.14 (t, J_{HP} = 5.25, H_α, 9%).

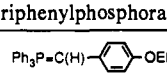
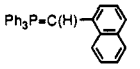
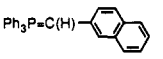
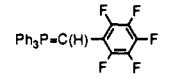
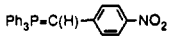
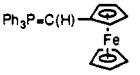
with the exception of Me_3CCH_2I[31] and $CpFeC_5H_4CH_2PPh_3I$.[32] Phosphonium salts were generally synthesized by refluxing a 1:1 mixture of triphenylphosphine and the organic halide overnight in THF and then filtering. However, $Me_3CCH_2PPh_3I$ and $Me_3SiCH_2PPh_3I$ were synthesized by refluxing triphenylphosphine in a small excess of the corresponding halide.[33] Ylides were synthesized by deprotonation of the phosphonium salt with an excess of NaH in refluxing THF until evolution of H_2 ceased. After filtering the solution, the ylide was recrystallized at low temperature. Me_3COLi was synthesized by the deprotonation of Me_3COH by 1 equiv of freshly titrated BuLi.[34] The syntheses of $WCl_4(NAr)$ complexes,[17] $WCl_2(NPh)(PMePh_2)_3$,[11] and $(CF_3)_2CH_3COLi$[17] are reported elsewhere, and the syntheses of $Ph_3P{=}CH{-}C_6H_4{-}C_6H_4{-}CH{=}PPh_3$ and its precursors are included in the supplementary material.

Survey of Alkylidene Transfer from *ortho*-, *meta*-, and *para*-Substituted Aryl Ylides $Ph_3P{=}CHAr'$ to $WCl_2(NPh)(PMePh_2)_3$ (Table VI). $WCl_2(NPh)(PMePh_2)_3$ (10 mg, 0.011 mmol, 0.018 M) was dissolved in 600 μL of toluene-d_8 (0.014 M mesitylene internal standard) together with 1 equiv of the respective triphenylphosphorane. The solution was transferred to an NMR tube, the NMR tube was capped with a septum, and the septum was wrapped with Parafilm. The tube was rotated at room temperature for a total of 24.33 h; ^1H NMR spectra were acquired periodically. (All four reactions were run simultaneously, and the tubes were rotated together at the same rate.) Subsequently, the tube was heated in an oil bath at 70 °C without any external mixing for 8 h, and a ^1H NMR spectrum was then acquired and integrated. Yields of tungsten alkylidene products are based upon the integration of the diagnostic H_α resonances and are reported in Table VI.

Survey of the Reactivity of Phosphoranes with $WCl_2(NPh)(PMePh_2)_3$ (Table VII). $WCl_2(NPh)(PMePh_2)_3$ (10 mg, 0.011 mmol, 0.018 M) was dissolved in 600 μL of solvent [either toluene-d_8 (0.014 M mesitylene internal standard) or THF-d_8 (0.0034 M mesitylene internal standard)] together with 1 equiv of the respective triphenylphosphorane. The solution was transferred to an NMR tube, the NMR tube was capped with a septum, and the septum was wrapped with Parafilm. The tube was heated in an oil bath at 60–65 °C without any external mixing for several hours, and a ^1H NMR spectrum was then acquired and integrated. Reaction conditions and NMR spectral data are reported in Table VII.

$W(=CHPh)Cl_2(NPh)(PMePh_2)_2$ (1). An orange solution of $Ph_3P{=}CHPh$ (0.765 g, 2.17 mmol) in 60 mL of benzene was transferred via cannula into a Schlenk flask containing 2.05 g (2.17 mmol) of $WCl_2(NPh)(PMePh_2)_3$ dissolved in 40 mL of benzene. After refluxing for 21.5 h, the solvent was removed in vacuo, and the remaining brown oil was washed twice with 40-mL portions of pentane to yield a golden-yellow powder. The powder was dissolved in 20 mL of toluene, and the resulting solution was filtered, layered with pentane, and cooled to −50 °C. Yellow-brown crystals (1.1 g, 61%) were isolated: ^1H NMR (C_6D_6) δ 12.52 (t, 1, J_{HP} = 4.77, H_α), 7.8–6.5 (m, 30, H_{aryl}), 2.47 (t, 6, N = 9.14, P*Me*Ph_2); ^{13}C NMR (CD_2Cl_2) δ 290.9 (t, J_{CH} = 126.5, J_{CP} = 12.0, J_{CW} = 132.8, C_α), 152.8 (t, J_{CP} = 1.9, J_{CW} = 37.6, NPh C_{ipso}), 146.7 (t, J_{CP} = 3.0, CH*Ph* C_{ipso}), 133.8 (t, J_{CP} = 23.4, PMe*Ph*Ph′ C_{ipso}), 132.9 (t, J_{CP} = 5.1, PMe*Ph*Ph′ C_o), 132.7 (t, J_{CP} = 21.2, PMePh*Ph′* C_{ipso}), 132.5 (t, J_{CP} = 5.2, PMePh*Ph′* C_o), 130.8 (CH*Ph* C_o), 130.3 (PMe*Ph*Ph′ C_p), 129.9 (PMePh*Ph′* C_p), 129.6 (CH*Ph* C_p), 128.04 (t, J_{CP} = 5.04, PMe*Ph*Ph′ C_m), 127.97 (t, J_{CP} = 4.92, PMePh*Ph′* C_m), 127.8 (CH*Ph* C_m), 127.5 and 127.4 (NPh C_o and C_m), 126.9 (NPh C_p), 13.9 (t, N = 32.8, P*Me*Ph_2); ^{31}P NMR (CD_2Cl_2) δ 11.9 (J_{PW} = 283.2). Anal. Calcd for $C_{39}H_{37}Cl_2NP_2W$: C, 56.00; H, 4.46; N, 1.67. Found: C, 55.47; H, 4.32; N, 1.60.

Table VII. Survey of the Reactivity of Phosphoranes with $WCl_2(NPh)(PMePh_2)_3$

triphenylphosphorane	solvent, time color	yield ^1H NMR data for H_α of [W](=CHR)
	tol-d_8, 7 h yellow	69% δ 12.34 (t, J_{HP} = 4.6) 15% δ 12.26 (t, J_{HP} = 4.6) 16% $WCl_2(NPh)(PMePh_2)_3$ unreacted.
	tol-d_8, 10 h orange	71% δ 13.46 (t, J_{HP} = 4.6) 25% $WCl_2(NPh)(PMePh_2)_3$ unreacted.
	tol-d_8, 7 h yellow	~73% δ 12.59 (t, J_{HP} = 4.6) ~23% δ 12.47 (t, J_{HP} = 4.9) 4% $WCl_2(NPh)(PMePh_2)_3$ unreacted.
	tol-d_8, 7 h yellow	70% δ 11.96 (br m) 33% $WCl_2(NPh)(PMePh_2)_3$ unreacted.
	THF-d_8, min's	Not acquired—precipitate formed.
	tol-d_8, 7 h magenta	12% δ 12.36 (t, J_{HP} = 4.15) Unreacted $WCl_2(NPh)(PMePh_2)_3$.
$Ph_3P{=}CH$-*t*-Bu	THF-d_8, 10 h yellow	No reaction.
$Ph_3P{=}CHSiMe_3$	THF-d_8, 10 h yellow	No reaction.
$Ph_3P{=}CH_2$	THF-d_8, 1 h yellow	20% δ 10.70 (m, C*H*H′) δ 10.30 (m, CH*H*′) 23% $WCl_2(NPh)(PMePh_2)_3$ unreacted.[a]
$Ph_3P{=}CHMe$	THF-d_8, 1 h red	1% δ 12.47 (m) 1% δ 12.15 (m) 7% δ 10.77 (m) 39% $WCl_2(NPh)(PMePh_2)_3$ unreacted.[a]

[a] Tungsten-containing decomposition compounds formed the remainder of the product mixture.

$W(=CHC_6H_4$-*p*-Me$)Cl_2(NPh)(PMePh_2)_2$ (2). Benzene (100 mL) was added to a solid mixture of $WCl_2(NPh)(PMePh_2)_3$ (1.98 g, 2.09 mmol) and $Ph_3P{=}CHC_6H_4$-*p*-Me (0.77 g, 2.09 mmol) to yield a deep red-brown solution. The reaction mixture was stirred at 80 °C for 6 h to give a yellow-brown solution. The solvent was removed in vacuo, and the resulting orange-brown oil was left under dynamic vacuum for 12 h. Upon washing with pentane (2 × 30 mL), the oil solidified and formed a mustard-gold powder. The powder was dissolved in 35 mL of toluene, and the resulting solution was cooled to give brown-orange crystals (1.04 g, 58.4%): ^1H NMR (CD_2Cl_2) δ 12.21 (t, 1, J_{HP} = 4.64, H_α), 7.6–6.7 (m, 29, H_{aryl}), 2.53 (s, 3, CH*Ar′*, *p*-Me), 2.43 (t, 6, N = 8.80, P*Me*Ph_2); ^{13}C NMR (CD_2Cl_2) δ 290.7 (m, J_{CH} = 126.7, C_α), 153.2 (t, J_{CP} = 2.3, NPh C_{ipso}), 144.3 (t, J_{CP} = 3.3, CH*Ar′* C_{ipso}), 140.2 (CH*Ar′* C_p), 134.1 (t, J_{CP} = 23.5, PMe*Ph*Ph′ C_{ipso}), 133.1 (t, J_{CP} = 21.1, PMePh*Ph′* C_{ipso}), 133.1 (t, J_{CP} = 5.1, PMe*Ph*Ph′ C_o), 132.7 (t, J_{CP} = 5.1, PMePh*Ph′* C_o), 130.4 (PMe*Ph*Ph′ C_p), 130.0 (PMePh*Ph′* C_p), 128.2 (t, J_{CP} = 5.1, PMe*PhPh′* C_m), 131.2, 128.1, 128.0, and 127.7 (NPh C_o and C_m and CH*Ar′* C_o and C_m), 126.9 (NPh C_p), 14.1 (t, N = 33.0, P*Me*Ph_2); ^{31}P NMR (CD_2Cl_2) δ 12.5 (J_{PW} = 283). Anal. Calcd for $C_{40}H_{39}Cl_2NP_2W$: C, 56.49; H, 4.62; N, 1.65. Found: C, 56.79; H, 4.40; N, 1.32.

$W(=CHC_6H_4$-*p*-$CF_3)Cl_2(NPh)(PMePh_2)_2$ (3). Benzene (100 mL) was added to a solid mixture of $WCl_2(NPh)(PMePh_2)_3$ (2.02 g, 2.13 mmol) and $Ph_3P{=}CHC_6H_4$-*p*-CF_3 (0.90 g, 2.13 mmol) to yield a deep red-brown solution. The reaction mixture was stirred at 80 °C for 6.5 h to give an orange-brown solution. The solvent was removed in vacuo, and the resulting orange-brown oil was left under dynamic vacuum for 12 h. The oil was washed twice (2 × 25 mL) with pentane, and the resulting powder was then dissolved in toluene (30 mL) at 40 °C. The toluene solution was layered with pentane and cooled to −50 °C. Gold crystals (805 mg, 42%) were isolated: ^1H NMR (CD_2Cl_2) δ 12.13 (t, 1, J_{HP} = 4.63, H_α), 7.6–6.7 (m, 29, H_{aryl}), 2.43 (t, 6, N = 8.92, P*Me*Ph_2); ^{13}C NMR (CD_2Cl_2) 288.3 (t, J_{CH} = 128.6, J_{CP} = 12.2, J_{CW} = 131.6, C_α), 152.4 (t, J_{CP} = 1.8, J_{CW} = 37.5, NPh C_{ipso}), 149.8 (CH*Ar′* C_{ipso}), 133.5 (t, J_{CP} = 21.8, PMe*Ph*Ph′ C_{ipso}), 132.7 (t, J_{CP} = 5.1, PMe*Ph*Ph′ C_o), 132.4 (t, J_{CP} = 5.1, PMePh*Ph′* C_o), 132.2 (t, J_{CP} = 21.7, PMePh*Ph′* C_{ipso}), 130.4 (PMe*Ph*Ph′ C_p), 130.3 (PMePh*Ph′* C_p), 129.9 (q, J_{CF} = 32.1, CH*Ar′* C_p), 128.0 (t, J_{CP} = 5.0, PMe*Ph*Ph′ C_m), 128.0 (t, J_{CP} =

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4.9, PMePh*Ph'* C_m), 129.9, 127.8, 127.6, and 127.2 (NPh C_o, C_m, and C_p and CHAr' C_o), 124.1 (q, J_{CF} = 3.5, CH*Ar'* C_m), 124.1 (q, J_{CF} = 271.8, *C*F_3), 13.8 (t, J_{CP} = 33.2, P*Me*Ph_2); ^{31}P NMR (CD_2Cl_2) δ 11.9 (J_{PW} = 280); ^{19}F NMR (CD_2Cl_2) δ −62.3 (CF_3). Anal. Calcd for $C_{40}H_{36}Cl_2F_3NP_2W$: C, 53.12; H, 4.01; N, 1.55. Found: C, 53.09; H, 3.99; N, 1.44.

W[=CH(2-Np)]Cl_2(NPh)(PMePh_2)$_2$ (4). A mixture of WCl_2(NPh)(PMePh_2)$_3$ (3.09 g, 3.27 mmol) and Ph_3P=CH(2-Np) (1.50 g, 3.29 mmol) was dissolved in 60 mL of toluene and stirred for 4 h at 83 °C. After the solution was stored at −20 °C for 1 day, the supernatant was transferred into another Schlenk tube via a cannula equipped with a filter. Approximately 35 mL of the solvent was removed in vacuo, and the remaining brown solution was transferred via cannula into 150 mL of rapidly stirring pentane. Filtration yielded 2.58 g (89.0%) of yellow powder, which was dried in vacuo: ^{1}H NMR (CD_2Cl_2) δ 12.31 (t, 1, J_{HP} = 4.72, H_α), 7.8–6.6 (m, 32, H_{aryl}), 2.45 (t, 6, N = 9.00, P*Me*Ph_2); ^{13}C NMR (CD_2Cl_2, only selected C_{aryl} chemical shifts are listed) δ 290.4 (t, J_{CH} = 125.3, J_{CP} = 12.1, J_{CW} = 132.3, C_α), 153.0 (t, J_{CP} = 1.9, J_{CW} = 37.6, NPh C_{ipso}), 144.4 (t, J_{CP} = 3.2, CH*Ar'* C_{ipso}), 133.9 (t, J_{CP} = 21.1, PMe*Ph*Ph' C_{ipso}), 133.9 (t, J_{CP} = 23.5, PMePh*Ph'* C_{ipso}), 133.0 (t, J_{CP} = 5.1, PMe*Ph*Ph' C_o), 132.8 (t, J_{CP} = 5.1, PMePh*Ph'* C_o), 130.4 (PMe*Ph*Ph' C_p), 130.0 (PMePh*Ph'* C_p), 128.2 (t, J_{CP} = 5.1, PMe*Ph*Ph' C_m), 128.2 (t, J_{CP} = 4.9, PMePh*Ph'* C_m), 14.2 (t, N = 32.8, P*Me*Ph_2); ^{31}P NMR (CD_2Cl_2) δ 11.8 (J_{PW} = 281). Anal. Calcd for $C_{43}H_{39}Cl_2NP_2W$: C, 58.26; H, 4.43; N, 1.58. Found: C, 57.95; H, 4.29; N, 1.64.

W(=CHC_6F_5)Cl_2(NPh)(PMePh_2)$_2$ (5). A mixture of WCl_2(NPh)(PMePh_2)$_3$ (3.07 g, 3.25 mmol) and Ph_3P=CHC_6F_5 (1.62 g, 3.67 mmol) was dissolved in 30 mL of benzene and stirred at 75 °C for 4.25 h. Most of the benzene (~23 mL) was removed in vacuo, and 150 mL of pentane was added to the reaction mixture. Upon vigorous stirring, a bright-yellow powder formed, and the reaction mixture was then filtered. At this point, the ^{1}H NMR spectrum of the yellow powder indicated a 28:72 mixture of WCl_2(NPh)(PMePh_2)$_3$ and W(=CHC_6F_5)Cl_2(NPh)(PMePh_2)$_2$. The powder was redissolved in 30 mL of benzene together with 543 mg (1.23 mmol) of Ph_3P=CHC_6F_5, and the solution was stirred for 2 h at 75 °C. After the benzene was removed in vacuo, the yellow powder was washed with 30 mL of pentane and then dissolved in a mixture of 100 mL of toluene and 30 mL of pentane. This solution was filtered, and subsequent removal of the solvent in vacuo yielded an oil. The oil was partially dissolved in 17 mL of benzene. Slow addition of 50 mL of hexane and subsequent filtration resulted in the isolation of 1.78 g (56.7%) of yellow powder: ^{1}H NMR (CD_2Cl_2) δ 11.71 (t, 1, J_{HP} = 4.12, H_α), 7.69–6.51 (m, 25, H_{aryl}), 2.42 (t, 6, N = 9.10, P*Me*Ph_2); ^{13}C NMR (CD_2Cl_2) δ 261.5 (t, J_{CH} = 133.9, J_{CP} = 12.0, J_{CW} = 146, C_α), 152.3 (t, J_{CP} = 1.9, J_{CW} = 39, NPh C_{ipso}), 133.0 (t, J_{CP} = 22.8, PMe*Ph*Ph' C_{ipso}), 132.8 (t, J_{CP} = 5.3, PMe*Ph*Ph' C_o), 132.7 (t, J_{CP} = 5.0, PMePh*Ph'* C_o), 131.9 (t, J_{CP} = 22.6, PMePh*Ph'* C_{ipso}), 130.5 (PMe*Ph*Ph' C_p), 130.0 (PMePh*Ph'* C_p), 128.2 (t, J_{CP} = 4.9, PMe*Ph*Ph' C_m), 127.9 (t, J_{CP} = 4.8, PMePh*Ph'* C_m), 127.74, 127.69, and 127.67 (NPh C_o, C_m, and C_p), 14.9 (t, N = 33.6, P*Me*Ph_2), multiplets for the CHC_6F_5 ring carbons were observed between 145 and 124 ppm; ^{19}F NMR (CD_2Cl_2) δ −136.68 (d, J_{FF} = 25.7, F_o), −158.13 (t, J_{FF} = 20.1, F_p), −164.87 (t, J_{FF} = 22.0, F_m); ^{31}P NMR (CD_2Cl_2) δ 13.7 (J_{PW} = 280). Anal. Calcd for $C_{39}H_{32}Cl_2F_5NP_2W\cdot{}^1/_2C_6H_6$: C, 52.25; H, 3.65; N, 1.45. Found: C, 51.94; H, 3.29; N, 1.27. (Inclusion of half of a molecule of benzene was supported by the ^{1}H and ^{13}C NMR spectra.)

W(=CH—CH=CMe_2)Cl_2(NPh)(PMePh_2)$_2$ (6). WCl_2(NPh)(PMePh_2)$_3$ (10.24 g, 10.82 mmol) and Ph_3P=CH—CH=CMe_2 (3.66 g, 11.1 mmol) were placed together in a Schlenk flask equipped with a reflux condenser, dissolved in 150 mL of benzene, and stirred for 20.5 h at 90 °C. After ~40 mL of benzene was removed in vacuo, the solution was transferred via a cannula equipped with a filter into 300 mL of rapidly stirring pentane. A golden-yellow powder (7.24 g, 82.2%) precipitated and was filtered away from the pentane solution. The complex was always isolated as a mixture of syn and anti rotamers of the alkylidene ligand, the relative amounts of which varied according to the reaction time. The thermodynamic (major) isomer was the rotamer with the more upfield H_α resonance: ^{1}H NMR (CD_2Cl_2) major isomer δ 12.22 (d of t, 1, J_{HH} = 12.77, J_{HP} = 4.14, H_α), 8.00 (d, 1, J_{HH} = 12.73, H_β), 7.7–6.8 (m, 25, H_{aryl}), 2.44 (t, 6, N = 8.78, P*Me*Ph_2), 2.30 (s, 3, =C*Me*Me'), 1.90 (s, 3, =CMe*Me'*); minor isomer δ 12.45 (d of t, 1, J_{HH} = 13.11, J_{HP} = 4.35, H_α), 7.9 (d, 1, H_β), 2.41 (t, 6, J_{HP} = 4.32, P*Me*Ph_2), 2.15 (s, 3, =C*Me*Me'), 1.98 (s, 3, =CMe*Me'*); ^{13}C NMR (CD_2Cl_2) major isomer δ 284.0 (t, J_{CH} = 134.4, J_{CP} = 11.6, J_{CW} = 129.3, C_α), 153.2 (t, J_{CP} = 1.9, J_{CW} = 38.2, NPh C_{ipso}), 140.0 (t, J_{CH} = 155.6, J_{CP} = 3.9, C_β), 138.7 (t, J_{CP} = 3.7, C_γ), 134.4 (t, J_{CP} = 23.3, PMe*Ph*Ph' C_{ipso}), 133.3 (t, J_{CP} = 21.1, PMePh*Ph'* C_{ipso}), 132.8 (t, J_{CP} = 5.1, PMe*Ph*Ph' C_o), 132.7 (t, J_{CP} = 5.2, PMePh*Ph'* C_o), 130.0 (PMe*Ph*Ph' C_p), 129.8 (PMePh*Ph'* C_p), 128.1 (t, J_{CP} = 4.9, PMe*Ph*Ph' C_m), 128.0 (t, J_{CP} = 4.8, PMePh*Ph'* C_m), 127.9 and 127.8 (NPh C_o and C_m), 126.5 (NPh C_p), 25.2 (=C*Me*Me'), 18.0 (=CMe*Me'*), 13.6 (t, J_{CP} = 16.0, P*Me*Ph_2); minor isomer (only selected C_{aryl} chemical shifts are listed) δ 274.2 (t, J_{CH} = 126.3, J_{CP} = 11.9, C_α), 153.9 (t, J_{CP} = 1.7, NPh C_{ipso}), 138.1 (C_γ), 136.9 (J_{CH} = 159.7, C_β), 24.9 (=C*Me*Me'), 17.8 (=CMe*Me'*), 13.4 (t, N = 36.4, PMePh$_2$); ^{31}P NMR (CD_2Cl_2) δ 12.0 (J_{PW} = 283, major isomer), 11.5 (J_{PW} = 276, minor isomer). Anal. Calcd for $C_{37}H_{39}Cl_2NP_2W$: C, 54.57; H, 4.83; N, 1.72. Found: C, 54.56; H, 4.60; N, 1.45.

Cl_2(PhN)(Ph_2MeP)$_2$W(=CH—C_6H_4—C_6H_4—CH=)WCl_2(NPh)(PMePh_2)$_2$ (7). A suspension of 1.48 g (1.79 mmol, assumed to contain 217.4 mg, 5.13 mol of LiCl) of Ph_3P=CH—C_6H_4—C_6H_4—CH=PPh_3 and 3.91 g (4.13 mmol) of WCl_2(NPh)(PMePh_2)$_3$ in 150 mL of benzene was stirred at 80 °C for 18 h. The yellow reaction mixture was filtered, and the filtrate was added slowly into 500 mL of rapidly stirring pentane. The yellow precipitate was collected and recrystallized from CH_2Cl_2/THF at −20 °C to give 7 in 80% yield (2.43 g, 1.45 mmol): ^{1}H NMR (CD_2Cl_2) δ 12.14 (t, 2, J_{HP} = 4.7, H_α), 7.60–7.56 (m, 8, PMe*Ph*$_2$ $H_{o'}$), 7.55–7.47 (m, 12, PMe*Ph*$_2$ H_o and NPh H_o), 7.36–7.31 (m, 4, PMePh$_2$ $H_{p'}$), 7.29–7.24 (m, 8, PMePh$_2$ $H_{m'}$), 7.21–7.18 (m, 4, PMePh$_2$ H_p), 7.15–7.09 (m, 12, PMePh$_2$ H_m and biphenyl H), 6.99–6.96 (m, 4, NPh H_m), 6.70 (d, 4, J = 7.6, biphenyl H), 2.40 (t, 12, N = 9.0, PMePh$_2$); ^{13}C NMR (CD_2Cl_2, −10 °C) δ 288.83 (t, J_{CH} = 126, J_{CP} = 12, J_{CW} = 156, C_α), 152.65 (NPh C_{ipso}), 145.79 (t, J_{CP} = 2.5, biphenyl C_{ipso}), 140.54 (biphenyl C_p), 133.68 (t, J_{CP} = 23.5, PMe*Ph*$_2$ C'_{ipso}), 132.88 (t, J_{CP} = 5.0, PMe*Ph*$_2$ $C_{o'}$), 132.61 (t, J_{CP} = 23.5, PMe*Ph*$_2$ C_{ipso}), 132.38 (t, J_{CP} = 5.0, PMe*Ph*$_2$ C_o), 131.47 (biphenyl C_o), 130.35 (PMe*Ph*$_2$ $C_{p'}$), 129.91 (PMe*Ph*$_2$ C_p), 128.08 (t, J_{CP} = 4.6, PMe*Ph*$_2$ $C_{m'}$), 128.02 (t, J_{CP} = 4.6, PMePh$_2$ C_m), 127.72 (NPh C_m), 127.59 (NPh C_o), 126.88 (NPh C_p), 125.71 (biphenyl C_m), 13.65 (t, N = 32.8, P*Me*Ph_2); ^{13}P NMR (CD_2Cl_2) δ 12.25 (J_{PW} = 281). Anal. Calcd for $C_{78}H_{72}Cl_4N_2P_4W_2$: C, 56.07; H, 4.34; N, 1.68. Found: C, 55.90; H, 4.35; N, 1.41.

WCl_2(NPh)[OCMe(CF_3)$_2$]$_2$(THF) (8). A solution of $(CF_3)_2$MeCOLi (18.72 g, 99.55 mmol) in 120 mL of THF was added via cannula over a 15-min period to a suspension of WCl_4(NPh) (20.74 g, 47.74 mmol) in 120 mL of THF cooled to 0 °C. After the solution was stirred for 16 h at room temperature, the solvent was removed in vacuo, and the product was dissolved in 90 mL of Et_2O. The solution was filtered and then cooled to −50 °C to give 34.89 g of bright-orange crystals (93.7%, 3 crops): ^{1}H NMR (CD_2Cl_2) δ 7.63 (dd, 2, NPh H_m), 7.30 (d, 2, J = 7.57, NPh H_o), 7.14 (t, 1, J = 7.57, NPh H_p), 4.40 (m, 4, THF), 2.06 (m, 4, THF), 1.75 (s, 6, OC*Me*$(CF_3)_2$); ^{13}C NMR (CD_2Cl_2) δ 150.7 (NPh C_{ipso}), 132.3 (NPh C_p), 128.6 and 128.3 (NPh C_o and C_m), 123.7 (q, J_{CF} = 290, CF_3), 86.2 (septet, J_{CF} = 30, O*C*Me$(CF_3)_2$), 73.0 (THF), 25.9 (THF), 17.7 (OC*Me*$(CF_3)_2$). Anal. Calcd for $C_{18}H_{19}Cl_2F_{12}NO_3W$: C, 27.71; H, 2.46; N, 1.80. Found: C, 27.84; H, 2.47; N, 1.83.

WCl_2(N-2,6-C_6H_3-Me_2)[OCMe(CF_3)$_2$]$_2$(THF) (9). Two equivalents of $(CF_3)_2$MeCOLi (17.14 g, 91.17 mmol) were dissolved in 90 mL of THF. The resulting solution was added slowly via cannula to a −78 °C solution of WCl_4(N-2,6-C_6H_3-Me_2)(Et_2O) (23.24 g, 44.79 mmol) in 60 mL of THF. After being warmed to room temperature, the solution was stirred for 19 h before the solvent was removed in vacuo. The red powder was then dissolved in 150 mL of Et_2O, and the solution was filtered. Recrystallization at −50 °C afforded red crystals in 93.4% yield (33.8 g, 2 crops): ^{1}H NMR (C_6D_6) δ 6.80 (d, 2, J = 7.6, NAr H_m), 6.35 (t, 1, J = 7.6, NAr H_p), 4.25 (m, 4, THF), 2.93 (s, 6, NAr Me), 1.54 (s, 6, OCMe$(CF_3)_2$), 1.29 (m, 4, THF); ^{13}C NMR (C_6D_6) δ 148.7 (NAr C_{ipso}), 144.9 (NAr C_o), 131.5 (NAr C_p), 127.8 (NAr C_m), 123.8 (q, J_{CF} = 288, CF_3), 85.8 (septet, J_{CF} = 30, O*C*Me$(CF_3)_2$), 72.2 (THF), 25.1 (THF), 19.8 and 16.4 (NAr Me and OC*Me*$(CF_3)_2$). Anal. Calcd for $C_{20}H_{23}Cl_2F_{12}NO_3W$: C, 29.73; H, 2.87; N, 1.73. Found: C, 29.72; H, 2.86; N, 1.76.

WCl_2[N-2,6-C_6H_3-(*i*-Pr)$_2$][OCMe(CF_3)$_2$]$_2$(THF) (10). Two equivalents of $(CF_3)_2$MeCOLi (7.20 g, 38.3 mmol) were dissolved in 40 mL of THF. The resulting solution was added over a period of 10 min to a suspension of WCl_4[N-2,6-C_6H_3-(*i*-Pr)$_2$] (9.59 g, 19.1 mmol) in 40 mL of THF at 0 °C. After being warmed to room temperature, the solution was stirred for 15 h before the solvent was removed in vacuo. The red solid was dissolved in pentane, and the solution was filtered and slowly cooled to −50 °C. Red crystals (13.68 g) were isolated in 82.7% yield (2 crops): ^{1}H NMR (C_6D_6) δ 7.07 (d, 2, J = 8.06, NAr H_m), 6.57 (t, 1, J = 8.06, NAr H_p), 4.61 (septet, 2, J = 6.59, C*H*Me_2), 4.25 (m, 4, THF), 1.58 (s, 6, OCMe$(CF_3)_2$), 1.29 (m, 4, THF), 1.28 (d, 12, J = 6.59, CH*Me*$_2$); ^{13}C NMR (C_6D_6) δ 154.1 (NAr C_o), 146.6 (NAr C_{ipso}), 132.1 (NAr Cp), 123.5 (NAr C_m), 123.8 (q, J_{CF} = 288, CF_3), 86.5 (septet, J_{CF}

= 30, $OCMe(CF_3)_2$), 72.1 (THF), 27.6 ($CH(CH_3)_2$), 25.1 (THF), 24.9 ($CH(CH_3)_2$), and 17.1 ($OCMe(CF_3)_2$). Anal. Calcd for $C_{24}H_{31}Cl_2F_{12}NO_3W$: C, 33.35; H, 3.62; N, 1.62. Found: C, 33.60; H, 3.65; N, 1.75.

Observation of W(=CHAr')(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(PPh$_3$) (11). Representative Procedure: A 600-μL C_6D_6 solution containing WCl_2(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(THF) (30 mg, 0.037 mmol) and 1 equiv of Ph_3P=CHAr' was added to an excess (~6–8 equiv) of 1% Na(Hg) in an NMR tube in the drybox. The NMR tube was capped with a septum, the septum was wrapped with Parafilm, and the tube was then mechanically rotated for 4 h. The NMR tube was returned to the drybox, and the reaction mixture was poured into a vial. After allowing the salts to settle, the orange-brown solution was transferred via pipet off of the spent sodium amalgam and placed in the NMR tube again. ^1H and ^{31}P NMR spectra of the product were acquired after the solution was centrifuged.

W(=CHPh)(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(PPh$_3$) (11a): ^1H NMR (C_6D_6) δ 12.32 (d, 1, J_{HP} = 6.87, H_α), 7.5–6.5 (m, H_{aryl}), 2.63 (s, 3, NAr Me), 2.16 (s, 3, $OCMe(CF_3)_2$), 1.80 (s, 3, NAr Me), 1.44 (s, 3, $OCMe(CF_3)_2$); ^{31}P NMR (C_6D_6) δ 37.4 (J_{PW} = 284).

W(=CHC_6H_4-*p*-Me)(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(PPh$_3$) (11b): ^1H NMR (C_6D_6) δ 12.31 (d, 1, J_{HP} = 6.87, H_α), 8.0–6.5 (m, H_{aryl}), 2.63 (s, 3, NAr Me), 2.36 (s, 3, CHAr' Me), 2.19 (s, 3, $OCMe(CF_3)_2$), 1.81 (s, 3, NAr Me), 1.45 (s, 3, $OCMe(CF_3)_2$); ^{31}P NMR (C_6D_6) δ 35.7 (J_{PW} = 283).

W(=CHC_6H_4-*m*-Me)(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(PPh$_3$) (11c): ^1H NMR (C_6D_6) δ 12.32 (d, 1, J_{HP} = 6.87, H_α), 7.9–6.2 (m, H_{aryl}), 2.64 (s, 3, NAr Me), 2.27 (s, 3, CHAr' Me), 2.19 (s, 3, $OCMe(CF_3)_2$), 1.82 (s, 3, NAr Me), 1.45 (s, 3, $OCMe(CF_3)_2$); ^{31}P NMR (C_6D_6) δ 37.6 (J_{PW} = 283).

W(=CHC_6H_4-*o*-Me)(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(PPh$_3$) (11d): ^1H NMR (C_6D_6) δ 12.65 (d, 1, J_{HP} = 6.84, H_α). (Not as stable as the other derivatives—decomposes within ~12 h.)

W(=CHC_6H_4-*p*-OEt)(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(PPh$_3$) (11e): ^1H NMR (C_6D_6) δ 12.26 (d, 1, J_{HP} = 6.37, H_α), 8–6 (m, H_{aryl}), 3.61 (q, 2, J = 6.87, OCH_2CH_3), 2.64 (s, 3, NAr Me), 2.19 (s, 3, $OCMe(CF_3)_2$), 1.81 (s, 3, NAr Me), 1.49 (s, 3, $OCMe(CF_3)_2$), 1.12 (t, 3, J = 6.87, OCH_2CH_3); ^{31}P NMR (C_6D_6) δ 35.8 (J_{PW} = 283).

W(=CHPh)(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(PMe$_3$) (12). A solution of Ph_3P=CHPh (2.25 g, 6.38 mmol) and WCl_2(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(THF) (5.05 g, 6.25 mmol) in 50 mL of benzene was added to a 1% sodium amalgam (1.47 g of Na, 64.1 mmol) and stirred for 3 h. After 1.98 mL of PMe_3 (3 equiv, 19.1 mmol) was added via syringe and the mixture was stirred for an additional 16 h, the mixture was allowed to settle. The golden-brown solution was separated from the residual sodium amalgam, which was then washed with 45 mL of benzene. The solvent was removed in vacuo, and the brown residue was dissolved in 90 mL of Et_2O. After the solution was filtered, it was added via cannula to 0.66 g (6.6 mmol) of CuCl and stirred for 15 h. The Et_2O was removed in vacuo, and the solid was then extracted with 230 mL of pentane to give a yellow-brown solution. After the solution was filtered and concentrated, recrystallization at –50 °C afforded 2.51 g of yellow-brown crystals (48.3%): (This complex was isolated as an 18:1 mixture of isomers. Spectroscopic data for the major isomer is reported here.) ^1H NMR (C_6D_6) δ 12.16 (d, 1, J_{HP} = 9.59, H_α), 7.27 (t, 2, J = 7.57, H_{aryl}), 7.13 (m, 2, H_{aryl}), 6.91 (d, 2, J = 7.57, H_{aryl}), 6.78 (m, 1, H_{aryl}), 6.73 (t, 1, J = 7.57, H_{aryl}), 2.54 (s, 3, NAr Me), 2.43 (s, 3, NAr Me), 2.14 (s, 3, $OCMe(CF_3)_2$), 1.40 (s, 3, $OCMe(CF_3)_2$), 0.79 (d, 9, J_{HP} = 9.28, PMe_3); ^{13}C NMR (C_6D_6) δ 266.5 (J_{CH} = 144, J_{CP} = 14, J_{CW} = 154, C_α), 153.8 (NAr C_{ipso}), 141.09 (d, CH*Ph* C_{ipso}), 136.7 (NAr C_o), 134.4, 128.7, 128.1, 127.9, and 126.7 (all C_{aryl}), 125.7 (q, J_{CF} = 289, CF_3), 125.1 (q, J_{CF} = 289, CF_3), 82.8 (septet, J_{CF} = 29, $OCMe(CF_3)_2$), 80.4 (septet, J_{CF} = 28, $OCMe(CF_3)_2$), 19.2, 18.7, and 17.4 (NAr Me and $OCMe(CF_3)_2$), 14.2 (d, J_{CP} = 29, PMe_3); ^{31}P NMR (CD_2Cl_2) δ 12.7 (J_{PW} = 318, PMe_3). Anal. Calcd for $C_{26}H_{30}F_{12}NO_2PW$: C, 37.56; H, 3.64; N, 1.68. Found: C, 37.74; H, 3.69; N, 1.84.

W(=CHC_6H_4-*o*-OMe)(NPh)[$OCMe(CF_3)_2$]$_2$(THF) (13). A solution of Ph_3P=CHC_6H_4-*o*-OMe (7.82 g, 20.5 mmol) and WCl_2(NPh)[OCMe-$(CF_3)_2$]$_2$(THF) (15.49 g, 19.85 mmol) in 160 mL of benzene and 5 mL of THF was added to a 1% sodium amalgam (3.66 g of Na, 8.02 equiv) and then stirred for 4.5 h. After the mixture settled, the solution was added via cannula to 2.07 g (20.9 mmol) of CuCl, and the residual sodium amalgam was washed with 60 mL of benzene. The combined benzene solutions were stirred with CuCl for 13 h before the solvent was removed in vacuo, and the brown solid was then extracted with 135 mL of pentane. THF (4 mL) was added to the red solution, which was then filtered and slowly cooled to –50 °C. Burnt-orange crystals (10.5 g, 63.8%) were obtained: ^1H NMR (THF-d_8) δ 10.46 (s, 1, H_α), 7.38 (dd, 2, NPh H_m), 7.23 (d, 2, J = 7.69, NPh H_o), 7.11 (m, 3, H_{aryl}), 6.68 (t, 1, J = 7.69, H_{aryl}), 6.39 (d, 1, J = 7.69, CHAr' H_m), 4.09 (s, 3, OMe), 3.61 (m, 4, THF), 1.78 (m, 4, THF), 1.14 (s, 6, $OCMe(CF_3)_2$); ^{13}C NMR (THF-d_8) δ 246.4 (J_{CH} = 149, J_{CW} = 161, C_α), 159.6 and 156.2 (CHAr' *C*OMe and NPh C_{ipso}), 133.5 (CH*Ar'* C_{ipso}), 129.0, 128.8, 126.5, 126.3, 125.0, and 122.6 (all C_{aryl}), 108.4 (1, CH*Ar'* C_m), 125.6 (q, J_{CF} = 288, CF_3), 125.4 (q, J_{CF} = 290, CF_3), 80.9 (septet, J_{CF} = 28, $OCMe(CF_3)_2$), 68.2 (THF), 57.1 (OMe), 26.4 (THF), 18.0 ($OCMe(CF_3)_2$). Anal. Calcd for $C_{26}H_{27}F_{12}NO_4W$: C, 37.66; H, 3.28; N, 1.69. Found: C, 37.93; H, 3.45; N, 2.16.

W(=CHC_6H_4-*o*-OMe)(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(THF) (14). WCl_2(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(THF) (16.0 g, 19.8 mmol) and Ph_3P=CHC_6H_4-*o*-OMe (7.78 g, 20.3 mmol) were dissolved in 160 mL of benzene and 2.5 mL of THF, and the solution was then added to a 1% sodium amalgam (3.59 g of Na, 7.90 equiv). After being stirred for 8 h at room temperature, the mixture was allowed to settle, and the orange-brown supernatant was added via cannula to 2.07 g of CuCl (20.9 mmol). The residual sodium amalgam was washed with a total of 120 mL of Et_2O, and the combined benzene/Et_2O solution was stirred with CuCl for 12 h before the solvent was removed in vacuo. The brown solid was then extracted with 260 mL of Et_2O. After 2 mL of THF was added to the extract, the solution was filtered and then slowly cooled to –50 °C to give 12.0 g (70.6%) of an olive-yellow powder: ^1H NMR (C_6D_6) δ 10.81 (s, 1, H_α), 6.96 (m, 1, H_{aryl}), 6.95 (d, 2, J = 8.06, NAr H_m), 6.75 (m, 1, H_{aryl}), 6.53 (d, 1, J = 7.32, CH*Ar'* H), 6.48 (m, 1, H_{aryl}), 6.26 (d, 1, J = 7.32, CH*Ar'* H_m), 3.93 (m, 4, THF), 3.59 (s, 3, OMe), 2.66 (s, 6, NAr Me), 1.37 (m, 4, THF), 1.19 (s, 6, $OCMe(CF_3)_2$); difference NOE experiments irrad. of δ 10.81 enhances δ 6.26, 2.66; irrad. of δ 3.93 enhances δ 3.59, 2.66, 1.37; irrad. of δ 3.59 enhances δ 6.53, 3.93; irrad. of δ 2.66 enhances δ 10.81, 6.95, 3.93; irrad. of δ 1.19 enhances δ 10.81; ^1H NMR (toluene-d_8, –70 °C) δ 10.78 (s, 1, H_α), 6.99 (m, 3, H_{aryl}), 6.80 (m, 1, H_{aryl}), 6.48 (m, 2, H_{aryl}), 6.11 (d, 1, J = 7.32, H_{aryl}), 4.11 (br s, 4, THF), 3.40 (s, 3, OMe), 2.92 (s, 3, NAr Me), 2.37 (s, 3, NAr Me), 1.25 (s, 6, $OCMe(CF_3)_2$), 1.22 (br s, 4, THF); ^{13}C NMR (C_6D_6) δ 240.2 (J_{CH} = 151, J_{CW} = 160, C_α), 158.0 (CHAr' *C*OMe), 153.5 (NAr C_{ipso}), 134.9 and 132.5 (CH*Ar'* C_{ipso} and NAr C_o), 128.0, 127.8, 125.6, 124.3, and 122.3 (all C_{aryl}), 107.8 (CH*Ar'* C_m), 124.8 (q, J_{CF} = 291, CF_3), 124.6 (q, J_{CF} = 290, CF_3), 81.0 (septet, J_{CF} = 28, $OCMe(CF_3)_2$), 70.3 (THF), 56.1 (OMe), 25.6 (THF), 18.9 and 18.1 (NAr Me and $OCMe(CF_3)_2$). Anal. Calcd for $C_{28}H_{31}F_{12}NO_4W$: C, 39.22; H, 3.64; N, 1.63. Found: C, 39.33; H, 3.71; N, 1.65.

W(=CHC_6H_4-*o*-OMe)[N—2,6-C_6H_3—(*i*-Pr)$_2$][$OCMe(CF_3)_2$]$_2$(THF) (15). A solution of Ph_3P=CHC_6H_4-*o*-OMe (7.12 g, 18.6 mmol) and WCl_2[N—2,6-C_6H_3—(*i*-Pr)$_2$][$OCMe(CF_3)_2$]$_2$(THF) (15.16 g, 17.54 mmol) in 150 mL of benzene and 4 mL of THF was added via cannula to a 1% sodium amalgam (3.37 g of Na, 8.35 equiv) and stirred for 8 h at room temperature. After the mixture settled, the orange-brown supernatant was added via cannula to CuCl (1.79 g, 18.1 mmol). Next, the residual sodium amalgam was washed with a total of 120 mL of benzene, and the combined benzene solutions were stirred with the CuCl for 12 h before the solvent was removed in vacuo. Diethyl ether (330 mL) was used to extract the product from the brown solid. After being filtered, the Et_2O solution was cooled to –50 °C to yield 7.3 g of golden crystals (46%): ^1H NMR (THF-d_8) δ 10.60 (s, 1, H_α), 7.17 (d, 2, J = 7.69, NAr H_m), 7.13 (m, 2, H_{aryl}), 6.98 (t, 1, J = 7.69, NAr H_p), 6.72 (m, 1, H_{aryl}), 6.41 (d, 1, J = 7.33, CH*Ar'* H_m), 4.03 (s, 3, OMe), 3.63 (m, 4, THF), 3.62 (m, 2, $CH(CH_3)_2$), 1.78 (m, 4, THF), 1.34 (br s, 12, $CH(CH_3)_2$), 1.18 (s, 6, $OCMe(CF_3)_2$); ^{13}C NMR (THF-d_8) δ 248.1 (J_{CH} = 148, J_{CW} = 167, C_α), 159.8 (CH*Ar'* *C*OMe), 151.3 (NAr C_{ipso}), 145.8 and 133.1 (CH*Ar'* C_{ipso} and NAr C_o), 129.3, 126.2, 125.2, 123.3, and 122.4 (all C_{aryl}), 108.7 (CH*Ar'* C_m), 125.6 (q, J_{CF} = 290, CF_3), 125.4 (q, J_{CF} = 291, CF_3), 80.8 (septet, J_{CF} = 28.3, $OCMe(CF_3)_2$), 68.1 (THF), 56.9 (OMe), 28.6 ($CH(CH_3)_2$), 26.4 (THF), 24.4 ($CH(CH_3)_2$), 18.0 ($OCMe(CF_3)_2$). Anal. Calcd for $C_{32}H_{39}F_{12}NO_4W$: C, 42.08; H, 4.30; N, 1.53. Found: C, 42.22; H, 4.33; N, 1.82.

W(=CHC_6H_4-*o*-OMe)(N—2,6-C_6H_3—Me_2)[$OCMe(CF_3)_2$]$_2$(PMe$_3$) (16). W(=CHC_6H_4-*o*-OMe)(N—2,6-C_6H_3—Me_2)[OCMe-$(CF_3)_2$]$_2$(THF) (2.01 g, 2.34 mmol) was dissolved in 50 mL of benzene. Three equivalents of PMe_3 (0.73 mL, 7.1 mmol) were added, and the red solution turned golden brown within a few minutes. After the reaction mixture was stirred for 12 h, the solvent was removed in vacuo, and the product was recrystallized from pentane at –50 °C to give 1.44 g of golden crystals (71.4%). This complex was isolated as a 12:1 mixture of isomers. Spectroscopic data for the major isomer is reported here: ^1H NMR (CD_2Cl_2) δ 12.48 (d, 1, J_{HP} = 7.08, H_α), 7.32 (d, 1, J = 7.57, H_{aryl}), 7.22 (d, 2, J = 7.57, NAr H_m), 7.18 (m, 1, H_{aryl}), 7.04 (m, 3, H_{aryl}),

Table VIII. Polymerization of Norbornene at −40 °C by **14**

time (min)	[norbornene] (M)	[polynorbornene] (M)
0	0.590	0.007
10.23	0.559	0.036
20.03	0.514	0.077
30.01	0.478	0.121
40.01	0.433	0.158
49.96	0.404	0.196
60.08	0.372	0.227
70.06	0.341	0.251
79.99	0.319	0.277

4.05 (s, 3, OMe), 2.79 (s, 6, NAr Me), 2.07 (s, 3, OC*Me*$(CF_3)_2$), 1.45 (s, 3, OC*Me*$(CF_3)_2$), 1.37 (d, 9, J_{HP} = 9.52, PMe_3); ^{13}C NMR (CD_2Cl_2, CF_3 quartets were not assigned) δ 259.5 (J_{CH} = 147, J_{CW} = 148, J_{CP} = 15, C_α), 154.3 and 153.9 (CH*Ar'*COMe and NAr C_{ipso}), 136.4 and 132.4 (CH*Ar'* C_{ipso} and NAr C_o), 131.4, 130.3, 128.5, 126.8, and 121.1 (all C_{aryl}), 109.9 (CH*Ar'* C_m), 82.4 (septet, J_{CF} = 28, OCMe$(CF_3)_2$), 80.6 (septet, J_{CF} = 28, OCMe$(CF_3)_2$), 56.6 (OMe), 19.7, 19.4, and 18.2 (NAr Me and OC*Me*$(CF_3)_2$), 15.3 (d, J_{CP} = 29, PMe_3); ^{31}P NMR (CD_2Cl_2) δ 11.0 (J_{PW} = 324). Anal. Calcd for $C_{27}H_{32}F_{12}NO_3PW$: C, 37.65; H, 3.74; N, 1.63. Found: C, 37.89; H, 3.79; N, 1.56.

W(=CHC$_6$H$_4$-*o*-OMe)(NAr)[OCMe(CF$_3$)$_2$]$_2$ (17). W(=CHC$_6$H$_4$-*o*-OMe)(N—2,6-C$_6$H$_3$—Me$_2$)[OCMe(CF$_3$)$_2$]$_2$ (17a). A 150-mL toluene solution of the THF adduct W(=CHC$_6$H$_4$-*o*-OMe)(N—2,6-C$_6$H$_3$—Me$_2$)-[OCMe$(CF_3)_2]_2$(THF) (7.92 g, 9.17 mmol) was heated to 50 °C as the solvent was removed in vacuo. The resulting red powder was dissolved in 30 mL of toluene, and the solution was filtered, layered with 120 mL of pentane, and cooled to −10 °C to give red crystals in 73% yield (5.2 g, 2 crops): ^1H NMR (C_6D_6) δ 10.94 (s, 1, H_α), 6.93 (m, 1, H_{aryl}), 6.90 (d, 2, J = 7.69, NAr H_m), 6.73 (t, 1, J = 7.69, NAr H_p), 6.49 (m, 2, H_{aryl}), 6.37 (d, 1, J = 6.96, CH*Ar'* H_m), 3.75 (s, 3, OMe), 2.69 (s, 6, NAr Me), 1.11 (s, 6, OC*Me*$(CF_3)_2$); ^{13}C NMR (C_6D_6) δ 228.1 (J_{CH} = 155, J_{CW} = 172, C_α), 156.3 (CH*Ar'*COMe), 153.0 (NAr C_{ipso}), 135.6 and 132.4 (CH*Ar'* C_{ipso} and NAr C_o), 127.9, 126.8, 126.6, 123.6, and 122.6 (all C_{aryl}), 107.6 (CH*Ar'* C_m), 124.2 (q, J_{CF} = 287, CF_3), 124.1 (q, J_{CF} = 288, CF_3), 82.3 (septet, J = 29, OCMe$(CF_3)_2$), 56.7 (OMe), 18.73 and 18.66 (NAr Me and OC*Me*$(CF_3)_2$). Anal. Calcd for $C_{24}H_{23}F_{12}NO_3W$: C, 36.71; H, 2.95; N, 1.78. Found: C, 36.90; H, 3.03; N, 1.70.

W(=CHC$_6$H$_4$-*o*-OMe)[N—2,6-C$_6$H$_3$—(*i*-Pr)$_2$][OCMe(CF$_3$)$_2$]$_2$ (17b). Removal of THF from W(=CHC$_6$H$_4$-*o*-OMe)[N—2,6-C$_6$H$_3$—(*i*-Pr)$_2$]-[OCMe$(CF_3)_2]_2$(THF) was much more difficult than that for the (dimethylphenyl)imido analog. After the above procedure was repeated twice, the product was dissolved in pentane, filtered, and cooled to −10 °C. Red single crystals of **17b** precipitated from solution along with a small amount of yellow single crystals of the THF adduct **15**. Due to the differences in color, the crystals were easily separated by hand, and pure **17b** was then characterized: ^1H NMR (CD_2Cl_2) δ 10.79 (s, 1, H_α), 7.28 (d, 2, J = 8.06, NAr H_m), 7.18 (t, 1, J = 6.96, H_{aryl}), 7.14 (t, 1, J = 7.70, H_{aryl}), 7.09 (d, 1, J = 8.06, CH*Ar'* H_o), 6.81 (t, 1, J = 7.89, H_{aryl}), 6.59 (d, 1, J = 7.33, CH*Ar'* H_m), 4.22 (s, 3, OMe), 4.06 (septet, 2, J = 6.96, C*H*$(CH_3)_2$), 1.34 (d, 2, J = 6.96, CH$(CH_3)_2$), 1.29 (s, 6, OC*Me*$(CF_3)_2$); ^{13}C NMR (CD_2Cl_2) δ 229.4 (J_{CH} = 155, J_{CW} = 176, C_α), 156.6 (CH*Ar'*COMe), 150.4 (NAr C_{ipso}), 146.4 and 132.4 (CH*Ar'* C_{ipso} and NAr C_o), 127.5, 127.0, 123.9, 123.1, and 122.8 (all C_{aryl}), 107.9 (CH*Ar'* C_m), 124.0 (q, J_{CF} = 289, CF_3), 123.9 (q, J_{CF} = 289, CF_3), 82.5 (septet, J_{CF} = 29.3, OCMe$(CF_3)_2$), 57.4 (OMe), 28.6 (*CH*$(CH_3)_2$), 24.3 (CH(*CH*$_3)_2$), 19.0 (OC*Me*$(CF_3)_2$). Anal. Calcd for $C_{28}H_{31}F_{12}NO_3W$: C, 39.97; H, 3.71; N, 1.66. Found: C, 40.11; H, 3.73; N, 1.82.

Observation of W(=CHC$_6$H$_4$-*o*-OMe)(N—2,6-C$_6$H$_3$—Me$_2$)(O-*t*-Bu)$_2$(PMe$_2$Ph). W(=CHC$_6$H$_4$-*o*-OMe)(N—2,6-C$_6$H$_3$—Me$_2$)(O-*t*-Bu)$_2$ was formed upon mixing **13** with 2 equiv of NaO-*t*-Bu, but numerous difficulties were encountered in separating this complex from free $LiOCMe(CF_3)_2$. After several manipulations of the product, it was discovered that the addition of PMe_2Ph, which binds reversibly to tungsten, to a pentane solution of the *tert*-butoxide complex and subsequent filtration enabled the removal of the free alkoxide. The PMe_2Ph adduct was then recrystallized from pentane: ^1H NMR (C_6D_6) δ 10.55 (br s, 1, H_α), 7.35–6.54 (m, 12, H_{aryl}), 3.72 (s, 3, OMe), 2.79 (s, 6, NAr *Me*$_2$), 1.18 (s, 18, OC*Me*$_3$), 1.07 (s, 6, P*Me*$_2$Ph); ^{13}C NMR (CD_2Cl_2, selected C_{aryl} only) δ 2.08 (br, C_α), 155.4 (br, CH*Ar'*COMe), 154.0 (NAr C_{ipso}), 136.4 (br, CH*Ar'* C_{ipso}), 134.7 (NAr C_o), 107.9 (CH*Ar'* C_m), 80.0 (OCMe$_3$), 56.3 (OMe), 32.6 (OC*Me*$_3$), 19.4 (NAr *Me*$_2$), 14.6 (P*Me*$_2$Ph).

Polymerization of Norbornene by 14 (Table VIII). Norbornene (35.9 mg, 0.381 mmol) was dissolved in 300 μL of toluene-d_8 and transferred via pipet into a small flask equipped with a Kontes valve. Complex **14** (6.3 mg, 0.0073 mmol) and 4.9 mg (0.041 mmol) of mesitylene were dissolved in 300 μL of toluene-d_8 and transferred via pipet into a sealable NMR tube. After both solutions were freeze–pump–thaw-degassed several times, the toluene-d_8 solution of norbornene was vacuum-transferred onto the solution of **14** ([**14**] = 0.012 M; [norbornene] = 0.635 M, 52.9 equiv), and the tube was sealed and then stored in liquid nitrogen before it was placed in the probe of the 400-MHz NMR at −82 °C. After an initial spectrum was acquired at −82 °C, the probe was warmed to −61 °C and the polymerization was monitored at this temperature for 50 min. After 50 min, integration versus the mesitylene internal standard indicated that [norbornene] = 0.606 M and [polynorbornene] = 0.002 M. The probe was then warmed to −40 °C, and the polymerization was again monitored for 80 min. For the data reported in Table VIII, a plot of the rate of disappearance of norbornene versus time was linear with rate = 17.5 equiv/h.

Table IX. Polymerization of Norbornene at −61 °C by **17a**

time (min)	[norbornene] (M)	[polynorbornene] (M)
0	0.630	0.004
9.98	0.606	0.023
20.02	0.590	0.052
29.97	0.546	0.084
40.05	0.516	0.121
50.02	0.480	0.158
60.00	0.432	0.188
70.03	0.405	0.233
80.03	0.367	0.273
110.02	0.269	0.377
120.02	0.234	0.400

Table X. Isomerization of *cis*-2-Pentene by **17a**

time (min)	[*cis*-2-pentene] (M)	time (min)	[*cis*-2-pentene] (M)
0	0.416	65.5	0.114
10.4	0.372	75.0	0.100
23.7	0.319	85.4	0.095
34.8	0.283	106.1	0.089
49.2	0.176	128.7	0.091
57.0	0.136		

Polymerization of Norbornene by 17a (Table IX). Norbornene (35.6 g, 0.378 mmol) was dissolved in 300 μL of toluene-d_8 and transferred via pipet into a small flask equipped with a Kontes valve. Complex **17a** (5.7 mg, 0.0073 mmol) and 4.5 mg (0.037 mmol) of mesitylene were dissolved in 300 μL of toluene-d_8 and transferred via pipet into a sealable NMR tube. After both solutions were freeze–pump–thaw-degassed several times, the toluene-d_8 solution of norbornene was vacuum-transferred onto the solution of **17a** ([**17a**] = 0.012 M; [norbornene] = 0.630 M, 52.5 equiv), and the tube was sealed and then stored in liquid nitrogen before it was placed in the probe of the 400-MHz NMR at −82 °C. After an initial spectrum was acquired at −82 °C, the probe was warmed to −61 °C and the polymerization was monitored at this temperature for 120 min. For the data reported in Table IX, a plot of the rate of disappearance of norbornene versus time was linear with rate = 16.5 equiv/h. The starting alkylidene peak disappeared during the polymerization at low temperature and then reappeared when the solution was warmed to room temperature. This observation, together with the occurrence of a doublet at 4.77 ppm and a triplet at 0.65 ppm, may indicate that the resting state of the catalyst is the norbornene metallacycle at low temperature.[10a,35]

Observation of the Olefination of Carbonyl Compounds by 14.[27] A small excess of the carbonyl compound and 25 mg of **14** were dissolved together in 600 μL of C_6D_6, and the reaction was monitored by ^1H NMR spectroscopy. The reactions were carried out at room temperature unless specified otherwise for the following: EtC(O)H, PhC(O)H, PhC(O)Me, PhC(O)Ph, MeC(O)OEt (65 °C), and $MeC(O)NMe_2$ (65 °C). A mixture of trans and cis isomers was observed in all cases for the alkene products.

Isomerization of *cis*-2-Pentene by 17a (Table X). Complex **17a** (14.1 mg, 0.0018 mmol, 0.0030 M), *cis*-2-pentene (17.5 mg, 0.250 mmol, 0.416 M, 140 equiv), and mesitylene (internal standard, 2.8 mg, 0.023 mmol) were dissolved together in 600 μL of toluene-d_8, and the reaction was monitored by ^1H NMR spectroscopy; the data are reported in Table X. An equilibrium mixture of *cis*- and *trans*-2-pentene was obtained within

(35) (a) Feldman, J.; Davis, W. M.; Schrock, R. R. *Organometallics* **1989**, *8*, 2266–2268. (b) Feldman, J.; Davis, W. M.; Thomas, J. K.; Schrock, R. R. *Organometallics* **1990**, *9*, 2535–2548.

75 min, establishing a lower limit of 1.4 equiv/min for the metathesis of *cis*-2-pentene by **17a**.

X-ray Data Collection, Structure Determination, and Refinement for W(=CHC$_6$H$_4$-*p*-Me)Cl$_2$(NPh)(PMePh$_2$)$_2$ (2). A yellow crystal of approximate dimensions 0.23 × 0.40 × 0.47 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 was carried out by previously described techniques similar to those of Churchill.[36] Low-temperature (168 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation.

All 8664 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[37] 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[38] or the SHELXTL PLUS program set.[39] The analytical scattering factors for neutral atoms were used throughout the analysis;[40a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[40b] 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. Refinement of the model led to convergence with R_F = 3.0%, R_{wF} = 4.1%, and GOF = 1.08 for 415 variables refined against those 7811 data with $|F_o| > 3.0\sigma(|F_o|)$. A final difference Fourier map yielded ρ(max) = 1.25 eÅ^{-3} at a distance of 1.53 Å from tungsten.

X-ray Data Collection, Structure Determination, and Refinement for W(=CHC$_6$H$_4$-*o*-OMe)(N—2,6-C$_6$H$_3$—Me$_2$)[OCMe(CF$_3$)$_2$]$_2$(THF) (14). A yellow-gold crystal of approximate dimensions 0.32 × 0.34 × 0.40 mm was immersed in Paratone-N (lube-oil additive), mounted on a glass fiber, and transferred to the Nicolet 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 was carried out by previously described techniques similar to those of Churchill.[36] Low-temperature (173 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation.

All 6054 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[38] or the SHELXTL PLUS program set.[39] The analytical scattering factors for neutral atoms were used throughout the analysis;[40a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[40b] were included. The quantity minimized during least-squares analysis was $\sum w(|F_o| - |F_c|)^2$, where $w^{-1} = \sigma^2(|F_o|) + 0.0005(|F_o|)^2$.

The structure was solved via an automatic Patterson routine (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. Refinement of positional and anisotropic thermal parameters led to convergence with R_F = 3.8%, R_{wF} = 4.4%, and GOF = 1.39 for 415 variables refined against all 5269 unique data with $|F_o| > 0$ (R_F = 3.1% and R_{wF} = 4.1% for those 4576 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference Fourier map yielded ρ(max) = 2.29 eÅ^{-3} at a distance of 0.95 Å from tungsten.

X-ray Data Collection, Structure Determination, and Refinement for W(=CHC$_6$H$_4$-*o*-OMe)[N—2,6-C$_6$H$_3$—(*i*-Pr)$_2$][OCMe(CF$_3$)$_2$]$_2$ (17b). A bright-red crystal of approximate dimensions 0.20 × 0.30 × 0.32 mm was immersed in Paratone-N (lube-oil additive), 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 was carried out by previously described techniques similar to those of Churchill.[36] Low-temperature (183 K) intensity data were collected via a θ–2θ scan technique with Mo Kα radiation.

All 6092 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[38] or the SHELXTL PLUS program set.[39] The analytical scattering factors for neutral atoms were used throughout the analysis;[40a] both the real ($\Delta f'$) and imaginary ($i\Delta f''$) components of anomalous dispersion[40b] 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 via an automatic Patterson routine (SHELXTL PLUS) and refined by full-matrix least-squares techniques. All hydrogen atoms were located from a series of difference Fourier syntheses and included in the refinement with isotropic temperature factors. Full-matrix least-squares refinement of the model led to convergence with R_F = 3.4%, R_{wF} = 4.1%, and GOF = 1.00 for 530 variables refined against all 5195 unique data with $|F_o| > 0$ (R_F = 2.5% and R_{wF} = 3.7% for those 4434 data with $|F_o| > 6.0\sigma(|F_o|)$). A final difference Fourier map showed no significant features; ρ(max) = 1.17 eÅ^{-3} at a distance of 1.06 Å from tungsten.

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Supplementary Material Available: Procedures for the synthesis of Ph$_3$P=CH—C$_6$H$_4$—C$_6$H$_4$—CH=PPh$_3$ and its precursors, tables of experimental data, atomic coordinates, bond lengths, and bond angles for the X-ray diffraction studies of **2**, **14**, and **17b** (54 pages); tables of observed and calculated structure factors for the X-ray diffraction studies of **2**, **14**, and **17b** (57 pages). Ordering information is given on any current masthead page.

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