

2-Alkylidenephosphiranes

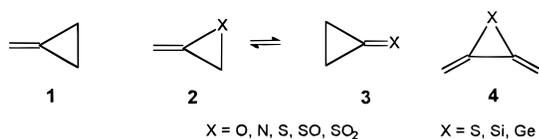
Steffen Krill, Bing Wang, Jui-Te Hung, Chris J. Horan, Gary M. Gray, and Koop Lammertsma*

Contribution from the Department of Chemistry, University of Alabama at Birmingham, UAB Station, Birmingham, Alabama 35294-1240, and Faculty of Chemistry, Vrije Universiteit, De Boelelaan 1083, 1081 HV Amsterdam, The Netherlands

Received April 28, 1997[Ⓢ]

Abstract: Three stable alkylidenephosphiranes have been synthesized from the addition of the terminal phosphinidene complex Ph–P–W(CO)₅ to allene, 1,1-dimethylallene, and tetramethylallene. Isopropylidenephosphirane **16b** was characterized by a single-crystal X-ray structure determination. Demetalation of its W(CO)₅ group provides the uncomplexed compound. The addition reaction with tetramethylallene also yields vinylphosphirane epimers, which rearrange to phospholene **20**. Ab initio MP2/6-31G* structures and energies are presented for the parent uncomplexed methylenephosphirane and its dimethyl derivatives.

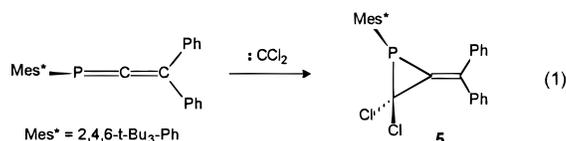
Ring strain augmented by the presence of an exocyclic double bond makes the heteroatom analogues of methylenecyclopropanes (**1**) fascinating compounds.^{1,2} Strain underlies, for example, the biradical interconversion of the valence isomers **2** and **3**, which consequently have received particular attention.^{3–5} While synthesizing such systems is inherently challenging, their presence as reactive and versatile intermediates has been well established. Expectantly, the stability of the methylene derivatives of the aziridines, oxiranes, and thiiranes increases with bulky substituents on the heteroatom, ring, and/or double bond. These sterically congested systems are typically generated via ring closure reactions, either thermally or photochemically induced, rather than by, e.g., the epoxidation of or the nitrene addition to allenes.^{1,6} Our interest in these heterocycles and their even more strained higher homologues, the radialenes **4**,⁷ arose because of the noticeable elusive phosphorus analogues.⁸



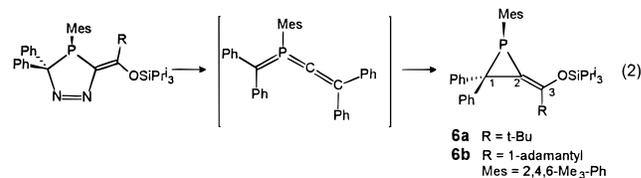
* To whom correspondence should be addressed at Vrije Universiteit.

Ⓢ Abstract published in *Advance ACS Abstracts*, August 15, 1997.(1) For a review, see: L'abbé, G. *Angew. Chem., Int. Ed. Engl.* **1980**, *19*, 276.(2) Doering, W. v. E.; Sachdev, K. *J. Am. Chem. Soc.* **1974**, *96*, 65. Doering, W. v. E.; Roth, H. D. *Tetrahedron* **1970**, *26*, 2825. Gajewski, J. *J. Am. Chem. Soc.* **1968**, *90*, 7178. Dolbier, W. R.; Alonso, J. H. *J. Am. Chem. Soc.* **1973**, *95*, 4421. Roth, W. R.; Wegener, G. *Angew. Chem., Int. Ed. Engl.* **1975**, *14*, 758. Dowd, P. *Acc. Chem. Res.* **1972**, *5*, 242. Berson, J. A. *Acc. Chem. Res.* **1978**, *11*, 446.(3) Osamura, Y.; Borden, W. T.; Morokuma, K. *J. Am. Chem. Soc.* **1976**, *98*, 7081. Wasserman, H. H.; Berdahl, D. R.; Lu, T.-J. In *The Chemistry of the Cyclopropyl Group*; Rappoport, Z., Ed.; Wiley: New York, 1987; Part 2, pp 1455–1532. Turecek, F.; Drinkwater, D. E.; McLafferty, F. W. *J. Am. Chem. Soc.* **1991**, *113*, 5950.(4) Block, E.; Schwan, A.; Dixon, D. A. *J. Am. Chem. Soc.* **1992**, *114*, 3492. Block, E.; Penn, R. E.; Ennis, M. D.; Owens, T. A.; Yu, S. L. *J. Am. Chem. Soc.* **1978**, *100*, 7436. Jongejan, E.; Buys, Th. S. V.; Steinberg, H.; de Boer, Th. *Recl. Trav. Chim. Pays-Bas* **1978**, *97*, 215. Ando, W.; Itami, A.; Furuhashi, T.; Tokitoh, N. *Tetrahedron Lett.* **1987**, *28*, 1787. Ando, W.; Choi, N.; Kabe, Y. *J. Am. Chem. Soc.* **1990**, *112*, 4574. Schhaumann, E.; Behr, H.; Adiwidjaja, G.; Tangerman, A.; Lammerink, B. H. M.; Zwanenburg, B. *Tetrahedron* **1981**, *37*, 219.(5) Quast, H.; Risler, W. *Angew. Chem., Int. Ed. Engl.* **1973**, *12*, 414. Quast, H.; Jacobi, H. *Chem. Ber.* **1991**, *124*, 1613.(6) Bingham, E. M.; Gilbert, J. C. *J. Org. Chem.* **1975**, *40*, 224. Herges, R.; Hoock, C. *Synthesis* **1991**, 1151. Green, M.; Verkoczy, B.; Lown, E. M.; Strausz, O. P. *Can. J. Chem.* **1985**, *63*, 667.

Only recently did Yoshifuji et al.⁹ report the first synthesis of a congested methylenephosphirane, **5**, via the addition of dichlorocarbene to a sterically protected 1-phosphaallene (eq 1). No structural details were provided. Subsequently, Manz



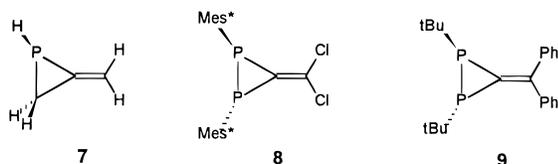
and Maas¹⁰ reported two similarly congested methylenephosphiranes **6a,b**. These stable compounds were obtained from thermal N₂-extrusion of diazaphosphole precursors, thereby extending the method explored in detail by Quast and co-workers¹¹ for the syntheses of the O-, S-, and N-analogues. Product formation is presumed to occur via ring closure of the reactive 2-phosphacumulene intermediates (eq 2). The yields



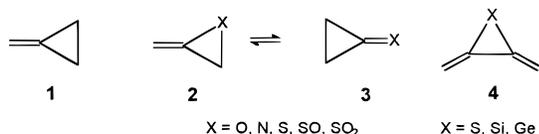
are modest due to competing biradical H-abstractions. The difference between the *ab initio* geometry of the parent methylenephosphirane, C₃H₅P (**7**),¹² and the single-crystal X-ray structure of **6a** emphasizes the effect of steric crowding (see also later).¹⁰ These two synthetic routes are, however, rather limited in scope due to the high sensitivity of phosphaallene and 2-phosphacumulenes.⁸ A third route has been attempted,

(7) For sila- and thia[3]radialenes, see: Ando, W.; Hanyu, Y.; Kumamoto, Y.; Takata, T. *Tetrahedron Lett.* **1986**, *42*, 1989. Yamamoto, T.; Kabe, Y.; Ando, W. *Organometallics* **1993**, *12*, 1996. For a review on carbon [n]radialenes, see: Hopf, H.; Maas, G. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 931.(8) (a) Regitz, M.; Scherer, O. Eds. *Multiple bonds and low coordination in phosphorus chemistry*; Georg Thieme Verlag: Stuttgart, 1990. (b) Mathey, F. *Chem. Rev.* **1990**, *90*, 997.(9) Yoshifuji, M.; Toyota, K.; Yoshimura, H.; Hirotsu, K.; Okamoto, A. *J. Chem. Soc. Chem. Commun.* **1991**, 124.(10) Manz, B.; Maas, G. *J. Chem. Soc., Chem. Commun.* **1995**, 25.(11) Kinderman, M. K.; Poppek, R.; Rademacher, P.; Fuss, A.; Quast, H. *Chem. Ber.* **1990**, *123*, 1161. Quast, H.; Fuss, A.; Jacobi, H. *Chem. Ber.* **1991**, *124*, 1747. Quast, H.; Hergenröther, T. *Chem. Ber.* **1992**, *125*, 2095.(12) Bachrach, S. M. *J. Phys. Chem.* **1993**, *97*, 4996.

i.e., the simple addition of Bu_3P to phenylallene, but the intermediacy of a reactive derivative of **7**, as suggested by Gasparyan et al.,¹³ however, is speculative at best.



Only two methylenediphosphiranes have been reported, both of which are again highly congested. Yoshifuji et al.⁹ employed also in this case the CCl_2 carbene addition to a 1,3-diphosphaallene to form **8**, while Baudler¹⁴ used a condensation route instead for the synthesis of **9**. Single-crystal X-ray structures were reported for both. Likewise, there are only two reports on the more strained phospha[3]radialenes. Yoshifuji et al.¹⁵ employed again the CCl_2 carbene addition to phosphabutatriene followed by a rearrangement to give **10**, while Maercker and Brieden¹⁶ used a condensation reaction to synthesize **11** from dichlorophosphines and 3,4-dilithio-2,5-dimethyl-2,4-hexadiene.



We decided to explore an alternative access to the methylenephosphiranes, namely, the addition of singlet, transition-metal-complexed phosphinidenes ($\text{R}-\text{P}-\text{M}$) to allenes. Since Mathey's pioneering work on the development of such *in situ* generated¹⁷ electrophilic phosphinidenes, their use toward the syntheses of organophosphorus compounds has become a viable option.¹⁸ While Gaspar, Cowley, and co-workers¹⁹ showed recently by ESR spectroscopy that the parent $\text{Ph}-\text{P}$ has a triplet ground state, conforming to theoretical predictions,²⁰ the transition-metal-complexed phosphinidenes $\text{R}-\text{P}-\text{W}(\text{CO})_5$ are believed to be singlet carbene-like species.^{21,22} Its cycloaddition to olefins (eq 3) is a convenient route for the synthesis of phosphiranes. Those of the parent **13** and the smallest phosphaspiro compound **14** are illustrative.²³ In the present study,

(13) Gasparyan, G.; Ovakimyan, M. Zh.; Abramyan, T. A.; Indzhikyan, M. G. *Arm. Khim. Zh.* **1984**, *37*, 520; *Chem Abstr.* **1985**, *102*, 78993v. The reported reaction of Bu_3P with phenylallene followed by addition of HBr/MeBr to give phosphonium salts probably occurs via betaines.

(14) Baudler, M.; Saykowski, F.; Hintze, M.; Tebbe, K.-F.; Heinlein, T.; Vissers, A.; Fehér, M. *Chem. Ber.* **1984**, *117*, 1542.

(15) Toyota, K.; Yoshimura, H.; Uesugi, T.; Yoshifuji, M. *Tetrahedron Lett.* **1991**, *32*, 6879.

(16) Maercker, A.; Brieden, W. *Chem. Ber.* **1991**, *124*, 933.

(17) (a) Marinetti, A.; Mathey, F. *Organometallics* **1984**, *3*, 456. (b) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, J. *J. Am. Chem. Soc.* **1982**, *104*, 4484. (c) Marinetti, A.; Mathey, F. *Organometallics* **1982**, *1*, 1488. (d) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, J. *J. Chem. Soc., Chem. Commun.* **1982**, 667.

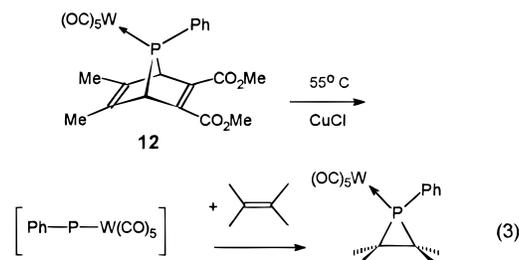
(18) (a) Mathey, F. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 275. (b) Mathey, F. *Pure Appl. Chem.* **1987**, *59*, 993.

(19) Li, X.; Weissman, S. I.; Lin, T.-S.; Gaspar, P. P.; Cowley, A. H.; Smirnov, A. I. *J. Am. Chem. Soc.* **1994**, *116*, 7899.

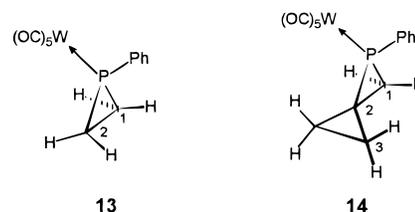
(20) The triplet-singlet energy gap for PhP amounts to 24 kcal/mol at CISD/6-31G*: Hamilton, T. P. Personal communication. See also: Cowley, A. H.; Gabbai, F.; Schluter, R.; Atwood, D. *J. Am. Chem. Soc.* **1992**, *114*, 3142. For the triplet-singlet energy gap of 22.6 kcal/mol for CH_3P , see: Kim, S.-J.; Hamilton, T. P.; Schaefer, H. F. *J. Phys. Chem.* **1993**, *97*, 1872.

(21) (a) Cowley, A. H.; Barron, A. R. *Acc. Chem. Res.* **1988**, *21*, 81. (b) Gonbeau, D.; Pfister-Guillouzo, G.; Marinetti, A.; Mathey, F. *Inorg. Chem.* **1985**, *24*, 4133.

(22) (a) Lammertsma, K.; Chand, P.; Yang, S.-W.; Hung, J.-T. *Organometallics* **1988**, *7*, 1875. (b) Hung, J.-T.; Yang, S.-W.; Chand, P.; Gray, G. M.; Lammertsma, K. *J. Am. Chem. Soc.* **1994**, *116*, 10966. (c) Wang, B.; Lammertsma, K. *J. Am. Chem. Soc.* **1994**, *116*, 10486.



the use of this terminal phosphinidene complex for the syntheses of several methylenephosphiranes, including its parent, will be described.



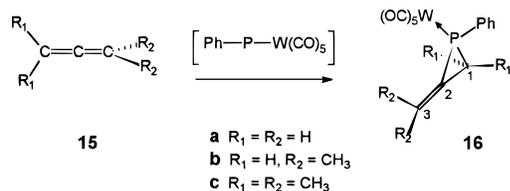
Results and Discussion

Reaction of the phosphinidene precursor **12** with allene and its 1,1-dimethyl and tetramethyl derivatives affords the new methylenephosphiranes **16a**, **16b**, and **16c**, respectively. These are formed with surprising ease in reasonable yields and at a modest temperature of ca. 55 °C. The crystalline products are remarkably stable and can be stored for weeks in air at ambient temperatures without showing signs of decomposition. They are characterized by ^1H , ^{13}C , and ^{31}P NMR spectroscopic data and by a single-crystal X-ray structure determination for **16b**. The geometrical, electronic, and reactivity aspects of these methylenephosphiranes will be discussed. We start with addressing the allene reactivities toward the phosphinidene complex, followed by a structural analysis of **16b** to illustrate that stable methylenephosphiranes do not need to be heavily substituted. We then elaborate on the demetalation of **16b** and use theoretical data for structure and energy evaluations.

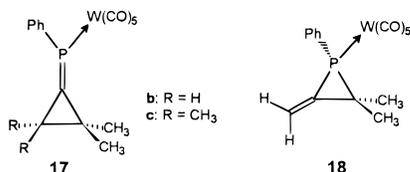
Phosphinidene Addition. The carbene-like cycloaddition of the *in situ* generated $\text{Ph}-\text{P}-\text{W}(\text{CO})_5$ to the parent allene (**15a**) yields a stable methylenephosphirane under mild conditions. The surprise is not in the ease of the addition, because $\text{Ph}-\text{P}-\text{W}(\text{CO})_5$ adds with equal ease to gaseous ethylene and methylenecyclopropane, for example, to form the parent phosphirane **13** and spirophosphapentane **14**, respectively.²³ Rather, the stability of the product **16a** appears to stand out. The synthesis of methylenephosphiranes via the addition of a phosphinidene to allenes appears then as a viable alternative to the carbene addition to phosphacumulenes (eq 1) and to the cyclization of phosphacumulenes (eq 2), the difference being that the phosphinidene precursors are inherently more stable than the phosphacumulenes and phosphacumulenes which typically require bulky substituents to be synthetically accessible, thereby limiting their synthetic scope. Because the transition metal group of **16** can be removed (see later) and its P-substituent can be varied (*e.g.*, alkyl, phenyl, alkoxy, amine),¹⁸ the phosphinidene-allene addition is a versatile route.

Not surprisingly then, methylenephosphiranes can also be generated from the 1,1-dimethyl- (**15b**) and tetramethylallenes (**15c**). The phosphinidene complex adds exclusively to the unsubstituted double bond of **15b** to give **16b**, but gives in the case of **15c** besides **16c** a mixture of the *anti/syn*-vinylphos-

(23) Hung, J. T.; Yang, S.-W.; Gray, G. M.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 6786.



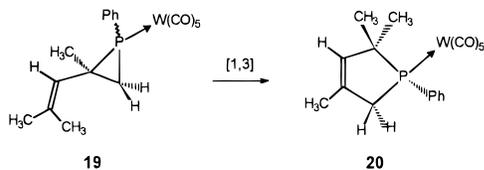
phiranes **19**. The chemical stability of the complexed methylenephosphiranes is startling in comparison with methylenephosphiranes, -aziridines, and -cyclopropanes, which are prone to isomerization, polymerization, and decomposition reactions.¹ The substituted derivatives **16b** and **16c** do not show any sign of decomposition or rearrangement when heated in solution at 80 °C for two days. The absence of any formation of phosphamethylenecyclopropane **17** contrasts the reported $2 \rightleftharpoons 3$ biradical rearrangement of the analogous oxy, thio, and imino derivatives.^{3,4,5} Attempts to alkylate the phosphirane ring of **16b** in a manner analogous to that employed for methylenephosphiranes²⁴ proved fruitless.



The high intramolecular selectivity for $\text{Ph}-\text{P}-\text{W}(\text{CO})_5$ addition to **15b** is somewhat surprising in light of the intermolecular olefin competition reactions which showed isobutylene to react slightly faster than other (poly)methylated olefins.^{22b} This selective formation of **16b** over **18** may be thermodynamically controlled, but it is also sterically the least demanding pathway. Addition of $\text{Ph}-\text{P}-\text{W}(\text{CO})_5$ to **15c** to give **16c** illustrates, however, that the higher substituted olefinic bond is sterically accessible.

The reaction with **15c** is, as noted, accompanied by the formation of the *syn*- and *anti*-phosphiranes **19**. Formally, these represent the (*syn*- and *anti*-) addition of $\text{Ph}-\text{P}-\text{W}(\text{CO})_5$ to 2,4-dimethyl-1,3-pentadiene, which we confirmed independently. However, we can only speculate on their formation since tetramethylallene does not rearrange to 2,4-dimethyl-1,3-pentadiene at 70 °C in the presence of CuCl nor does isolated **16c** rearrange to **19**. Interaction of the electrophilic $\text{Ph}-\text{P}-\text{W}(\text{CO})_5$ with the hyperconjugatively weakened $\text{C}-\text{CH}_3$ single bond or a biradical addition, each followed by a subsequent [1,3]-H-shift, might explain the formation of these products.

Prolonged heating of the mixture of vinylphosphiranes **19** gives as the main product phospholene **20**, which evidently results from a [1,3]-sigmatropic shift. Recently, we²⁵ and others^{17a,26} have reported on such rearrangements.



Experimental Structures. The ORTEP plot of **16b** is shown in Figure 1. Its relevant bond distances and angles are

- (24) Quast, H.; Weise, A. *Angew. Chem., Int. Ed. Engl.* **1974**, *13*, 342.
 (25) (a) Wang, B.; Lammertsma, K. *J. Am. Chem. Soc.* **1996**, *118*, 1690.
 (b) Lammertsma, K.; Hung, J.-T.; Chand, P.; Gray, P. M. *J. Org. Chem.* **1992**, *57*, 6557. (c) Hung, J.-T.; Lammertsma, K. *J. Org. Chem.* **1993**, *58*, 1800.
 (26) Richter, W. *J. Chem. Ber.* **1985**, *118*, 1575.

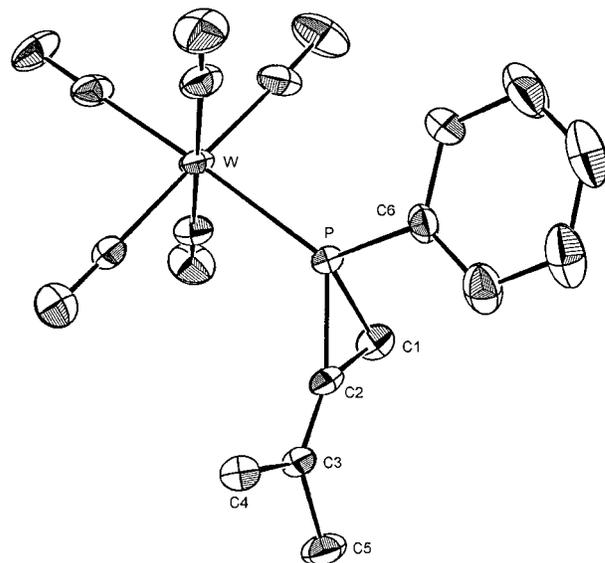


Figure 1. Crystal structure of **16b** (thermal ellipsoids with 50% probability). Selected bond lengths (Å) and angles (deg): P–C1 1.85(1), P–C2 1.776(8), C1–C2 1.47(1), C2–C3 1.31(1), C3–C4 1.47(1), C3–C5 1.50(1), P–C6 1.799(7), W–P 2.500(2), C1–P–C2 47.8(4), W–P–C6 124.0(3), C1–C2–C3 142.3(8), C2–C3–C4 123.0(7), C2–C3–C5 120.4(7).

Table 1. Selected Bond Distances (Å) and CPC Angles (deg) for the X-ray Structures of **16b**, **6a**, **14**, and **13**, the Microwave Structure of Phosphirane $\text{C}_2\text{H}_5\text{P}$, and the Theoretical Structures of $\text{C}_3\text{H}_5\text{P}$ and $\text{C}_2\text{H}_5\text{P}^e$

bond	16b ^a	6a ^b	14 ^c	7 ^d	13 ^e	$\text{C}_2\text{H}_5\text{P}^e$
P–C(1)	1.85(1)	1.967	1.855(7)	1.905	1.83(2)	1.867
P–C(2)	1.776(8)	1.790	1.794(6)	1.818	1.80(2)	1.867
C(1)–C(2)	1.47(1)	1.490	1.508(9)	1.460	1.50(2)	1.502
C(2)–C(3)	1.31(1)	1.331	1.470(1)	1.330		
			1.475(10)			
P–C(6)	1.799(7)	1.839	1.819(7)		1.80(1)	
C(1)PC(2)	47.8(4)	46.4	48.6(3)	51.2	48.6(7)	47.4

^a This study. ^b Reference 10; reported estimated standard deviations are 0.003–0.004 Å for bond lengths and 0.1° for the bond angle. ^c Reference 24. ^d This study, MP2(fc)/6-31G*. ^e Reference 30.

summarized in Table 1 together with those reported for the X-ray structures of methylenephosphirane **6a**,¹⁰ the related $\text{W}(\text{CO})_5$ -complexed spirophospha[2.2]pentane **14**,²³ and the parent $\text{W}(\text{CO})_5$ -complexed phosphirane **13**.²³ Comparison of their important bond distances and bond angles illustrates that the phosphirane ring of structure **16b** differs from that of the more congested **6a**. Instead, the resemblance with the spiro compound **14** is much better. For example, the P–C(1) bond length of **16b** of 1.85(1) Å is similar to the 1.855(7) Å bond length of **14** but substantially shorter than the 1.967 Å bond length reported for **6a**. The much longer P–C(1) bond of the latter must be attributed to its high degree of substitution, reflecting the repulsion between the two phenyl groups and the *P*-mesityl substituent, as noted by Manz and Maas.¹⁰ The other phosphirane PC bond is in all three cases much shorter than the P–C(1) bond. For **16b** this difference is a significant 0.07 Å (4%). This shorter P–C(2) bond of **16b** of 1.776(8) Å is within experimental uncertainties the same as in **6a** and **14**, and deviates little, if any, from those reported for $\text{W}(\text{CO})_5$ -complexed phosphiranes (ca. 1.81 Å) and phosphirenes (ca. 1.79 Å).^{8b,17b} Thus, while the difference in hybridization contributes to the difference in lengths between the $\text{P}(\text{sp}^3)-\text{C}(1)(\text{sp}^3)$ and $\text{P}(\text{sp}^3)-\text{C}(2)(\text{sp}^2)$ bonds, this effect appears to be rather small. Evidently, the phosphirane P–C(1) bond is elongated. Additional strain resulting from the distal olefinic bond is the likely

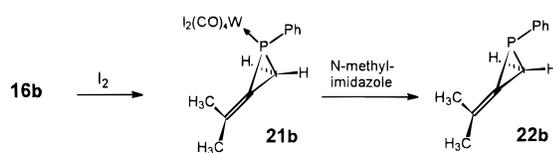
cause of this effect; noteworthy is the similar influence of the cyclopropyl ring. Small differences in the phosphirane CC bond may suggest a conjugative effect with the exocyclic double bond. Thus, the C(1)–C(2) bond of **16b** of only 1.47(1) Å is shorter than those of both **6a** and **14**, albeit that the differences fall within the error margins.^{8b,23} However, the 1.31(1) Å short double bond of **16b** would argue against such an electronic effect.

Because of its simple substitution pattern, **16b** shows no signs of steric distortion, which sets it apart not only from **6a** but also from the sterically congested methylenediphosphiranes **8** and **9**. For example, structure **9** has a 2-fold axis, and the exocyclic =CCl₂ group of structure **8** is twisted by 20.4°. Also the phenyl rings of **8** are deformed into boat forms which underscores the presence of significant steric strain. Methylenephosphirane **6a** shows a similar twisting of the double bond; *i.e.*, the C(1)–C(2)–C(3)–C(4) torsion angle is 26.9(6)°. In sharp contrast, the isopropylene group (C(3), C(4), and C(5)) of structure **16b** is within 1.1° coplanar with the phosphirane ring, and the *P*-phenyl ring is planar within 1.8°.

These geometrical comparisons indicate that the phosphirane rings of **16b** and spirophospha[2.2]pentane **14** are surprisingly similar, which may suggest these systems to have similar ring strain as well.

The ³¹P NMR chemical shifts, which are a sensitive electronic probe, also suggest similarity between the methylenephosphiranes **16a** and **16b** and spirophospha[2.2]pentane **14**. The slightly more shielded chemical shifts of **16a** ($\delta = -164.9$ ppm) and **16b** ($\delta = -162.4$ ppm) may suggest a marginally smaller CPC angle as in **14** ($\delta = -154.8$ ppm).^{8b,27} The X-ray structures point in the same direction (47.8(4)° for **16b**), but the differences are within the error margins.

Demetalation. Emboldened by the chemical stability of **16b**, we attempted decomplexation of its W(CO)₅ group.²⁸ Successive addition of iodine at –30 °C in the dark, and monitoring of the reaction by ³¹P NMR for complete conversion to **21b** ($\delta = -183.3$ ppm), followed by quenching with *N*-methylimidazole yielded after chromatography the parent isopropylidene-phosphirane **22b**, which was characterized by NMR spectro-



scopic methods. The expected reduced stability of this uncomplexed compound is reflected in its slow decomposition at room temperature, but **22b** keeps reasonably well in solution below –10 °C. Maercker and Brieden¹⁶ reported a similar air sensitivity for 2,3-diisopropylidene-1-phenylphosphirane, which is a phosphirane with an exocyclic allene.

The W(CO)₅ decomplexation is clearly reflected in the NMR features. The change in phosphorus coordination is evident from the ³¹P NMR chemical shifts. Thus, decomplexation results in a 39.7 ppm upfield shift of the ³¹P NMR chemical shift from $\delta = -162.4$ ppm for **16b** to $\delta = -202.1$ ppm for **22b**. This resonance is at much higher field than those of the highly substituted methylenephosphiranes **5** ($\delta = -93.4$ ppm) and **6a** ($\delta = -134.5$ ppm), which is in accordance with expectations.

(27) Goldwhite, H.; Rowsell, D.; Vertal, L. E.; Bowers, M. T.; Cooper, M. A.; Manatt, S. L. *Org. Magn. Reson.* **1983**, *21*, 494.

(28) (a) Marinetti, A.; Mathey, F.; Fischer, J.; Mitschler, J. *J. Chem. Soc., Chem. Commun.* **1984**, 45. (b) Marinetti, A.; Fischer, J.; Mathey, J. *F. J. Am. Chem. Soc.* **1985**, *107*, 5001.

Table 2 Absolute (au) and Relative Energies (kcal/mol) of C₃H₅P and C₅H₉P Isomers

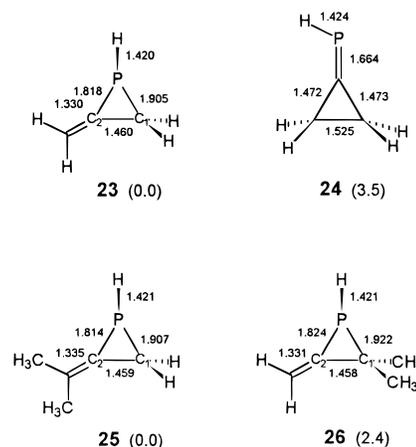
Compd	MP2(fc)/6-31G*	ZPVE ^a	ΔE ^b
23	–457.64570	45.83	0.00
24	–457.63957	46.20	3.52
25	–535.99143	83.52	0.00
26	–535.98761	83.60	2.47

^a Zero-point vibrational energies at HF/6-31G* (kcal/mol). ^b Relative MP2(fc)/6-31G* with inclusion of 0.89-scaled ZPVE.

For comparison, $\delta(^{31}\text{P})$ for the W(CO)₅-complexed triphenylphosphirene is –161.4 and –190.3 ppm for the uncomplexed form.^{28a}

The demetalation is also reflected in the NMR coupling constants. Thus, while **22b** has sizable ¹J_{P–C} couplings of 40.8 Hz for the olefinic carbon and 21.3 Hz for the methylene carbon of the phosphirane ring, the W(CO)₅-complexed parent **16a** and its dimethyl derivative **16b** display an absence of these couplings.^{8b} Such a difference is not unexpected as transition metal complexation significantly reduces the negative ¹J_{P–C} coupling constant due to an increase in the phosphorus coordination number from 3 to 4. In the case of **16a** and **16b** this apparently results in a coincidental absence of ¹J_{P–C} for the ring carbons. The large ¹J_{P–C} coupling constant of 40.8 Hz for the olefinic carbon of uncomplexed **22b** compares well with the 47.6 Hz coupling constant of **6a** and the 43.9 Hz coupling constant in triphenylphosphirene.^{28a} Likewise, the smaller coupling of 21.3 Hz for the methylene carbon in **22b** is similar to the 21.3 Hz coupling reported for the CPh₂ carbon in **6a**.

Theoretical Structures and Stabilities. *Ab initio* quantum mechanical calculations were performed at MP2(fc)/6-31G* for 2-methylenephosphirane (**23**), its isomeric phosphamethylenecyclopropane (**24**), and its dimethyl derivatives **25** and **26**. For



computational simplification, these parent systems have no transition metal complex and the P-atom carries a hydrogen instead of a phenyl substituent. Bachrach¹² has reported earlier on the geometry of **23**, its P–H inversion barrier, and its ring strain energy. The MP2(fc)/6-31G* structures of this species and **24–26** are shown with relative energies (kcal/mol) in parentheses. Absolute and relative energies with 0.89-scaled zero-point vibrational energy (HF) corrections (ZPVE) are listed in Table 2.

All methylenephosphiranes have P–C(1) bonds that are ca. 0.1 Å longer and therefore presumably also weaker than the P–C(2)= bonds in accordance with the X-ray structure of **16b**. The differences between this structure and that calculated for **25** are modest. Both P–C bonds of the experimental structure are shorter by 0.04–0.06 Å, which is mainly attributed to

complexation by the $W(CO)_5$ group and to a lesser extent to *P*-phenyl stabilization.²⁹ The same difference in P–C bond lengths exists between the X-ray structure of the $W(CO)_5$ -complexed phosphirane **13**²³ and the microwave structure³⁰ of the parent phosphirane C_2H_5P . This “tightening” effect in the $W(CO)_5$ -complexed phosphiranes is in line with their remarkable stabilities. The comparison of the phosphirane bond lengths indicates that the observed methylenephosphirane **16b** is not particularly strained. This is also supported by the reported “modest” 30 kcal/mol ring strain energy (HF/6-31G*) for **23**.¹² For phosphirane itself (C_2H_5P) Bachrach¹² reported a ring strain energy of only 20 kcal/mol. For comparison, methylenecyclopropane has a ring strain energy of 37 kcal/mol and cyclopropanone of 26 kcal/mol, and those of methyleneaziridine and aziridine are 39 and 27 kcal/mol, respectively (same level). These energies underscore that the methylenephosphiranes do not need stabilizing substituents to be synthetically accessible. It is also evident that blocking the reactive, tricoordinate phosphorus with a transition metal group limits its reactivity.

2-Isopropylidene phosphirane (**25**) is a modest 2.5 kcal/mol more stable than the isomeric 2,2-dimethyl-3-methylenephosphirane (**26**), which is in line with the observed formation of **16b**. The minor geometrical differences between the two isomers are as expected. Both P–C bonds of structure **25** are shorter than the corresponding ones of its isomer **26**. Introduction of two methyl groups on the ring carbon lengthens the P–C(1) bond by nearly 0.02 Å. It is not surprising that large sterically repulsive, but electronically stabilizing groups, as in **6a**, lengthen this bond even more. Cleavage of the P–C(1) bond would give a phosphatrimethylene biradical from which a phosphamethylenecyclopropane could result. However, this is not a likely event because **24** is 3.5 kcal/mol less stable than **23** at MP2(fc)/6-31G* + ZPE. Dimethyl substitution will not influence this energy difference much.

Conclusions. The important observation of this work is that stable methylenephosphiranes can be synthesized with surprising ease using the carbene-like addition of the phosphinidene complex $Ph-P-W(CO)_5$ to allenes. These additions have been accomplished with the parent allene, and its 1,1-dimethyl and tetramethyl derivatives. The X-ray structure of 2-isopropylidene-1-phosphirane **16b** shows no signs of steric distortion. Its geometrical parameters compare, in fact, well with those of the reported X-ray structure of the $W(CO)_5$ -complexed spirophospha[2.2]pentane **14**. Demetalation of the $W(CO)_5$ group from **16b** was accomplished to give the uncomplexed product **22b**. Theoretical *ab initio* calculations on model systems are in agreement with the experimental data, underscoring the stability of these systems.

This leads to the conclusion that the addition of phosphinidenes to allenes is a convenient and versatile synthetic route to simply substituted, but stable, methylenephosphiranes. It is a welcome alternative method to the carbene-1-phosphaallene and 2-phosphacumulene cyclization routes, both of which are more limited by their accessibility of the phosphorus-containing unsaturated systems.

Experimental Section

NMR spectra were recorded on a Bruker ARX 300, wide-bore spectrometer. Chemical shifts are referenced in parts per million to internal Me_4Si for the ¹H and ¹³C NMR spectra and to external 85% H_3PO_4 for the ³¹P NMR spectra. Downfield shifts are reported as

(29) For example, the P–C bond lengths of triphenylphosphirene (1.8197 Å, X-ray structure)^{28c} are shortened by 0.03–0.05 Å on $W(CO)_5$ complexation (*i.e.*, 1.7901 and 1.7868 Å, X-ray structure).^{17b}

(30) Bowers, M.; Baudet, R. A.; Goldwhite, H.; Tang, R. *J. Am. Chem. Soc.* **1969**, *91*, 17.

positive. Mass spectra were recorded on a HP 5985 at 70 eV. Melting points were determined on an electrothermal melting point apparatus and are uncorrected. Elemental analyses were performed by Atlantic Microlab, Inc., Norcross, GA. All materials were handled under an atmosphere of dry, high-purity nitrogen. Reagents and solvents were used as purchased, except for THF, which was distilled from sodium–benzophenone prior to use, and toluene, which was dried over molecular sieves. Chromatographic separations were performed on silica gel columns (230–400 mesh, EM Science). The synthesis of [5,6-dimethyl-2,3-bis(methoxycarbonyl)-7-phenyl-7-phosphanorbornadiene]pentacarbonyltungsten (**12**) is described in ref 17c.

(2-Methylene-1-phenyl-1-phosphirane)pentacarbonyltungsten (16a). Allene (**15a**) was passed through a 30 mL toluene solution containing complex **12** (0.77 mmol, 0.50 g) and CuCl (30 mg, 0.3 mmol) at 55–60 °C for 2.5 h and monitored by TLC. Following evaporation of the solvent, chromatography of the reaction mixture on silica (hexane–benzene, 4:1) and crystallization of the product gave 210 mg (55%) of **16a** as colorless crystals. Mp: 102–103 °C. ³¹P NMR (C_6D_6): δ = –164.9 (¹*J*_{P–W} = 251.1 Hz). ¹³C NMR (C_6D_6): δ = 197.7 (d, ²*J*_{P–C} = 29.3 Hz, *trans*-CO), 195.7 (d, ²*J*_{P–C} = 7.2 Hz, *cis*-CO), 132.1 (s, *H*₂C=), 131.4 (d, ²*J*_{P–C} = 17.7 Hz, *o*-phenyl), 130.7 (s, *p*-phenyl), 128.9 (m, *m*-phenyl), 121.1 (s, =C–), 18.4 (s, PCH₂). ¹H NMR (C_6D_6): δ = 7.29–6.91 (m, phenyl, 5 H), 5.88 (dm, ³*J*_{P–H} = 13.5 Hz, 1H, =CH₂), 5.76 (dm, ³*J*_{P–H} = 31.5 Hz, 1H, =CH₂), 1.51 (d, ²*J*_{H–H} = 12.0 Hz, 1H, PCH₂), 1.29–1.33 (m, 1H, PCH₂).

(2-Isopropylene-1-phenyl-1-phosphirane)pentacarbonyltungsten (16b). Complex **12** (1 mmol, 0.64 g) and a 3–4-fold excess of 1,1-dimethylallene (**15b**) were heated at 55–60 °C in 5 mL of benzene with CuCl (10 mg, 0.1 mmol) for 2 h in a sealed autoclave to give after workup a yield of 385 mg (77%) of **16b** as colorless crystals. Mp: 84–86 °C. ³¹P NMR (C_6D_6): δ = –162.4 (¹*J*_{P–W} = 252.0 Hz). ¹³C NMR (C_6D_6): δ = 198.0 (d, ²*J*_{P–C} = 29.5 Hz, *trans*-CO), 195.7 (d, ²*J*_{P–C} = 6.9 Hz, *cis*-CO), 142.8 (s, Me₂C=), 134.3 (d, ¹*J*_{P–C} = 23.8 Hz, *P*-phenyl), 131.3 (d, ²*J*_{P–C} = 13.8 Hz, *o*-phenyl), 130.4 (s, *p*-phenyl), 128.8 (³*J*_{P–C} = 9.9 Hz, *m*-phenyl), 116.4 (s, Me₂C=C–), 25.0 (d, ³*J*_{P–C} = 3.3 Hz, CH₃), 23.3 (d, ³*J*_{P–C} = 8.4 Hz, CH₃), 17.9 (s, PCH₂). ¹H NMR: δ = 7.37–7.3 and 6.96–6.93 (m, phenyl, 5 H), 1.86 (d, ⁴*J*_{P–H} = 2.7 Hz, CH₃), 1.62 (d, ⁴*J*_{P–H} = 3.0 Hz, CH₃), 1.60–1.53 (m, 1H) and 1.44–1.37 (m, 1H, CH₂). MS (¹⁸⁴W): *m/z* (rel intens) 500 (M, 21.1), 444 (M – 2CO, 18.0), 416 (M – 3CO, 19.9), 388 (M – 4CO, 25.9), 376 (PhPW(CO)₃, 4.2), 360 (M – 5CO, 93.6), 348 (PhPW(CO)₂, 50.4), 320 (PhPW(CO), 46.9), 292 (PhPW, 100). Anal. Calcd for C₁₆H₁₃PWO₅: C, 38.41; H, 2.60. Found: C, 38.50; H, 2.62.

(2-Isopropylene-3,3-dimethyl-1-phenyl-1-phosphirane)pentacarbonyltungsten (16c). Complex **12** (1 mmol, 0.65 g) and tetramethylallene (**15c**) (1 mmol, 0.09 g) were heated at 45–50 °C in 20 mL of toluene with CuCl (100 mg) under an atmosphere of nitrogen for 1 h to give after workup 430 mg (58%) of a 1:1 isomeric mixture of **16c**, **19a**, and **19b**, as determined by their ³¹P NMR chemical shifts at δ = –134.8 (¹*J*_{P–W} = 245 Hz), –137.4 (¹*J*_{P–W} = 255.0 Hz), and –142.5 (¹*J*_{P–W} = 255.0 Hz) ppm, respectively. After chromatography **16c** was obtained as a colorless oil. ³¹P NMR ($CDCl_3$): δ = –134.8 (¹*J*_{P–W} = 245.0 Hz). ¹³C NMR ($CDCl_3$): δ = 195.0 (d, ²*J*_{P–C} = 12.1 Hz, *cis*-CO), 125.9 (s, C=), 124.2 (d, ¹*J*_{P–C} = 7.7 Hz, PC=), 127.1–131.4 (m, Ph), 29.3 (m, CH₃), 24.3 (m, CH₃), 21.9 (s, CH₃), 19.1 (d, ¹*J*_{P–C} = 45.9 Hz, PCMe₂). ¹H NMR ($CDCl_3$): δ = 7.54–7.20 (m, Ph, 5H), 2.12 (s, CH₃, 3H), 1.85 (d, ³*J*_{P–H} = 13.5 Hz, CH₃, 3H), 1.50 (m, CH₃, 3H), 1.16 (d, ³*J*_{P–H} = 10.7 Hz, CH₃, 3H).

(2-(1'-Isobutylene)-2-methyl-1-phenyl-1-phosphirane)pentacarbonyltungsten (19a). Complex **12** (1 mmol, 0.65 g) and 2,4-dimethylpenta-2,3-diene (**15e**) (2 mmol, 0.18 g) were heated at 55 °C in 20 mL of toluene with CuCl (100 mg) under an atmosphere of nitrogen for 1 h to give after workup 430 mg (58%) of a 1:1 isomeric mixture of **19a** and **19b**, as determined by their ³¹P NMR chemical shifts at δ = –137.4 and –142.5, respectively. After chromatography and crystallization **19a** was obtained as a colorless oil. ³¹P NMR ($CDCl_3$): δ = –137.4 (¹*J*_{P–W} = 258.6 Hz). ¹³C NMR ($CDCl_3$): δ = 196.4 (d, ²*J*_{P–C} = 8.0 Hz, *cis*-CO), 140.5 (d, ³*J*_{P–C} = 10.1 Hz, C=), 127.4 (s, CH=), 129.1–132.8 (m, Ph), 30.6 (d, ¹*J*_{P–C} = 17.4 Hz, CH₂), 25.8 (t, ¹*J*_{P–C} = 11.0 Hz, C), 25.9 (m, CH₃), 23.3 (s, CH₃), 20.4 (s, CH₃). ¹H NMR ($CDCl_3$): δ = 7.40–7.15 (m, Ph, 5H), 5.15 (d, ³*J*_{P–H} = 12.8 Hz, CH=), 1.83 (s, CH₃, 3H), 1.67 (d, ⁴*J*_{H–H} = 4.41 Hz, CH₃,

3H), 1.47 (d, $^3J_{P-H} = 19.8$ Hz, CH₂, 1H), 1.43 (d, $^3J_{P-H} = 29.9$ Hz, CH₂, 1H), 1.10 (d, $^3J_{P-H} = 11.8$ Hz, CH₃, 3H).

(2,2,4-Trimethyl-1-phenyl-3-phospholene)pentacarbonyl tungsten (20). Monitoring of the reaction of **15c** with complex **12** at 45 °C using ^{31}P NMR showed the appearance not only of $\delta = -134.8$ ppm (**16c**) but also of two additional resonances at $\delta = -137.4$ ($^1J_{P-W} = 255$ Hz) and -142.5 ppm ($^1J_{P-W} = 255$ Hz) (**19a,b**). On continued heating **19a,b** disappeared with the simultaneous emergence of a resonance at $\delta = 40.0$ ppm ($^1J_{P-W} = 231$ Hz) (**20**). This phospholene **20** was separated by preparative thin layer chromatography. ^{31}P NMR (CDCl₃): $\delta = 40.0$ ($^1J_{P-W} = 230.6$ Hz). ^{13}C NMR (CDCl₃): $\delta = 198.9$ (d, $^2J_{P-C} = 21.7$ Hz, *trans*-CO), 197.1 (d, $^2J_{P-C} = 7.1$ Hz, *cis*-CO), 135.9 (s, =C-CH₃), 135.6 (d, $^3J_{P-C} = 5.1$ Hz, =C-H), 134.6 (d, $^1J_{P-C} = 30.3$ Hz, ipso-Ph), 131.7 (d, $^2J_{P-C} = 10.2$ Hz, *o*-Ph), 129.9 (d, $^4J_{P-C} = 1.9$ Hz, *p*-Ph), 128.1 (d, $^3J_{P-C} = 8.8$ Hz, *m*-Ph), 48.2 (d, $^1J_{P-C} = 22.7$ Hz, C), 39.2 (d, $^1J_{P-C} = 27.8$ Hz, CH₂), 29.2 (d, $^2J = 15.4$ Hz, CH₃), 24.2 (s, CH₃), 18.7 (d, $^3J_{P-C} = 5.5$ Hz, =C-CH₃). ^1H NMR (CDCl₃): $\delta = 7.72-7.12$ (m, Ph, 5H), 5.17 (d, $^3J_{P-H} = 16.9$ Hz, CH=), 3.10 (m, CH₂), 1.93 (s, CH₃, 3H), 1.44 (d, $^3J_{P-H} = 28.4$ Hz, CH₃, 3H), 0.86 (d, $^3J_{P-H} = 12.9$ Hz, CH₃, 3H).

2-Isopropylene-1-phenyl-1-phosphirane (22b). To a stirred solution of complex **16b** (0.5 mmol, 250 mg) in 10 mL of CHCl₃ was added dropwise an equimolar amount of iodine in 10 mL of CHCl₃ at -30 °C in the dark over 1 h. The reaction was followed by ^{31}P NMR spectroscopy to minimize excess of iodine and to verify completion of the reaction to the W(CO)₄I₂ complex **21b**. ^{31}P NMR (C₆D₆): $\delta = -183.3$ ($^1J_{P-W} = 173.2$ Hz). The reaction mixture was allowed to warm to room temperature, and a 6-fold excess of *N*-methylimidazole was added over 5 min, after which the reaction mixture was chromatographed over silica with hexane to yield 48 mg (54%) of **22b** as a light yellow oil. ^{31}P NMR (CDCl₃): $\delta = -202.1$. ^{13}C NMR (CDCl₃): $\delta = 139.1$ (d, $^1J_{P-C} = 40.8$ Hz, *P*-phenyl), 136.0 (d, $^2J_{P-C} = 9.2$ Hz, Me₂C=), 131.8 (d, $^2J_{P-C} = 19.5$ Hz, *o*-phenyl), 128.5 (s, *p*-phenyl), 128.2 (d, $^3J_{P-C} = 5.2$ Hz, *m*-phenyl), 120.5 (d, $^1J_{P-C} = 40.8$ Hz, Me₂C=C-), 24.6 (s, CH₃), 23.8 (s, CH₃), 15.7 (d, $^1J_{P-C} = 21.3$ Hz, PCH₂). ^1H NMR (CDCl₃): $\delta = 7.37-7.14$ (m, phenyl, 5 H), 1.97 (s, CH₃), 1.93 (s, CH₃), 1.69-1.61 (m, 1H) and 1.34-1.16 ppm (m, 1H, CH₂). MS (^{184}W): *m/z* (rel intens) 176 (M, 44.9), 161 (M - CH₃, 54.7), 134 (M - C₃H₆, 100), 107 (PC₆H₄, 80.7).

Crystal Structure Analysis of 16b. C₁₆H₁₅O₅PW, *M* = 500.10, crystal size 0.28 × 0.56 × 0.15 mm, monoclinic, space group *P2*₁/*c*, *a* = 15.151(1) Å, *b* = 6.947(5) Å, *c* = 17.791(2) Å, $\beta = 104.276(8)^\circ$, *V* = 1814.8(3) Å³, *Z* = 4, $\rho_{\text{calc}} = 1.830$ g·cm⁻³, 4135 unique reflections were measured on an Enraf-Nonius CAD4 diffractometer (Ni-filtered monochromatized Cu K α radiation ($\lambda = 1.5418$ Å)) using an $\omega/2\theta$ scan mode (scan width 1.14°, background/scan ratio 0.5) up to $2\theta =$

148°, with index ranges $-18 \leq h \leq 18$, $-8 \leq k \leq 0$, $0 \leq l \leq 22$; 3272 were observed with $I > 3\sigma(I)$, abs coeff = 129.746 cm⁻¹, 209 parameters. The data manipulation and structure solution were carried out using the Enraf-Nonius MolEN software. Intensities were corrected for Lorentz and polarization effects; no decay was observed, and an empirical absorption correction ($T_{\text{max}} = 99.35\%$, $T_{\text{min}} = 42.25\%$) was applied. Variances were assigned on the basis of standard counting statistics, with the addition of an instrumental uncertainty term, $0.04F_o^2$. The structure was solved by standard Patterson and difference Fourier techniques and refined by weighted full-matrix least squares. The final model contains anisotropic thermal parameters for all non-hydrogens, and isotropic hydrogen atoms in calculated positions riding on their attached carbon atoms. The final difference Fourier map contained maximum $\Delta\rho$ values near the W atom ($\Delta\rho_{\text{max}} = 0.741$, $\Delta\rho_{\text{min}} = -0.400$), with no peaks interpretable as extra atoms. Final *R* = 5.54%, *R_w* = 7.69%, GOF = 2.526, $\Delta/\sigma_{\text{max}} = 0.00$.

Computational Methods. The *ab initio* calculations³⁰ were carried out using the GAUSSIAN 92 and 94 suite of programs.³¹ Geometries **23-26** were optimized at the SCF level with the d-polarized split-valence 6-31G* basis set and with inclusion of the effects of valence electron correlation by using Møller-Plesset perturbation theory at second order (MP2(fc)). The force constant matrices, vibrational harmonic frequencies, and zero-point vibrational energies (ZPVE) were calculated analytically for the HF-optimized geometries. All structures are minima, characterized by real frequencies only.

Acknowledgment is made to the National Science Foundation (Grant CHE-9500344) and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this study.

Supporting Information Available: Positional and thermal parameters and a complete listing of bond lengths and angles for **16b** (10 pages). See any current masthead page for ordering and Internet access instructions.

JA971340W

(31) Hehre, W. J.; Radom, L.; Schleyer, P. v. R.; Pople, J. A. *Ab Initio Molecular Orbital Theory*, Wiley: New York, 1986.

(32) GAUSSIAN 92, Revision B; GAUSSIAN 94, Revision B.1: Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Gill, P. M. W.; Johnson, B. G.; Robb, M. A.; Cheeseman, J. R.; Keith, T.; Petersson, G. A.; Montgomery, J. A.; Raghavachari, K.; Al-Laham, M. A.; Zakrzewski, V. G.; Ortiz, J. V.; Foresman, J. B.; Cioslowski, J.; Stefanov, B. B.; Nanayakkara, A.; Challacombe, M.; Peng, C. Y.; Ayala, P. Y.; Chen, W.; Wong, M. W.; Andres, J. L.; Replogle, E. S.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Binkley, J. S.; Defrees, D. J.; Baker, J.; Stewart, J. P.; Head-Gordon, M.; Gonzalez, C.; Pople, J. A., Gaussian, Inc., Pittsburgh, PA, 1995.