Dihydropyridines in Organometallic Synthesis. Formation of Pyridine and Dihydropyridine-Stabilized Alkylidene Complexes of Tungsten(0) and Chromium(0) from Fischer Carbene Complexes: Structure and Reactivity

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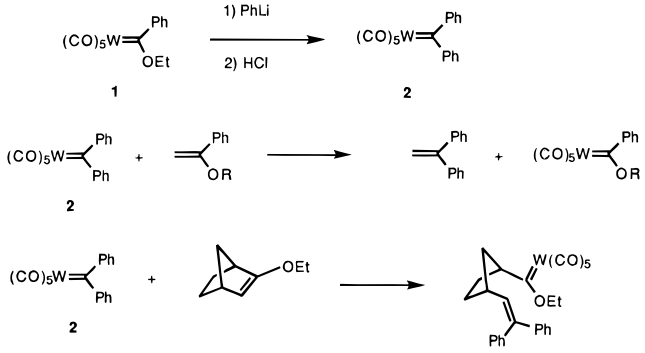
Abstract: 1,2- and 1,4-dihydropyridines react with alkoxycarbene complexes of chromium and tungsten to give, upon an unprecedented hydride transfer, alcohol elimination, and pyridine fixation on the carbene carbon, a new class of air-stable pyridinium ylide complexes. These pyridine-protected alkylidene complexes of chromium(0) and tungsten(0) were fully characterized by X-ray crystallography. In the case of $(CO)_5W{=}C(CH_3)(OEt)$ (**5a**), besides the pyridinium ylide complex $(CO)_5W^-{-}C(H)(CH_3)(pyridine)^+$ (**7a**), the dihydropyridinium complex $(CO)_5W^-{-}C(H)(CH_3)(2,5\text{-dihydropyridine})^+$ (**8a**) was also isolated. The intermediate tungstate $(CO)_5W^-{-}C(H)(CH_3)(OEt)(CH_3\text{-}NC_5H_5)^+$ could be easily obtained and characterized by using, as reducing agent, *N*-methyldihydropyridine. Whereas phenyl-substituted pyridinium complexes easily transferred the benzylidene moiety to alkenes, alkyl-substituted complexes appeared more reluctant to such a transfer: satisfactory results were observed in the case of nucleophilic olefins such as enol ethers. However, straightforward transfer of the tungsten(0) alkylidene group took place, even at room temperature, in the case of alkoxycarbene complexes tethered to alkenes, giving access, upon intramolecular cyclopropanation reactions, to polycyclic systems.

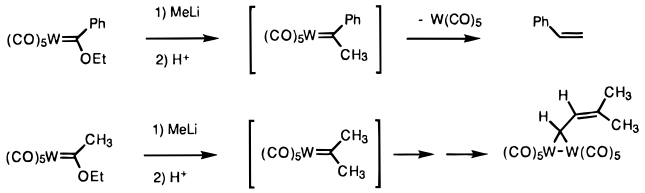
Introduction

Whereas methylene transfer had been observed by Fischer and co-workers as early as 1972 during the interaction of heteroatom-substituted carbene complexes with α,β-unsaturated esters and vinyl ethers,[1] the first alkylidene complex which mimicked both the metathesis and the cyclopropanation reactions of linear and cyclic olefins in a way consistent with the mechanistic proposal of Chauvin for these reactions was described in 1973 by Casey and had structure **2** (Scheme 1).[2−7] This tungsten(0) complex was obtained by successive treatment of $(CO)_5WC(OEt)Ph$ (**1**) with phenyllithium and an acid at low temperature and appeared to be less stable than its precursor **1**. A slightly modified method gave, later on, access to a series of diarylcarbene complexes of chromium and tungsten.[8] Attempts to synthesize and isolate other simple metal(0) alkylidene complexes of this type either failed due to fast β-elimination reactions or led to unexpected dinuclear complexes (Scheme 2).[9−11] However, a benzylidene complex, **3**, of W(0) (and later of Cr(0)) could be prepared in a two-step process by reacting successively $(CO)_5WC(OEt)Ph$ (**1**) with a complex hydride, $KHB(OiPr)_3$, and an acid.[12−17] Due to its unstability, complex

Scheme 1



Scheme 2



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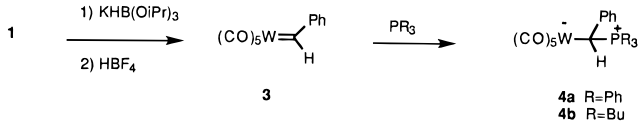
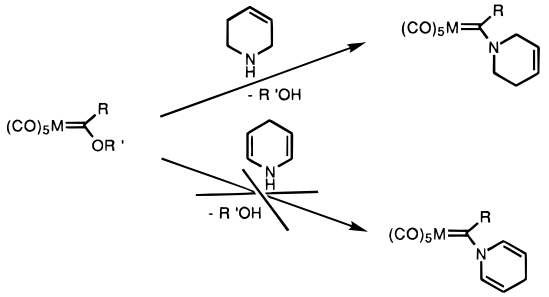
3 could only be handled at low temperature (−80 to −20 °C). Its reaction with phosphines led however to stable phosphorus ylides **4a**,**b**. Whereas **2** reacted with olefins to give both metathesis and cyclopropanation products, complex **3** only led to phenylcyclopropanes.



During the course of our investigations on the insertion of alkynes into aminocarbene complexes of chromium, tungsten, and molybdenum,[18−20] we were led to study, for the synthesis of the starting aminocarbene complexes, the aminolysis of alkoxycarbene complexes of these metals with *inter alia* unsaturated amines (Scheme 3). In the general case, no

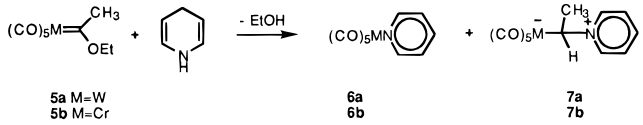
Scheme 3



problems were expected and indeed encountered during these attempts. However, in the special case of dihydropyridines, the reducing properties of which are well known both in biological systems and in classical organic chemistry,[21,22] no substitution of the alkoxy group by the amine took place. Instead, a new reaction linked to these reducing properties led to pyridine[23] and dihydropyridine-stabilized alkylidene complexes. The purpose of this paper is to describe on the one hand the interaction of a series of dihydropyridines with various alkoxycarbene complexes of tungsten and chromium, demonstrating the general scope of the reaction. On the other hand, the possible use of these complexes as stable cyclopropanation reagents and of the aforementioned reduction reaction for the direct intramolecular cyclopropanation reaction of alkene−alkoxycarbene complexes will be outlined.

Results and Discussion

Synthesis and Structure of Methyl-Substituted Pyridinium and Dihydropyridinium Ylide Complexes. When a yellow ethereal solution of $(CO)_5WC(OEt)CH_3$ (**5a**) was treated at 0 °C with a freshly prepared solution of pure 1,4-dihydropyridine in diethyl ether,[24] a deep-red color developed rapidly. After a few minutes complete consumption of the starting material and formation of two new complexes were observed. The faster moving yellow complex was assigned as structure **6a** on the grounds of its elemental analysis and its spectroscopic data. The ^{1}H NMR spectrum showed signals for only five aromatic protons of the pyridine ring system slightly shifted with respect to those of free pyridine (at δ 8.83 for 2H, 7.79 for 1H, and 7.28 for 2H vs δ 8.60, 7.64, and 7.64 ppm). Both the infrared and the ^{13}C NMR spectra confirmed the presence of the (pentacarbonyl)-tungsten(0) group (ν(CO) 2060, 1970, and 1930 cm^{-1}; δ(CO) 202.35 and 199.47 ppm).



The most striking feature of the ^{1}H NMR spectrum of the more polar complex **7a**, isolated in 66% yield as an orange solid, was the absence of signals due to the alkoxy group of the starting complex, an observation which confirmed that indeed a substitution reaction took place. However, no signals due to the protons of dihydropyridine were observed. Instead, signals due to the pyridine ring system were again present at δ 8.56 (2H, d), 7.85 (1H, t), and 7.63 (2H, t) ppm, thus only slightly different from the signals of free pyridine (Figure 1). Moreover, two signals for one proton at δ 4.91 ppm as a quartet and at δ 2.37 ppm for three protons as a doublet were attributable to a CHMe group. Confirmation of this and of the presence of a $W(CO)_5$ group was again obtained by infrared and ^{13}C NMR spectroscopies, with signals at δ 57.1 and 30.7 ppm giving, respectively, a doublet and a quartet in the off-resonance mode. Thus, hydride transfer from dihydropyridine to the carbene carbon with elimination of ethanol, together with addition of pyridine to the complex, took place. A similar result was observed starting instead from pure 1,2-dihydropyridine.

X-ray Structure of $(CO)_5WC(H)Me$(pyridine) (7a). The structure of this new complex was ascertained by an X-ray crystallographic study and appears in Figure 2 where the atom numbering scheme is also defined. The bond lengths (Å) and bond angles (deg) for this complex are presented in Tables 1 and 2. Structure **7a** consists of the pyridinium ylide of ethylidene and five CO ligands octahedrally coordinated to tungsten, the organic ligand being perpendicular to the plane defined by the equatorial carbonyl groups. The ethyl carbon(1)−tungsten bond length of **7a** is 2.32(2) Å, thus longer than the 2.28(1) Å benzilic carbon−metal single bond in $Cp_2W(CH_2Ar)_2$[25] but similar to the 2.34(1) Å carbon−metal bond in $(CO)_5W^--CH(Ph)(OMe)N(CH_2CH_3)_4^+$, the addition product of a hydride to complex **1**.[26] The angle between the axis of the pyridine ring and the axis of the W−C(1)−N(1) plane is equal to 161°, the methyl group being 0.63 Å beneath this latter plane. The geometry around C(1) corresponds to that of a deformed sp^3 hybridized carbon.

X-ray Structure of $(CO)_5WC(H)Me$(2,5-dihydropyridine) (8a). When however an excess of a mixture of 1,2- and 1,4-dihydropyridines was used (as obtained by sodium borohydride reduction of *N*-(methoxycarbonyl)pyridinium chloride),[24] a second complex, **8a**, slightly less polar than **7a**, could be

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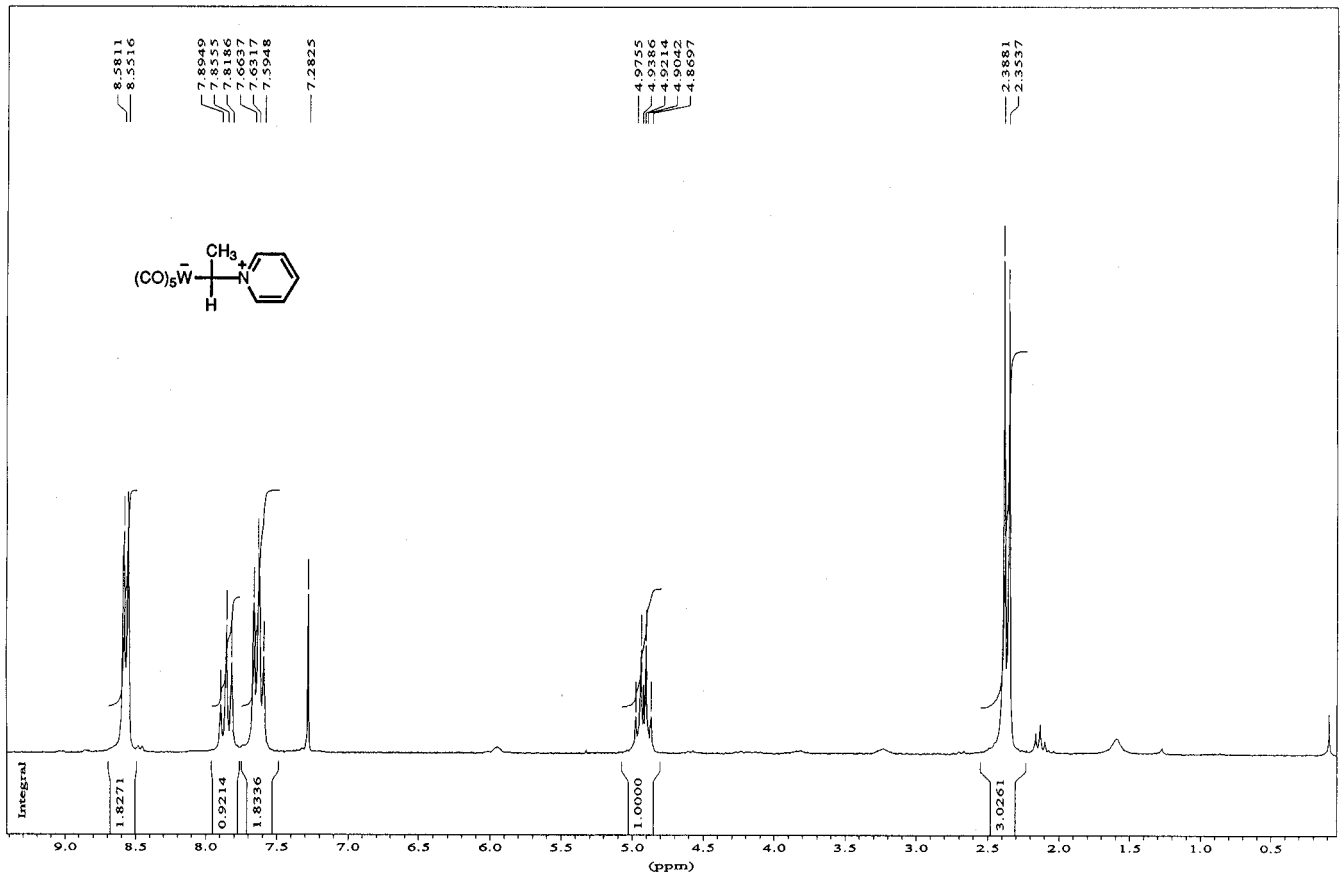


Figure 1. ^{1}H NMR spectrum ($CDCl_3$) of complex **7a**.

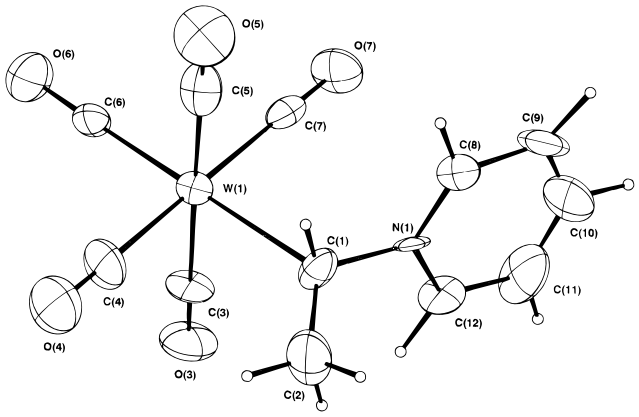


Figure 2. Perspective view and numbering scheme for $(CO)_5W^-$−C(H)$(CH_3)(C_5H_5N)^+$ (**7a**).

Table 1. Bond Distances (Å) for Complex **7a**

W(1)−C(1)	2.32(2)	W(1)−C(3)	1.99(2)
W(1)−C(4)	2.02(2)	W(1)−C(5)	2.05(2)
W(1)−C(6)	1.93(2)	W(1)−C(7)	2.02(2)
O(3)−C(3)	1.14(2)	O(4)−C(4)	1.12(2)
O(5)−C(5)	1.11(2)	O(6)−C(6)	1.18(2)
O(7)−C(7)	1.13(2)	N(1)−C(1)	1.49(2)
N(1)−C(8)	1.27(2)	N(1)−C(12)	1.36(2)
C(1)−C(2)	1.35(3)	C(8)−C(9)	1.43(4)
C(9)−C(10)	1.35(5)	C(10)−C(11)	1.30(4)
C(11)−C(12)	1.36(3)		

detected by TLC. Careful silica gel chromatography of the reaction mixture gave pure samples of this new complex which upon recrystallization led to crystals suitable for an X-ray structure determination. The ^{1}H NMR spectrum (Figure 3) confirmed again the presence as for complex **7a** of the CHMe group with a multiplet at δ 3.80 and a doublet at δ 2.11 ppm and the absence of the ethoxy group of the starting complex **5a**. Moreover, signals for seven protons appeared at δ 7.81 (br s), 5.91 (m, 2H), 4.90 (dt, 1H), 4.18 (dt, 1H), and 3.20 (m, 2H) ppm, a set compatible with that expected for a dihydropyridine. The observation of a broad singlet at low field agreed with the presence of a proton linked to an imine −N=C(H) function: thus, two methylene groups and a disubstituted double bond had to complete the dihydropyridine frame. Extensive irradiation experiments allowed the signals at δ 4.86, 4.17, and 3.20 ppm to be assigned to the two methylene groups and those at δ 5.90 ppm to the olefinic protons.

The structure of this unexpected complex is shown in Figure 4, the bond distances (Å) and the bond angles (deg) being gathered in Tables 3 and 4. It consists of the 2,5-dihydropyridinium ylide of ethylidene coordinated to (pentacarbonyl)-

Table 2. Bond Angles (deg) for Complex **7a**

C(1)−W(1)−C(3)	90.1(9)	C(1)−W(1)−C(4)	88.5(8)
C(3)−W(1)−C(4)	90.3(12)	C(1)−W(1)−C(5)	88.8(9)
C(3)−W(1)−C(5)	178.8(8)	C(4)−W(1)−C(5)	89.6(12)
C(1)−W(1)−C(6)	178.9(8)	C(3)−W(1)−C(6)	91.0(10)
C(4)−W(1)−C(6)	91.1(8)	C(5)−W(1)−C(6)	90.2(10)
C(1)−W(1)−C(7)	90.8(6)	C(3)−W(1)−C(7)	90.4(9)
C(4)−W(1)−C(7)	179.0(10)	C(5)−W(1)−C(7)	89.7(9)
C(6)−W(1)−C(7)	89.6(7)	C(1)−N(1)−C(8)	122.6(16)
C(1)−N(1)−C(12)	117.4(15)	C(8)−N(1)−C(12)	119.6(16)
W(1)−C(1)−N(1)	112.3(9)	W(1)−C(1)−C(2)	122.8(16)
N(1)−C(1)−C(2)	116.3(16)	W(1)−C(3)−O(3)	178.6(22)
W(1)−C(4)−O(4)	178.3(34)	W(1)−C(5)−O(5)	178.8(24)
W(1)−C(6)−O(6)	178.7(20)	W(1)−C(7)−O(7)	178.9(19)
N(1)−C(8)−C(9)	122.8(23)	C(8)−C(9)−C(10)	113.6(22)
C(9)−C(10)−C(11)	125.0(29)	C(10)−C(11)−C(12)	118.0(27)
N(1)−C(12)−C(11)	120.7(20)		

(26) Casey, C. P.; Polichnowsky, S. T.; Tuinstra, H. E.; Albin, L. D.; Calabrese, J. C. *Inorg. Chem.* **1978**, *17*, 3045.

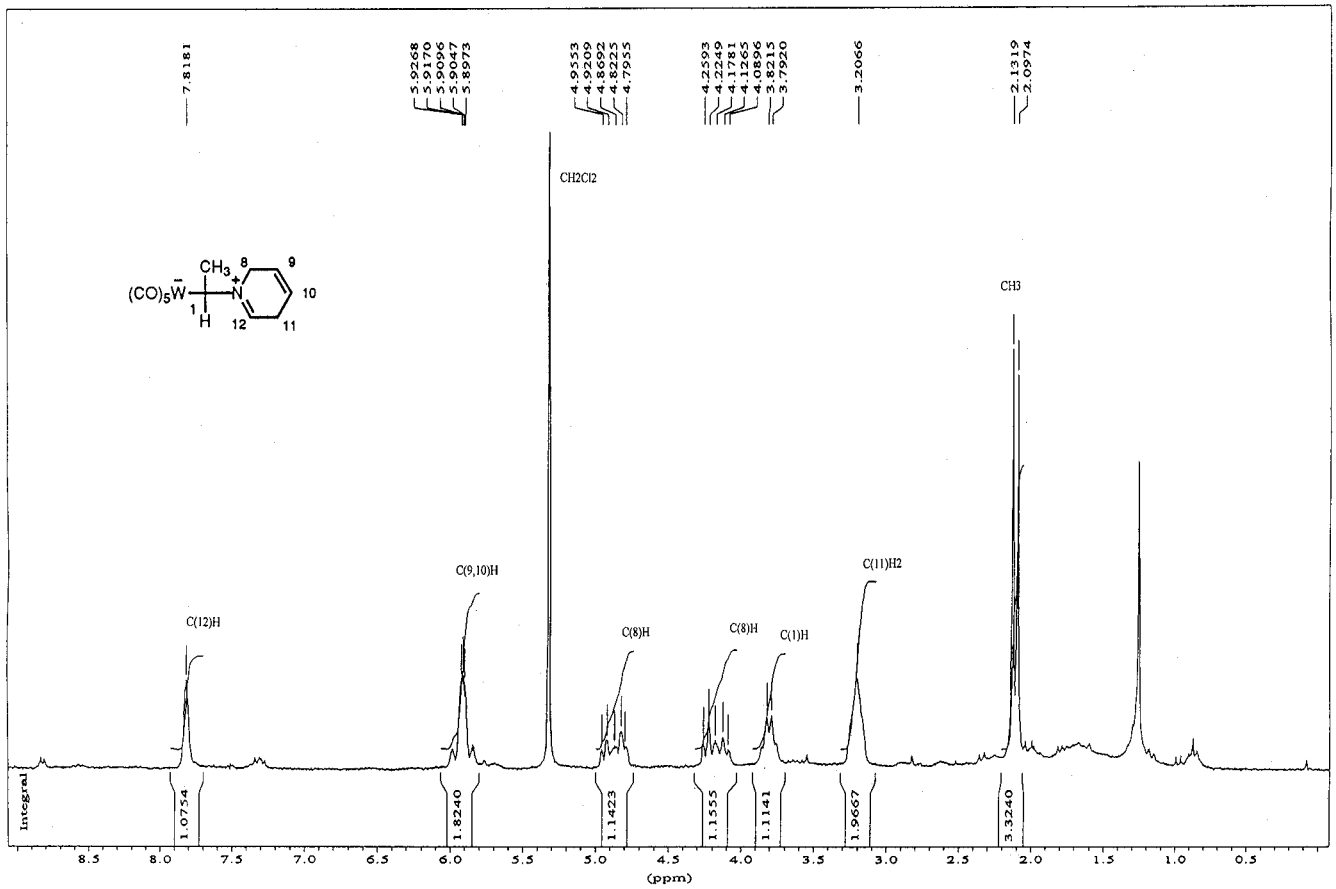


Figure 3. ^{1}H NMR spectrum (CD_2Cl_2) of complex **8a**.

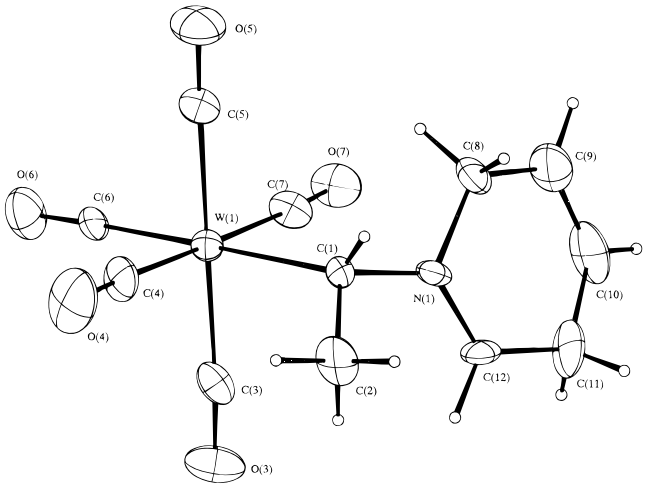


Figure 4. Perspective view and numbering scheme for $(CO)_5W^-$−$C(H)(CH_3)(C_5H_7N)^+$ (**8a**).

tungsten(0). Both the geometry around C(1) and the bond distances W−C(1) and C(1)−N(1) are very close to those observed for complex **7a**. The main difference is due to the presence in complex **8a** of two methylene groups in the α and δ positions with respect to the nitrogen atom: whereas perfect flatness is observed in the case of the pyridinium derivative **7a** (Figure 5a), a slightly twisted conformation of the dihydropyridinium ring system appears in the projection shown in Figure 5b, the C(8) and C(11) methylene groups being slightly below the N(1), C(9), C(10), C(11), and C(12) best plane. The bond distances N(1)−C(8) (1.46(2) Å), C(8)−C(9) (1.52(3) Å), C(12)−C(11) (1.44(3) Å), and C(11)−C(10) (1.46(4) Å) agree with those of carbon−nitrogen and carbon−carbon single bonds

Table 3. Bond Distances (Å) for Complex **8a**

W(1)−C(1)	2.34(2)	W(1)−C(3)	1.98(2)
W(1)−C(4)	2.01(2)	W(1)−C(5)	1.99(2)
W(1)−C(6)	1.94(2)	W(1)−C(7)	2.02(2)
O(3)−C(3)	1.17(3)	O(4)−C(4)	1.18(2)
O(5)−C(5)	1.16(2)	O(6)−C(6)	1.16(2)
O(7)−C(7)	1.18(2)	N(1)−C(1)	1.54(2)
N(1)−C(8)	1.46(2)	N(1)−C(12)	1.32(2)
C(1)−C(2)	1.48(2)	C(8)−C(9)	1.52(3)
C(9)−C(10)	1.37(4)	C(10)−C(11)	1.46(4)
C(11)−C(12)	1.44(3)		

Table 4. Bond Angles (deg) for Complex **8a**

C(1)−W(1)−C(3)	89.1(9)	C(1)−W(1)−C(4)	87.8(7)
C(3)−W(1)−C(4)	92.3(11)	C(1)−W(1)−C(5)	91.5(8)
C(3)−W(1)−C(5)	178.4(8)	C(4)−W(1)−C(5)	89.2(11)
C(1)−W(1)−C(6)	176.9(8)	C(3)−W(1)−C(6)	91.5(10)
C(4)−W(1)−C(6)	89.1(9)	C(5)−W(1)−C(6)	88.0(10)
C(1)−W(1)−C(7)	93.7(7)	C(3)−W(1)−C(7)	88.4(10)
C(4)−W(1)−C(7)	178.3(9)	C(5)−W(1)−C(7)	90.1(9)
C(6)−W(1)−C(7)	89.3(8)	C(1)−N(1)−C(8)	110.3(15)
C(1)−N(1)−C(12)	124.3(16)	C(8)−N(1)−C(12)	124.2(16)
W(1)−C(1)−N(1)	109.2(11)	W(1)−C(1)−C(2)	116.6(13)
N(1)−C(1)−C(2)	109.2(16)	W(1)−C(3)−O(3)	176.1(24)
W(1)−C(4)−O(4)	177.9(21)	W(1)−C(5)−O(5)	177.3(23)
W(1)−C(6)−O(6)	177.8(23)	W(1)−C(7)−O(7)	176.8(20)
N(1)−C(8)−C(9)	112.3(22)	C(8)−C(9)−C(10)	117.3(24)
C(9)−C(10)−C(11)	125.1(24)	C(10)−C(11)−C(12)	113.2(22)
N(1)−C(12)−C(11)	121.9(20)		

whereas N(1)−C(12) (1.32(2) Å) and C(9)−C(10) (1.37(4) Å) are compatible with carbon−nitrogen and carbon−carbon double bonds. This is confirmed by the values of the bond angles at C(8) (112.3(22)), C(9) (117.3(23)), C(10) (125.1(24)), C(11) (113.2(22)), and C(12) (121.9(20)) and the sum of the angles at N(1) (358.9°).

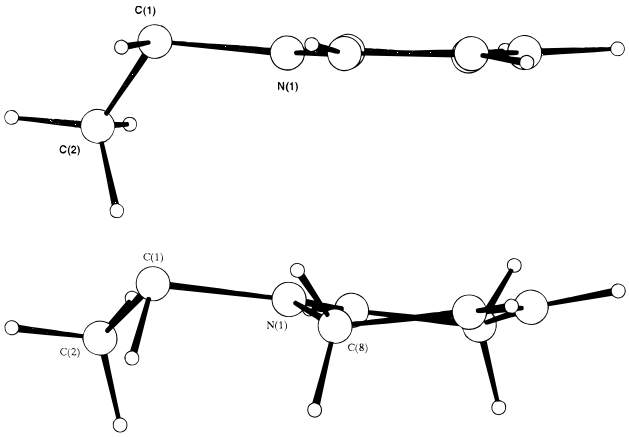
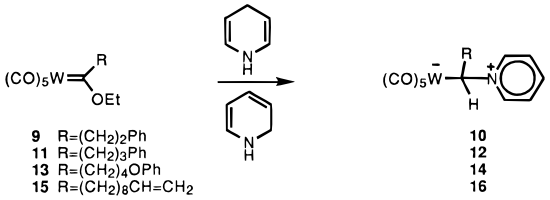


Figure 5. Projections of the ethylidene pyridinium (a, top) and dihydropyridinium (b, bottom) ylide fragments of complexes **7a** and **8a**.

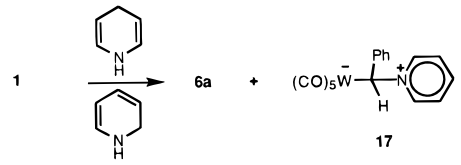
Reduction of the Chromium Complex $(CO)_5Cr{=}C(OEt)$-Me (5b). The same reaction could be carried out on the corresponding chromium complex **5b**: however, only a 20% yield of the reduction product **7b** was obtained after silica gel chromatography together with the corresponding known (pyridine)chromium pentacarbonyl complex (**6b**; 7.5%).[27]

Alkyl-Substituted Pyridinium Ylide Complexes of Tungsten. For synthetic purposes and in order to establish the scope of the new reduction reaction of alkoxycarbene complexes, the preparation of a series of alkyl-substituted pyridinium ylide complexes was attempted. The starting alkoxycarbene complexes of tungsten **9**, **11**, **13**, and **15** were either known complexes or were prepared from tungsten hexacarbonyl by the use of classical methods. Their preparation and spectroscopic data can be found in the experimental section.



These complexes reacted with dihydropyridine as in the previous cases to give the corresponding pyridinium ylides **10**, **12**, **14**, and **16** as orange air-stable solids. The spectroscopic data were in all respects in agreement with these structures with a typical chemical shift for all the carbons linked to the metal at about 63 ppm and a multiplet for the hydrogen bound to this carbon around 4.6 ppm.

Phenyl-Substituted Pyridinium Ylide Complexes. Under the same conditions as for complexes **5**, complex **1** led to a mixture of complexes **6a** and **17** in, respectively, 30 and 43% yield, thus to the pyridine protected form of complex **3**. The ^{1}H NMR spectrum of complex **17** disclosed signals for the

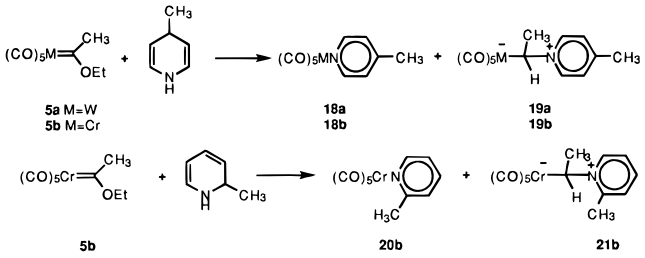


pyridinium protons at δ 8.92, 7.90, and 7.66 ppm together with a singlet for the proton of the carbene carbon at δ 6.01 ppm.

(27) Cotton, F. A.; Darensburg, D. J.; Fang, A.; Kolthammer, B. W. S.; Reed, D.; Thompson, J. L. *Inorg. Chem.* **1981**, *20*, 4090.

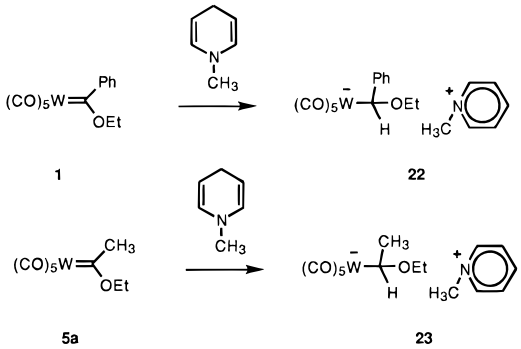
The ^{13}C NMR spectrum confirmed structure **17**: besides signals for the CO groups and the various aromatic carbons, a signal for the benzilic carbon is observed at δ 70.82 ppm. However, the related chromium complex failed to lead to the expected pyridinium ylide complex although it could be detected by TLC: decomposition mainly into benzaldehyde took place during attempts to purify it by silica gel chromatography.

Modifications of the Structure of the Dihydropyridines: Formation of *N*-Methylpyridinium Tungstates from *N*-Methylpyridine and Alkoxycarbene Complexes of Tungsten. In order to determine the influence of substituents on the dihydropyridine ring system, alkylated dihydropyridines[28,29] were prepared by known procedures and used to reduce various alkoxycarbene complexes. Thus, 2- and 4-methyldihydropyridines led, both in the case of chromium and tungsten, besides to the related pyridine (chromium or tungsten) pentacarbonyl complexes **18a,b** and **20b**, to the expected pyridinium ylide complexes **19a,b** and **21b**, yet in lower yields. No reaction was

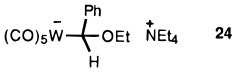


however observed in the case of more hindered dihydropyridines such as 2-phenyl- and 2,2-dimethyldihydropyridines. Moreover, removal of the hydrogen atoms at C(4) by dimethylation[30] completely inhibited the reaction: neither reduction nor aminolysis of the starting alkoxycarbene complexes was observed.

More interesting as far as the mechanism of the formation of these new ylide complexes and their use in organic synthesis is concerned was the reaction between complexes **1** and **5a** with *N*-methyldihydropyridine.[24] Thus, when complex **1** was treated



with a slight excess of *N*-methylpyridine at dry-ice/acetone temperature, a fast reaction leading to the pyridinium complex salt **22** was observed. The ^{1}H NMR spectrum of the new complex is very close to that of complex **24**, the intermediate

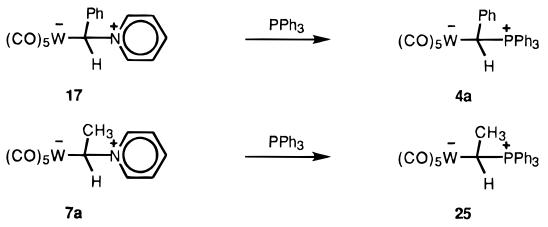


isolated by Casey[26] upon reduction of **1** with $KHB(OiPr)_3$, followed by cation exchange: one observes indeed a signal for

(28) Piers, E.; Soucy, M. *Can. J. Chem.* **1974**, *52*, 3563.
(29) Eisner, U.; Kuthan, J. *Chem. Rev.* **1972**, *72*, 1.
(30) Comins, D. L.; Abdullah, A. H. *J. Org. Chem.* **1982**, *47*, 4315.

the benzylic proton at δ 5.06 ppm (vs δ 4.88 ppm for **24**) and signals at δ 3.09 and 3.43 ppm as two doublets of quartets for the two diastereotopic protons of the ethoxy group. A similar reaction was observed starting from complex **5a** which gave **23**. Like **24**, these *N*-methylpyridinium (α-ethoxybenzyl or ethoxyalkyl)pentacarbonyl tungstates are slightly air sensitive.

Reactivity of the Pyridinium Ylide Complexes. Displacement of Pyridine by Triphenylphosphine. Exchange of pyridine could be carried out quite easily: reaction of triphenylphosphine with complex **17** led, after 15 min at room temperature, to the known phosphorus ylide complex **4** in 70% yield.[13] The substitution of pyridine in **7a** appeared to be more

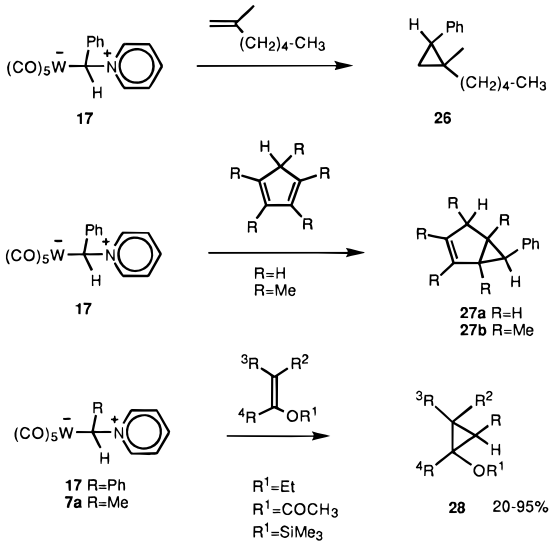


17 **4a** **7a** **25**

difficult since no reaction was observed after several hours at room temperature. However, heating in refluxing methylene chloride for 3 h led to complex **25** in 80% yield. The presence of the phosphine on the carbene carbon was confirmed both by the ^{1}H NMR spectrum which showed a doublet of doublets for the methyl group ($^3J_{HP}$ = 22.7 Hz, J_{HH} = 7 Hz) and a doublet of quartets for the hydrogen on the carbene carbon ($^1J_{HP}$ = 14.4 Hz, J_{HH} = 7 Hz) and by the ^{13}C NMR spectrum with a characteristic signal for the ylide carbon at δ −12.21 ppm as a doublet (J_{CP} = 15.2 Hz).

Reaction with Olefins: Intermolecular Cyclopropanation Reactions. Since the pyridinium ylide complexes described herein can be considered as the result of the interaction of pyridine with W(0) and Cr(0) alkylidene complexes (*vide infra*), one might address the question of the reversibility of this reaction. In such an event, a general access to alkylidene complexes such as **3** transferable to olefins would be possible: it has indeed been shown that simple olefins react with complex **3** at low temperature to give phenylcyclopropanes.[13,16] However, at first glance, no transformation of complexes **7a** and **17** was observed in solution by NMR spectroscopy. They appeared to be quite stable although slow oxidation to the corresponding aldehydes took place in the presence of oxygen.

In the hope that olefins might induce the elimination of pyridine, they were reacted both at room temperature and in refluxing dichloromethane or benzene with the ylide complexes. No reaction was however observed with terminal olefins such as 1-octene and complex **17** under these conditions. However, in the case of the more reactive 2-methyl-1-heptene, the transfer of the benzylidene group to the double bond took place in refluxing methylene chloride and gave **26** as a mixture of two isomers in 66% yield. In the same way, cyclopentene and norbornene reacted with **17** to give the corresponding known[31,32] phenylcyclopropanes **26a** and **26b** as mixtures of isomers in, respectively, 55 and 27% yield (see the Experimental Section). Olefins such as cyclopentadiene and pentamethylcyclopentadiene, the reactivity of which has been found to be extremely high toward complex **3** even at −20 °C,[17] led, at room temperature, to the same phenylcyclopropanes **27a,b** in 30 and 40% yield.

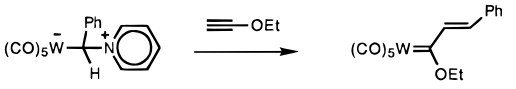


17 **26** **17** **27a** R=H **27b** R=Me **17** R=Ph **7a** R=Me **28**

Much better results were however observed in the case of electron-rich olefins such as enol ethers: the reaction with these substrates proved to be general and took place either at room temperature or at reflux temperature of methylene chloride or benzene. Thus, 2,3-dihydrofuran, the enol ethers of cyclopentanone, norcamphor, and isopropenyl acetate reacted with complex **17** at room temperature, leading to the isomeric phenylcyclopropanes **28a**−**d** in, respectively, 69, 79, 97, and 63% yield (see the Experimental Section).

Complex **7a** reacted more sluggishly: transfer of the ethylidene ligand occurred however again in the case of methyl-2-heptene yet in low yield (observed by ^{1}H NMR). In contrast, enol ethers of norcamphor and acetophenone proved again to be more reactive: they reacted in boiling benzene with complex **7a** to give moderate yields of the corresponding methylcyclopropanes **28e,f** (28 and 31% yield).

Reaction with Ethoxyacetylene. The nucleophilic alkyne ethoxyacetylene, which is known to give, upon insertion into complex **3**, a new carbene complex **29**,[13] reacted in the same way with complex **17** to give complex **29** yet in a very low 5% yield. Again, **7a** behaved differently: no complex arising from the monoinsertion of the alkyne could be detected; instead, a fast polymerization of ethoxyacetylene took place.

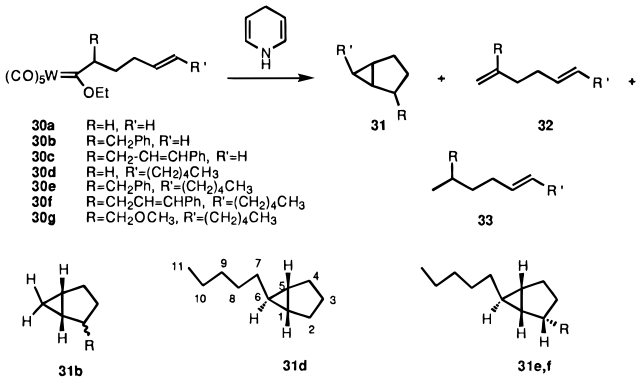


17 **29**

Direct Intramolecular Cyclopropanation Reactions. Intramolecular cyclopropanation reactions promoted by carbene complexes have found applications in the synthesis of natural products or analogues.[34,35] Although Fischer-type carbene complexes of tungsten and chromium react only sluggishly with olefins,[36] alkene−carbene complexes of this type are known to undergo easy intramolecular cyclopropanations provided that the carbene carbon and the alkene are separated by three or four methylene groups.[35,37,38] The first successful reactions have been observed in the case of complexes of the general structure

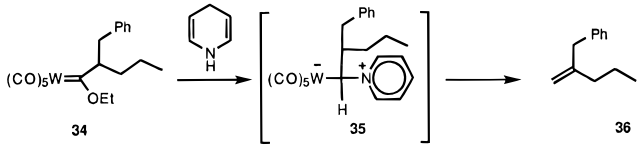
(31) Hesse, K.; Hurig, S.; Wenner, H. *Liebigs Ann. Chem*. **1982**, 2079.
(32) Creary, X. *J. Org. Chem*. **1980**, *45*, 4653.
(33) Catellani, M.; Chiusoli, G. P. *J. Organomet. Chem*. **1982**, *233*, C-21.
(34) Hoye, T. R.; Vyvyan, J. R. *J. Org. Chem*. **1995**, *60*, 4184.
(35) Söderberg, B. J.; Hegedus, L. S. *Organometallics* **1990**, *9*, 3113.
(36) Dötz, K. H. Carbene Complexes in Organic Chemistry. In *Transition Metal Carbene Complexes*; Seyferth, D., Ed.; Verlag Chemie: Weinheim, 1983; pp 192−226.
(37) Casey, C. P.; Vollendorf, N. W.; Haller, K. J. *J. Am. Chem. Soc*. **1984**, *106*, 3754.
(38) Alvarez, C.; Rudler, H.; Daran, J. C.; Jeannin, Y. *J. Chem. Soc., Chem. Commun*. **1984**, 574.

30a (R = R′ = H), a result portending a similar behavior of pyridinium ylide complexes derived from them. Since a successful intramolecular reaction of complex **30a** might lead to bicyclo(3.1.0)hexane, a compound difficult to isolate from the reaction medium due to its volatility, we choose to start from the α-benzylated complex **30b**.

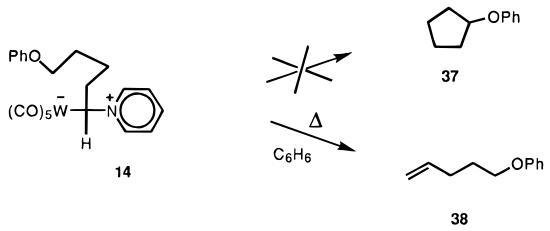


Surprisingly, when complex **30b** was submitted to a slight excess of dihydropyridine, a fast consumption of the starting material was again observed. However, in contrast to the previous cases, only trace amounts of the corresponding pyridinium ylide complex could be detected by TLC or by NMR. Moreover, when the reaction mixture was kept at room temperature for a further few hours, organic compounds of low polarity could be detected and isolated after workup and silica gel chromatography. We were delighted to discover that indeed a direct intramolecular cyclopropanation of the monosubstituted double bond of complex **30b** had taken place at room temperature. All the spectroscopic data of the less polar compound **31b**, obtained in 44% yield, and purified on silver nitrate impregnated silica gel, were in agreement with such a bicyclic structure. The ^{13}C NMR spectrum confirmed the presence of approximately a 1:1 mixture of isomers with 13 distinct signals for the 14 expected aliphatic carbons of the two compounds, whereas in the ^{1}H NMR spectrum overlap of most of the signals was observed, the signals for the hydrogens on the cyclopropane giving rise to multiplets between δ 0.8 and −0.01 ppm. Two side products were formed during this insertion reaction: the diene **32b** and the olefin **33b** in, respectively, 18 and 4% yield. Complexes **30c**−**g** behaved similarly and led to the bicyclic compounds **31c**−**g** in, respectively, 40, 70, 40, and 35% yield. However, subtle differences in the mode of formation of the various organic products could be noted. Whereas complexes **30c** and **30e**−**g** behaved like **30b** and gave directly, at room temperature, the cyclopropanation products **31c,e**−**g**, slightly more vigorous conditions had to be applied to complex **30d** for its transformation into **31d**: although the reduction reaction took place as in the other examples, the presence of the intermediate ylide complex for a long period of time was clearly established by ^{1}H NMR, with a characteristic signal for the W−C−H proton at δ 4.65 ppm. After one night at room temperature, the ylide complex was still detectable and the reaction could only be driven to completion upon reflux of the ethereal solution for an extra hour. The reaction products could again be separated by silica gel chromatography. According to the ^{1}H and ^{13}C NMR, the bicyclic compound **31d** was obtained as a single isomer in 70% yield. The shape and width (septuplet, 21 Hz) of the signal due to the cyclopropane proton at C(6) were in agreement with a *trans* geometry of the chain and the five-membered ring.[39] In contrast to **30b** which gave **31b** as a 1:1 mixture of isomers, **30e**, **30f**, and **30g** led to the formation of almost exclusively a single isomer (95%). The relative configurations of the substituents in these bicyclic compounds could be established through careful analysis of the ^{1}H NMR spectra along with NOE difference experiments, the alkyl chain at C(2) being cis to the hydrogen atoms at the ring junction.

Since a substituent in the α position with respect to the carbene carbon seemed to destabilize the ylide complex (or to hinder its formation), allowing thus a direct trapping of the alkylidene complex by the intramolecularly located double bond, the behavior of complex **34**, containing in contrast to **30** a saturated chain, was also examined. Confirmation of the previous observation could be established: indeed, **34** reacted with dihydropyridine to give instead of the ylide complex **35**, its decomposition product directly, the olefin **36** in 60% yield.



Thermolysis of Complex 14. Carbenes as well as alkylidene complexes are known to insert into carbon−hydrogen bonds especially when these are located α with respect to a heteroatom.[40−46] Complex **14** seemed to fulfill the structural requirements for such an intramolecular cyclization reaction. However, its thermolysis in boiling benzene did not lead to the expected ether **37**: a quantitative transformation into the alkene **38**, the product of β-elimination, was instead observed.



Discussion

These experimental data bring to light two striking features. The first one is the confirmation of the analogy which exists between carbonyl compounds and alkoxycarbene complexes: in both cases a smooth and clean reduction by the mild reducing agents dihydropyridines takes place. The second one is the possible application of the new reaction to the straightforward synthesis of polycyclic systems.

Mechanism of the Formation of the Ylide Complexes. On a formal point of view, these new pyridinium ylide complexes can be considered as the result of a double stabilization of a singlet carbene, by pyridine on the one hand and by a metal pentacarbonyl on the other. Pyridine is indeed a typical trap for singlet carbenes: the interaction of these species leads to

(39) Hoye, T. R.; Hanson, P. R.; Vyvyan, J. R. *J. Org. Chem.* **1994**, *59*, 4096.

(40) Fischer, H.; Zeuner, S.; Schmid, J.; Hofmann, J. In *Advances in Metal Carbene Chemistry*; Schubert, U., Ed.; NATO ASI Series C; Kluwer: Dordrecht, The Netherlands, 1989; Vol. 269, pp 185−188 and references therein.

(41) Adams, J.; Spero, D. M. *Tetrahedron* **1991**, *47*, 1765.

(42) Doyle, M. P.; van Oeveren, A.; Westrum, L. J.; Protopopova, M. N.; Clayton, T. W., Jr. *J. Am. Chem. Soc.* **1991**, *113*, 8982.

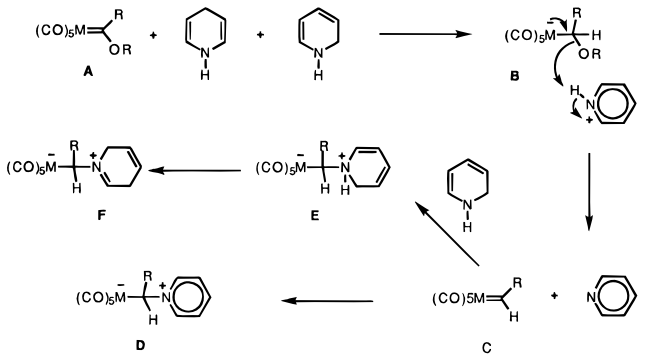
(43) Zhao, S. K.; Knors, C.; Helquist, P. *J. Am. Chem. Soc.* **1989**, *111*, 8527.

(44) Zhao, S. K.; Helquist, P. *J. Org. Chem.* **1990**, *55*, 5821.

(45) Zhao, S. K.; Mehta, G.; Helquist, P. *Tetrahedron Lett.* **1991**, *32*, 5753.

(46) Wang, S. L. B.; Su, J.; Wulff, W. D.; Hoogsten, K. *J. Am. Chem. Soc.* **1992**, *114*, 10665.

Scheme 4



organic pyridinium ylides detectable by UV/vis spectroscopy.[47] Stabilization is due here to the interaction of the pyridine nitrogen lone pair with the empty px orbital of the singlet carbene. According to our observations, an important improvement of the stability of this intermediate derives from the interaction of the remaining occupied nonbonding σ-orbital of the singlet carbene with an empty metal orbital of suitable energy and symmetry, in the present instance, of $W(CO)_5$ or $Cr(CO)_5$. The result of these interactions is a rehybridization of the carbene carbon from sp^2 to sp^3, a feature which appears in both crystal structures. A second way to describe these new complexes, which is more related to their mode of formation from alkoxycarbene complexes, is to consider them as the result of the trapping reaction of an unstable electrophilic alkylidene complex by pyridine. The role of dihydropyridine can thus be considered as being triplicate (Scheme 4): (1) The starting dihydropyridine transfers a hydride to the carbene complex with formation of a pyridinium (α-alkoxyalkyl or aryl) tungsten or chromium (pentacarbonyl) complex (**A** → **B**). This step is akin to the reduction of a carbonyl group by dihydropyridine.[48] (2) The pyridinium activates the alkoxy group for its elimination, by protonation. This gives the alkylidene complex and pyridine (**B** → **C**). (3) The resulting pyridine reacts with the electrophilic carbene carbon to lead to a stable pyridinium ylide complex (**C** → **D**). Evidence for such a mechanism is provided by the following observations: (1) The carbene complexes can also be reduced by *N*-methyldihydropyridine. In that case, pyridinium tungstates of type **B** are indeed formed and could be characterized. (2) From the work of Casey and Fischer, it is also known that such pyridinium tungstates readily eliminate alcohol under acidic conditions to give, for R = Ph, the corresponding isolable alkylidene complex (**1** → **3** vs **B** → **C**).[13,14] (3) Finally, since in the case of the alkylidene complex **3** the electrophilic nature of the carbene carbon is reflected by its reaction with triphenylphosphine, the last step of the reaction, the interaction of pyridine with the carbene carbon (Scheme 4, **C** → **D**), is easily understood. Moreover, at this stage competition between several nucleophiles of the reaction medium (in the present instance pyridine and dihydropyridines) can take place. One observes indeed the formation of two ylide complexes, **7a** and **8a**, from complex **5a** through the interaction of the transient electrophilic alkylidene complex with, respectively, pyridine and dihydropyridine. A plausible mechanism for the formation of **8a** is given in Scheme 4: interaction of the alkylidene complex **C** with 1,2-dihydropyridine might lead to the 1,2-dihydropyridinium ylide complex **E**, which upon a (1,3) hydride shift would give the 2,5-dihydropyridinium complex **8a**. Surprisingly, no complex resulting from the interaction of 1,4-dihydropyridine was observed. Since the reaction of dihydropyridine with **5a** leaves this latter complex unchanged, one can conclude that **8a** is not formed from **5a** via a substitution reaction of pyridine by dihydropyridine. Such substitution reactions can nevertheless occur: thus, in the case of phosphines, displacement of pyridine takes place. These reactions can be understood on the following grounds: the softer phosphine displaces the harder pyridine from the soft carbene carbon to give a complex in which the carbon−heteroatom bond is stronger than in the starting complex. This assertion is confirmed by the difference of reactivity with respect to olefins: complex **17** reacts with cyclopentene at room temperature to give the corresponding phenylcyclopropane whereas no reaction is observed in the case of complex **4a** even in refluxing benzene. The chemical shift of the proton geminated to the carbene carbon can be considered as a good criterion for the assessment of the relative carbon−nitrogen bond strengths in various complexes: the more this proton is deshielded, the weaker the bond between the carbene carbon and the heteroatom. This appears clearly for the series of tungsten complexes **4b**, **4a**, **17** (2.71, 3.81, 6.03 ppm), **7a**, and **25** (4.90, 2.47 ppm), in which pyridine has been exchanged by phosphines, **7a** and **8a** (4.90, 3.80 ppm), where one finds successively pyridine and the more basic dihydropyridine, and chromium complexes **21b**, **19b**, and **7b** (4.23, 4.56, 4.60 ppm) in which a weak influence of the methyl groups on pyridine can be detected.

Other pyridinium ylide complexes resulting from the interaction of pyridine with stable alkylidene complexes have recently been described and used as precursors for cyclopropanation reactions: their mode of formation is however completely different.[49] Moreover, to the best of our knowledge the stabilization of dihydropyridine by formation of an ylide complex is new, although it is known from organic chemistry that electron-withdrawing groups on nitrogen considerably stabilize dihydropyridines. At this point it is interesting to notice that since a carbon−nitrogen bond is formed upon interaction of the alkylidene complex **C** with 1,2-dihydropyridine, dihydropyridine reacts like an amine rather than an enamine: in this latter case formation of a carbon−carbon bond would have been expected. However, careful examination of the X-ray data completely excluded such a possibility. Up to now, dihydropyridines could be stabilized as tridentate ligands by coordination of the two double bonds and of nitrogen to $Cr(CO)_3$ or $W(CO)_3$.[50−53]

Reaction with Olefins. As far as the behavior of these complexes with respect to various olefins is concerned, the general lower reactivity of these ylide complexes as compared for example with the reactivity of complex **3** implies that displacement of pyridine prior to the reaction with the olefin must probably take place. This could involve either an associative or a dissociative mechanism, a fact which has yet to be established by kinetic measurements. The high reactivity of enol ethers can be considered as a good indication for a substitution of pyridine by the substrate as the limiting step of the reaction. This assumption is also confirmed by the easy insertion of the nucleophilic alkyne ethoxyacetylene into complex **17**. The difference of reactivity between phenyl- and alkyl-substituted pyridinium ylides already observed for tri-

(47) Modarelli, D. A.; Platz, M. S. *J. Am. Chem. Soc*. **1993**, *115*, 470 and references therein.

(48) Loewus, F. A.; Westheimer, F. H.; Vennesland, B. *J. Am. Chem. Soc*. **1953**, *75*, 5018.

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(51) Kutney, J. P.; Bagder, R. A.; Cullen, W. R.; Greenhouse, R.; Noda, M.; Ridaura-Sanz, V. E.; So, Y. H.; Zanarotti, A.; Worth, B. R. *Can. J. Chem*. **1979**, *57*, 300.

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(53) Ragauskas, A. J.; Stothers, J. B. *Can. J. Chem*. **1985**, *63*, 2969.

phenylphosphine is corroborated by their behavior toward olefins: satisfactory results could be obtained in the case of activated double bonds, the main reaction being otherwise the thermal β-elimination. The greatest achievements stem however from the direct intramolecular cyclopropanation reactions observed in the case of alkene−carbene complexes, although no attempts have been made, up to now, to optimize the reaction conditions. Several aspects of the cyclization reactions deserve a comment. First, complete retention of the stereochemistry of the alkene precursor is observed in the case of complex **30d** since **31d** was isolated as a single isomer.[54] This result is reminiscent of the reaction of complex **3** with (*E*)- and (*Z*)-olefins during which conservation of the stereochemistry was observed.[16] Second, complexes **30b** and **30c** gave rise to a 1:1 mixture of isomers. This means that a facial selectivity exists: if the transient carbene complex bearing in the α position the *pro-R* group gives a 80% addition to the *re* face of the double bond, then the carbene complex bearing the *pro-S* group leads to a 20% addition to this same face. Third, in the case of complexes **30e**−**g**, and in contrast to the previous cases, high diastereoselectivity is observed in spite of the presence of an α substituent. The exact reasons for this behavior are not clear for the moment.

Conclusion

Most of our efforts have been focused on the one hand on the generalization of the preparation and structure determination of these new ylide complexes and on the other hand on their thermolysis in the presence of olefins. Whereas in the case of alkenes tethered to carbene complexes the results were beyond our expectations, alkyl-substituted pyridinium ylides are still reluctant to release intermolecularly in a useful way their carbene moiety. It is however clear that these reactions might be induced otherwise, for instance by chemical or electrochemical oxidation or reduction, or by photochemistry which should also weaken the carbon−nitrogen bond and thus improve the reactivity. Work is in progress toward these goals and also to extend the intramolecular reactions first to 1,6-alkene−carbene complexes, which should lead to bicyclo(4.1.0)heptane systems common in natural products, and to alkyne-containing alkene−carbene complexes.

Experimental Section

General Methods. ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 200, ARX 400, and AM 500 spectrometers. IR spectra were recorded on a Perkin-Elmer 1420 spectrophotometer. Mass spectra were recorded on a ZAB HSQ (Fisons) instrument. Column chromatography was performed with Merck silica gel (70−230 mesh) using various ratios of ethyl acetate/light petroleum ether or dichloromethane/light petroleum ether as eluent. For the separation of the olefins, silica gel was impregnated with silver nitrate (5% by weight) and reactivated by heating under vacuum. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under an argon atmosphere in carefully dried glassware. Benzene, tetrahydrofuran (THF), and diethyl ether were distilled from sodium/benzophenone ketyl under a nitrogen atmosphere. Dichloromethane (CH_2Cl_2) was distilled from phosphorus pentoxide under a nitrogen atmosphere. Carbene complexes **1**, **5a**, **5b**, **9**, and **15** (R′ = R′ = H)[55−60] and the various dihydropyridines[24,29,30] were prepared according to published methods.

Table 5. Crystallographic Data for Complexes **7a** and **8a**

	$C_{12}H_{11}O_5NW$	$C_{12}H_9O_5NW$
Fw	433.07	431.0
a (Å)	11.050(5)	10.847(4)
b (Å)	15.215(6)	15.138(5)
c (Å)	9.299(3)	9.308(6)
α (deg)	90	90.
β (deg)	113.88(3)	113.64(5)
γ (deg)	90	90.
V (Å^3)	1430	1400
Z	4	4
crystal system	monoclinic	monoclinic
space group	*P*21/*a*	*P*21/*a*
linear absorption coefficient μ (cm^{-1})	82.7	84.4
density ρ (g·cm^{-3})	2.01	2.04
diffractometer	Philips PW1100	Philips PW1100
radiation	Mo Kα (λ = 0.710 69 Å)	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega/2\theta$	$\omega/2\theta$
scan range (deg)	1.20 + 0.345 tan θ	1.20 + 0.345 tan θ
θ limits (deg)	2−25	2−25
temperature of measurement	room temperature	room temperature
octants collected	*h*, −13, 12; *k*, 0, 18; *l*, 0, 11	*h*, −12, 11; *k*, 0, 18; *l*, 0, 10
no. of data collected	2797	2687
no. of unique data collected	2518	2416
no. of unique data used for refinement	1386 ($F_o^2 > 3\sigma(F^{02})$)	1451 ($F_o^2 > 3\sigma(F_o^2)$)
R(int)	0.069	0.061
$R = \sum\|\|F_o\| - \|F_c\|\|/\sum\|F_o\|$	0.0440	0.0477
$Rw = [\sum w(\|F_o\| - \|F_c\|)^2/\sum wF_o^2]^{1/2}$	0.0470 ($w = 1.0$)	0.0499 ($w = 1.0$)
absorption correction	DIFABS (min 0.78, max 1.43)	DIFABS (min 0.65, max 1.29)
extinction parameter ($\times 10^{-6}$)	no	no
goodness of fit *s*	1.02	1.31
no. of variables	173	172
$\Delta\rho$(min) (e·Å^{-3})	−0.75	−1.53
$\Delta\rho$(max) (e·Å^{-3})	0.97	0.86

X-ray Structure Determinations. Data were collected on an Enraf-Nonius CADA diffractometer. Accurate cell dimensions and orientation matrices were obtained by least-squares refinements of 25 accurately centered reflections. No significant variations were observed in the intensities of two checked reflections during data collections. Complete crystallographic data and collection parameters are listed in Table 5. The data were collected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS.[62] Scattering factors and corrections for anomalous absorption were taken from ref 63. The structures were solved by using standard Patterson−Fourier techniques and refined by full-matrix least squares with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinement, and only an overall isotropic thermal parameter was refined.

General Procedure for the Preparation of the Pyridinium Ylide Complexes: Reaction of $(CO)_5W{=}C(CH_3)OEt$ (5a) with 1,4-Dihydropyridine. Freshly prepared 1,4-dihydropyridine (obtained from *N*-carbomethoxydihydropyridine (6 mmol) and methyllithium according to the literature[24]) in diethyl ether (80 mL) was added at room

(54) Note added in proof: the reaction of the *Z* isomer **30d′** led also to a single isomer, confirming the high stereoselectivity of the cyclopropanation reaction (see the Experimental Section).

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temperature to the carbene complex **5a** (2.0 g, 3 mmol) in diethyl ether (20 mL). The solution turned rapidly from orange to red. Evaporation of the solvent gave a residue which was rapidly chromatographed on silica gel. Elution with dichloromethane/petroleum ether (20/80) gave $(CO)_5W$(pyridine) (**6a**) (0.15 g, 7.5%).[61] Elution with dichloromethane/petroleum ether (60/40) gave $(CO)_5W^--(CHCH_3)(pyridine)^+$ (**7a**) (0.86 g, 66%). Spectral data for **6a**: yellow crystals, from methylene dichloride/hexane, mp 114 °C; ^{1}H NMR ($CDCl_3$) δ 8.83 (dd, 2H, J = 5 and 1.4 Hz), 7.79 (tt, 1H, J = 7.7 and 1.4 Hz), 7.28 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 202.35 (CO), 199.47 (CO), 155.99, 137.39, 125.63; IR ($CHCl_3$) 2060, 1970, 1930 cm^{-1}. Anal. Calcd for $C_{10}H_5NO_5W$: C, 29.79; H, 1.24; N, 3.47. Found: C, 29.70; H, 1.28; N, 3.59. Spectral data for **7a**: orange crystals, from dichloromethane/hexane, mp 127 °C; ^{1}H NMR ($CDCl_3$) δ 8.55 (d, 2H, J = 6 Hz), 7.82 (t, 1H, J = 7.5 Hz), 7.59 (t, 2H, J = 6.7 Hz), 4.90 (q, 1H, J = 7 Hz, CHMe), 2.35 (d, 3H, J = 7 Hz, CH*Me*); ^{13}C NMR ($CDCl_3$) δ 204.51 (CO), 201.93 (CO), 139.22, 136.17, 126.61, 57.16 (CHMe), 30.72 (Me). Anal. Calcd for $C_{12}H_9NO_5W$: C, 33.42; H, 2.08; N, 3.25. Found: C, 33.49; H, 2.17; N, 3.35.

Reaction of $(CO)_5W$═$C(CH_3)OEt$ (5a) with a Mixture of 1,2- and 1,4-Dihydropyridines: Formation of $(CO)_5W^--C(H)(CH_3)(N^+C_5H_7)$ (8a). Under the same conditions as above, besides complexes **6a** and **7a**, pure fractions of complex **8a** could be eluted with methylene chloride/petroleum ether (20/80) and isolated in 17% yield. Spectral data for yellow crystals, mp 100 °C, from methanol/dichloromethane; ^{1}H NMR (CD_2Cl_2) δ 7.81 (br s, 1H, C(12)), 5.90 (m, 2H, C(9,10)-H), 4.95−4.79 (dt, 1H, J = 20 and 7 Hz, C(8)-H), 4.25−4.12 (dt, 1H, J = 20 and 7 Hz, C(8)-H), 4.19 (br q, 1H, C*H*Me), 3.20 (m, 2H, C(11)-H_2), 2.11 (d, 3H, J = 8 Hz, CH*Me*). Anal. Calcd for $C_{12}H_{11}NO_5W$: C, 33.26; H, 2.54; N, 3.23. Found: C, 32.23; H, 2.17; N, 3.19.

Reaction of $(CO)_5Cr$═$C(CH_3)OEt$ (5b) with 1,2-Dihydropyridine: Formation of the Pyridinium Ylide Complex $(CO)_5Cr^--C(H)(CH_3)(C_5H_5N)^+$ (7b). Under the same conditions as above, complex **5b** gave a mixture of complexes **6b** (8%) and **7b** (20%). Spectral data for **6b**: yellow solid, mp 95 °C; ^{1}H NMR ($CDCl_3$) δ 8.57 (dd, 2H, J = 6.5 and 1.6 Hz), 7.42 (tt, 1H, J = 7.6 and 1.5 Hz), 7.25 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 220.72 (CO), 214.32 (CO), 155.34, 137.17, 124.88. Anal. Calcd for $C_{10}H_5NO_5Cr$: C, 44.28; H, 1.84; N, 5.16. Found: C, 44.09; H, 1.95; N, 5.10. Spectral data for **7b**: orange solid, mp 112 °C, ^{1}H NMR ($CDCl_3$) δ 8.42 (d, 2H, J = 5.6 Hz), 7.75 (t, 1H, J = 4.5 Hz), 7.6 (t, 2H, J = 6 Hz), 4.6 (q, 1H, J = 7 Hz, C*H*Me), 2.10 (d, 3H, J = 7 Hz, *Me*); ^{13}C NMR ($CDCl_3$) δ 224.87 (CO), 220.06 (CO), 138.92, 135.77, 126.57, 63.83 (*C*HMe), 28.70 (*Me*). Anal. Calcd for $C_{12}H_9NO_5Cr$: C, 48.10; H, 3.01; N, 4.68. Found: C, 47.84; H, 3.10; N, 4.62.

Reaction of $(CO)_5W$═$C(Ph)OEt$ (1a) with 1,2-Dihydropyridine: Formation of the Pyridinium Ylide Complex $(CO)_5W^--C(H)(Ph)(C_5H_5N)^+$ (17). Under the same conditions as above, complex **1** gave a mixture of **6a** (31%) and **17** (43%). Spectral data for **17**: orange solid, mp 105 °C; ^{1}H NMR ($CDCl_3$) δ 8.92 (d, 2H, J = 5.6 Hz), 7.90 (t, 1H, J = 7.7 Hz), 7.66 (t, 2H, J = 7 Hz), 7.31 (m, 4H), 7.15 (m, 1H), 6.03 (t, 1H, J = 3.4 Hz); ^{13}C NMR ($CDCl_3$) δ 203.93 (CO), 201.56 (CO), 148.68, 141.92, 138.43, 128.7, 127.61, 126.70, 125.75, 70.82 (*C*HPh). Anal. Calcd for $C_{17}H_{11}NO_5W$: C, 41.38; H, 2.23; N, 2.84. Found: C, 41.27; H, 2.34; N, 2.71.

(1-Ethoxy-4-phenylbutylidene)pentacarbonyltungsten(0) (11). To a suspension of $W(CO)_6$ (10.55 g, 3×10^{-2} mol) in diethyl ether was added a solution of (3-phenylpropyl)lithium obtained from 3-phenylpropyl iodide (7.35 g, 3×10^{-2} mol) in diethyl ether (130 mL) and pentane (200 mL) and tBuLi (38 mL, 1.6 M in pentane, 6×10^{-2} mol). After 3 h at room temperature, the solvents were evaporated under vacuum. Water (180 mL) was added to the residue, followed by petroleum ether (80 mL) and triethyloxonium fluoroborate (6.3 g). Workup as usual gave complex **11** (12.71 g, 85%) as a yellow oil: ^{1}H NMR (CDCl) δ 7.35−7.16 (m, 5H, Ar), 4.88 (q, 2H, OCH_2), 2.64 (m, 2H, CH_2Ph), 1.82 (m, 2H, $-CH_2-$), 1.60 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 333.43 (W═C), 203.35 (CO), 197.37 (CO), 141.48, 128.52, 128.46, 126.17 (Ar), 80.75 (OCH), 64.69 (═CCH), 35.42 (C-Ph), 28.15 ($-CH_2-$), 14.60 (CH_2CH_3); HRMS calcd (obsd) for $C_{17}H_{16}O_6W^+$ 500.0456 (500.0457).

(1-Ethoxy-5-phenoxypentylidene)pentacarbonyltungsten(0) (13). This complex was obtained as above from the corresponding iodide and $W(CO)_6$ as a yellow oil in 52% yield: ^{1}H NMR ($CDCl_3$) δ 7.31−7.23 (m, 3H), 6.93−6.85 (m, 2H), 4.87 (q, 2H, OCH_2), 3.94 (t, 2H, $PhOCH_2$), 3.27 (t, 2H, W═CCH_2), 1.76 (m, 4H), 1.60 (t, 3H, CH_2-CH_3); ^{13}C NMR ($CDCl_3$) δ 333.46 (W═C), 203.28 (CO), 197.40 (CO), 158.99 (O−C), 129.51, 120.76, 120.54, 114.57, 80.83 (OCH_2), 76.47 (OCH_2), 67.35, 64.75, 28.60, 23.14; HRMS calcd (obsd) for $C_{18}H_{18}O_7W^+$ 530.0562 (530.0556).

Reaction of 1,2- and 1,4-Dihydropyridines with Complex 9: Formation of $(CO)_5W^--C(H)((CH_2)_2Ph)(C_5H_5N)^+$ (10). This complex was obtained as above in 47% yield as an orange solid: mp 113 °C; ^{1}H NMR ($CDCl_3$) δ 8.47 (d, 2H), 7.83 (t, 1H), 7.57 (t, 2H), 7.19 (m, 5H), 4.67 (dd, 1H, J = 9.5 and 5.6 Hz, W−C−H), 2.99−2.74 (m, 2H), 2.71−2.49 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 204.35 (CO), 201.78 (CO), 140.86, 139.98, 136.83, 128.51, 128.26, 128.74, 126.04 (Ar, Py), 63.50 (W−C), 45.34, 35.98. Anal. Calcd for $C_{19}H_{15}NO_5W$: C, 43.76; H, 2.88; N, 2.68. Found: C, 43.78; H, 3.02; N, 2.52.

Reaction of 1,2- and 1,4-Dihydropyridines with Complex 15: Formation of the Pyridinium Ylide Complex $(CO)_5W^--C(H)((CH_2)_8CH$═$CH_2)(C_5H_5N)^+$ (16). This complex was obtained as above in 42% yield as orange crystals: mp 50 °C; ^{1}H NMR ($CDCl_3$) δ 8.51 (d, 2H), 7.83 (t, 1H), 7.58 (t, 2H), 5.80 (m, 1H, CH═C), 4.92 (m, 2H, C═CH_2), 4.66 (dd, 1H, J = 10 and 5.5 Hz, W−C−H), 2.42 (m, 2H), 2.02 (m, 2H), 1.23 (m, 12 H); ^{13}C NMR ($CDCl_3$) δ 204.67 (CO), 202.08 (CO), 140.04, 139.26, 138.53, 136.67, 126.84, 114.22 (C═C, Py), 64.51 (W−C−H), 44.17, 33.84, 29.60, 29.53, 29.48, 29.35, 29.11 (CH_2). Anal. Calcd for $C_{21}H_{25}NO_5W$: C, 45.42; H, 4.51; N, 2.52. Found: C, 45.42; H, 4.56; N, 2.49.

Reaction of 1,2- and 1,4-Dihydropyridines with Complex 11: Formation of $(CO)_5W^--C(H)((CH_2)_3Ph)(C_5H_5N)^+$ (12). 12 was obtained from complex **11** (6.6 g, 0.13 mmol) as above: yellow solid (2.01 g, 28.5%), mp 128 °C; ^{1}H NMR ($CDCl_3$) δ 8.39 (d, 2H), 7.79 (t, 1H), 7.50 (t, 2H), 4.65 (dd, 1H, J = 5.6 and 10.2 Hz, W−C−H), 2.70−2.52 (m, 4H), 1.60−1.48 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 204.44 (CO), 201.96 (CO), 142.14, 139.67, 136.52, 128.45, 126.78, 125.97 (Ar, Py), 64.16 (W−C−H), 43.60, 35.45, 31.45 ($3CH_2$). Anal. Calcd for $C_{20}H_{17}NO_5W$: C, 44.87; H, 3.18; N, 2.62. Found: C, 44.98; H, 3.23; N, 2.55.

Reaction of 1,2- and 1,4-Dihydropyridines with Complex 13: Formation of the Pyridinium Ylide Complex $(CO)_5W^--C(H)((CH_2)_4OPh)(C_5H_5N)^+$ (14). This complex was obtained as above, in 50% yield as an orange solid: mp 69 °C; ^{1}H NMR ($CDCl_3$) δ 8.50 (d, 2H), 7.82 (t, 1H), 7.56 (t, 2H), 7.24 (m, 3H), 6.95−6.79 (m, 2H), 4.68 (1H, dd, J = 5.4 and 10 Hz), 3.93 (t, 2H, OCH_2), 2.69 (m, 1H, W−C−CH), 2.52 (m, 1H, W−C−CH), 1.29 (m, 2H), 1.39 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 204.5 (CO), 201.97 (CO), 158.9, 139.98, 136.69, 129.55, 126.65, 120.71, 114.45 (Ar, Py), 67.39, 64.20, 43.69, 28.64, 26.15. Anal. Calcd for $C_{21}H_{19}NO_6W$: C, 44.61; H, 3.36; N, 2.48. Found: C, 44.77; H, 3.46; N, 2.35.

Reaction of 4-Methyldihydropyridine with Complex 5b: Formation of the Pyridinium Ylide Complex $(CO)_5Cr^--C(H)(CH_3)(C_6H_8N)^+$ (19b). A solution of 4-methyldihydropyridine obtained from *N*-carbomethoxy-4-methyldihydropyridine (2.3 g, 15 mmol) and MeLi (28 mL, 45 mmol) was added to complex **5b** (4 g, 15 mmol) at room temperature. Workup as above followed by silica gel chromatography first gave complex **18b** (0.37 g, 9%) and then complex **19b** (1.2 g, 25%). Spectral data for **18b**: yellow solid, mp 97 °C; ^{1}H NMR ($CDCl_3$) δ 8.45 (d, 2H, J = 5 Hz), 7.08 (d, 2H, J = 6 Hz), 2.41 (s, 3H); ^{13}C NMR ($CDCl_3$) δ 220.78 (CO), 214.47 (CO), 154.79, 149.21, 125.84, 20.83. Anal. Calcd for $C_{11}H_{11}NO_5Cr$: C, 46.31; H, 2.46; N, 4.91. Found: C, 46.27; H, 2.53; N, 4.96. Spectral data for **19b**: orange crystals, mp 63 °C; ^{1}H NMR (CDCl) δ 8.36 (d, 2H, J = 5.7 Hz), 7.41 (d, 2H, J = 5.4 Hz), 4.56 (q, 1H, J = 7 Hz, W−C−H), 2.53 (s, 3H, Me), 2.11 (d, 3H, J = 7 Hz, CH*Me*); ^{13}C NMR ($CDCl_3$) δ 224.86 (CO), 220.36 (CO), 148.92, 138.42, 127.64, 62.9 (*C*HMe), 28.90 (Me), 21.18 (CH*Me*). Anal. Calcd for $C_{13}H_{11}NO_5Cr$: C, 49.84; H, 3.51; N, 4.47. Found: C, 49.98; H, 3.50; N, 4.57.

Reaction of 4-Methyl-1,4-dihydropyridine with Complex 5a: Formation of the Pyridinium Ylide Complex $(CO)_5W^--C(H)(CH_3)(C_6H_6N)^+$ (19a). This complex was obtained as above upon silica gel chromatography which gave first complex **18a** in 12% yield and then complex **19a** in 23% yield. Spectral data for complex **18a**: yellow crystals, mp 118 °C; ^{1}H NMR ($CDCl_3$) δ 8.66 (dd, 2H, J = 5.2 and 1

Hz), 7.07 (d, 2H, J = 6 Hz), 2.39 (s, 3H, Me); ^{13}C NMR ($CDCl_3$) δ 202.73 (CO), 199.22 5CO), 155.77, 149.93, 128.82, 21.39. Anal. Calcd for $C_{11}H_7NO_5W$: C, 31.65; H, 1.68; N, 3.35. Found: C, 31.81; H, 1.62; N, 3.40. Spectral data for complex **19a**: orange solid, mp 75 °C; ^{1}H NMR ($CDCl_3$) δ 8.36 (d, 2H, J = 6.7 Hz), 7.39 (d, 2H, J = 6.4 Hz), 4.80 (q, 1H, J = 7 Hz, CHMe), 2.46 (s, 3H, Me), 2.31 (d, 3H, J = 7 Hz, CH*Me*); ^{13}C NMR ($CDCl_3$) δ 204.69 (CO), 202.10 (CO), 149.42, 138.81, 127.25, 55.99 (CHMe), 30.99 (Me), 21.27 (CH*Me*). Anal. Calcd for $C_{13}H_{11}NO_5W$: C, 35.05; H, 2.47; N, 3.14. Found: C, 35.04; H, 2.47; N, 3.21.

Reaction of 2-Methyl-1,2-dihydropyridine with Complex 5b: Formation of the Pyridinium Ylide Complex $(CO)_5Cr^-$−C(H)-$(CH_3)(C_6H_6N)^+$ (21b). A solution of 2-methyl-1,2-dihydropyridine obtained from *N*-carbomethoxy-1,2-dihydropyridine (2.3 g, 15 mmol) and MeLi (28 mL, 45 mmol) was added to a solution of complex **5b** (4 g, 15 mmol) at room temperature. After workup and silica gel chromatography as above, complex **20b** (0.19 g, 4%) and then complex **21b** (0.36 g, 8%) were isolated. Spectral data for complex **20b**: yellow crystals, mp 99 °C; ^{1}H NMR ($CDCl_3$) δ 8.40 (d, 2H, J = 6 Hz), 7.04 (d, 2H, J = 6 Hz), 2.35 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 221.57 (CO), 214.8 (CO), 154.79, 149.57, 126.17, 126.0, 21.15 (Me). Anal. Calcd for $C_{11}H_7NO_5Cr$: C, 46.31; H, 2.46; N, 4.91. Found: C, 46.18; H, 2.42; N, 4.85. Spectral data for complex **21b**: orange crystals, mp 93 °C; ^{1}H NMR ($CDCl_3$) δ 8.58 (d, 1H, J = 6 Hz), 7.57 (m, 2H), 7.41 (d, 1H, J = 6 Hz), 4.25 (q, 1H, J = 6.8 Hz, Cr−C−H), 2.08 (d, 3H, J = 6.8 Hz, $CHCH_3$); ^{13}C NMR ($CDCl_3$) δ 225.25 (CO), 220.18 (CO), 148.68, 139.31, 135.03, 128.5, 127.43, 124.76, 55.66 (CHMe), 30.08 (C*Me*), 21.23 (CH*Me*). Anal. Calcd for $C_{13}H_{11}NO_5Cr$: C, 49.84; H, 3.51; N, 4.47. Found: C, 49.81; H, 3.56; N, 4.42.

Reaction of *N*-Methyl-1,4-dihydropyridine with Complex 1: Formation of $(CO)_5W^-$−C(Ph)(OEt)$HCH_3N^+(C_5H_5N)$ (22). A solution of *N*-methyl-1,4-dihydropyridine (0.085 g) in diethyl ether (20 mL) was added to a solution of complex **1** (1 g, 2.5 mmol) in dichloromethane (10 mL) at −78 °C. The solution turned instantly to dark red. After warming to 0 °C, the solvent was evaporated under vacuum to give an oil which was washed with ice-cold hexane: ^{1}H NMR ($CDCl_3$) δ 9.11 (d, 2H, J = 6 Hz, NHC), 8.71 (t, 1H, J = 7 Hz, ═CH), 8.30 (m, 2H, CH═), 4.64 (s, 3H, NCH_3), 3.64 (dq, 1H, OC*H*H), 3.23 (dq, 1H, OCH*H*), 3.14 (q, 1H, C*H*CH_3), 1.15 (t, 3H, C*H*$_3CH_2$), 0.90 (d, 3H, J = 6.6 Hz, CHC*H*$_3$); ^{13}C NMR ($CDCl_3$) δ 205.10 (CO), 192.37 (CO), 146.52 (NCH), 129.50, 128.04, 126.83, 122.43, 120.31 (Ar, PyMe), 79.83 (CH), 67.22 (OCH_2), 49.69 (NCH_3), 16.64 (CH_3).

Reaction of *N*-Methyl-1,4-dihydropyridine with Complex 5a: Formation of $(CO)_5W^-$−C(CH_3)(OEt)$HCH_3N^+(C_5H_5N)$ (23). Under the same conditions as above, complex **23** was isolated as a dark red oil which was not further purified. Spectral data: ^{1}H NMR ($CDCl_3$) δ 9.12 (d, 2H, J = 6 Hz), 8.72 (t, 1H, J = 7 Hz), 8.27 (m, 2H), 8.00−7.01 (m, 5H), 5.05 (s, 1H, C*H*Ph), 4.65 (s, 3H, N−CH_3), 3.42 (m, 1H, OC*H*H), 3.06 (m, 1H, OCH*H*), 1.09 (t, 3H, C*H*$_3CH_2O$); ^{13}C NMR (CD_3-$COCD_3$) δ 205.1, 192.37 (CO), 146.52 (NCH═), 129.17 (═CH), 97.43 (*C*HCH_3), 64.60 (OCH_2), 54.97 (NCH_3), 16.35 (CH*C*H_3), 16.0 (OCH_2*C*H_3).

Phosphorus ylide $(CO)_5W^-$−C(Ph)(H)P^+Ph_3 (4a) was obtained from complex **17** (0.2 g, 0.4 mmol) and PPh_3 (0.127 g, 1.2 equiv), in methylene chloride (10 mL) at room temperature for 15 min. Evaporation of the solvent followed by silica gel chromatography gave with petroleum ether/dichloromethane as eluent complex **4a** as a yellow solid (0.24 g, 90%). Its spectral data were in all respect identical to those of the literature: ^{31}P NMR ($CDCl_3$) δ 30.99 (J_{PW} = 83.23 Hz).

Phosphorus ylide $(CO)_5W^-$−C(CH_3)(H)P^+Ph_3 (25) was obtained upon refluxing complex **7a** (0.2 g, 0.46 mmol) and PPh_3 (0.145 g, 0.55 mmol) in methylene chloride (10 mL) for 3 h. The solution turned from orange to pale yellow. Evaporation of the solvent followed by silica gel chromatography first gave with petroleum ether/dichloromethane (80/20) as eluents complex **25** (0.2 g, 72%) and then with petroleum ether/methylene chloride (40/60) complex **7a** (0.045 g). Spectral data for **25**: yellow crystals, mp 109 °C; ^{1}H NMR ($CDCl_3$) δ 7.79−7.20 (m, 15H, PPh_3), 2.47 (dq, 1H, $^2J_{HP}$ = 14.4 Hz, J_{HH} = 7.0 Hz, CH), 1.97 (dd, 3H, $^3J_{HP}$ = 22.7 Hz, J_{HH} = 7.0 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 202.02 (CO), 200.78 (CO), 133.40−124.31 (PPh_3), 22.52 (d, J_{CP} = 3.0 Hz, CH_3), −12.21 (d, J_{CP} = 15.2 Hz, CH); ^{31}P ($CDCl_3$) δ 39.14 (J_{WP} = 81.8 Hz). Anal. Calcd for $C_{25}H_{19}WO_5P$: C, 48.87; H, 3.09. Found: C, 48.96; H, 3.21.

1-Phenyl-2-methyl-2-pentylcyclopropane (26) was obtained upon refluxing complex **17** (0.1 g, 0.2 mmol) and 2-methyl-1-heptene (0.15 mL, 5 equiv) in methylene chloride (10 mL) for 10 h. Evaporation of the solvent followed by silica gel chromatography gave with petroleum ether as the eluent compound **26** (0.027 g, 66%, 60/40 mixture of two isomers) as an oil: ^{1}H NMR ($CDCl_3$) δ 7.14−7.05 (m, 10H, Ar), 1.78 (m, 2H, CHPh), 1.38−1.18 (m, 10H), 1.10 (s, 3H, CH_3), 1.08−1.03 (m, 4H), 0.84−0.73 (m, 4H), 0.67 (s, 11H, $3CH_3$, 2CH); ^{13}C NMR ($CDCl_3$) δ 140.35, 140.17, 129.03, 128.95, 127.92, 127.83, 125.49 (Ar), 41.50 (CH_2), 33.68 (CH_2), 32.25 (CH_2), 32.10 (CH_2), 30.31 and 29.83 (Cph), 26.80 and 26.31 (CH_2), 24.74 (CH_3), 23.37 and 23.15 (C_q), 22.88 and 22.64 (CH_2), 17.94 and 17.76 (CH_2 cyclopropane), 17.64 (CH_3), 14.24 (CH_3), 14.09 (CH_3); HRMS calcd (obsd) for $C_{15}H_{22}^+$ 202.1721 (202.1722).

***exo*- and *endo*-6-phenylbicyclo(3.1.0)hexane (26a)** were obtained from complex **17** (0.38 g, 0.77 mmol) and cyclopentene (10 mL) at the reflux temperature of the olefin for 12 h. Workup as above gave a 3/1 mixture of the endo and exo isomers of **26a** (0.60 g, 55%), the physical properties of which were in agreement with those of the literature.[13]

***exo*-3-Phenyltricyclo(3.2.1.0^{2,4})octane (26b)** was obtained as above from complex **17** (0.20 g, 0.4 mmol) and norbornene (0.10 g, 0.5 mmol) at the reflux temperature of CH_2Cl_2 as an oil (0.02 g, 27%, mixture of two isomers), the physical properties of which were in agreement with those of the literature.[32]

2-Phenylbicyclo(3.1.0)hex-4-ene (27a) was obtained from complex **17** (0.25 g, 0.5 mmol) and cyclopentadiene (2 mL, 3 mmol) in CH_2Cl_2 at room temperature for 1 h. Evaporation of the solvent followed by silica gel chromatography gave **27a** as an oil (0.025 g, 30%, one isomer). The spectroscopic data of this product were in all respect identical with those of the known endo isomer.[22]

1,2,3,4,5-Pentamethyl-*endo*-6-phenylbicyclo(3.1.0)hex-2-ene (27b) was obtained as above from complex **17** (0.30 g, 0.6 mmol) and pentamethylcyclopentadiene (0.27 g, 2 mmol), in benzene at room temperature for 2 h. Workup as usual gave **27b** as an oil (0.054 g, 40%): ^{1}H NMR ($CDCl_3$) δ 7.25−6.96 (m, 5H, Ar), 1.97 (q, J = 7 Hz, C*H*CH_3), 1.70 (s, 1H, C*H*Ph), 1.65 (s, 3H, ═CCH_3), 1.30 (s, 3H, ═CCH_3), 1.10 (s, 3H, CH_3), 0.98 (d, J = 7 Hz, CHC*H*$_3$); HRMS calcd (obsd) for $C_{17}H_{25}^+$ 226.1721 (226.1721).

2-Oxa-6-phenylbicyclo(3.1.0)hexane (28a) was obtained from complex **17** (0.30 g, 0.6 mmol) and dihydrofuran (0.15 mL, 2 mmol), in benzene (8 mL) at room temperature. Workup as usual gave **28a** as an oil (0.66 g, 69%): ^{1}H NMR ($CDCl_3$) δ 7.27−7.14 (m, 5H, Ar), 4.16 (dd, J = 5 Hz, CHO), 3.71−2.46 (m, 2H, OCH_2), 2.04−1.71 (m, 2H, CH_2), 1.86 (m, 1H, CHPh), 1.83 (m, 1H, CH); ^{13}C NMR ($CDCl_3$) δ 135.0, 129.6, 127.7, 125.7 (Ar), 69.4 (CH_2), 61.6 (OCH), 26.0 (CHPh), 25.3 (CH_2), 20.7 (CH); HRMS calcd (obsd) for $C_{11}H_{12}O^+$ 160.0888 (160.0888).

1-Ethoxy-6-phenylbicyclo(3.1.0)hexane (28b) was obtained from complex **17** (0.54 g, 1.09 mmol) and the ethoxy enol ether of cyclopentanone (0.26 g, 2.1 equiv) in dichloromethane at room temperature for 24 h. Workup as above gave compound **28b** (0.175 g, 79%) as a 2/1 mixture of the endo/exo isomers. Spectral data for the exo isomer (minor): ^{1}H NMR ($CDCl_3$) δ 7.33−7.09 (m, 5H, Ar), 3.76−3.69 (m, 1H, OCH), 2.43 (d, 1H, CHPh), 2.07−1.98 (m, 3H, C(2)-H_2 and C(4)-H), 1.86−1.83 (m, 1H, C(5)-H), 1.60−1.55 (m, 1H, C(4)-H), 1.38−1.27 (m, 1H, C(3)-H), 1.26 (t, 3H, CH_3), 0.08−0.03 (m, 1H, C(3)-H); ^{13}C NMR ($CDCl_3$) δ 137.1, 129.0, 128.4, 125.0 (Ar), 74.5 (C(1)), 64.3 (C(7)), 29.9 (C(6)), 24.9 (C(4)), 22.3 (C(3)), 15.8 (C(8)). Spectral data for the major endo isomer: ^{1}H NMR ($CDCl_3$) δ 7.33−7.09 (m, 5H, Ar), 3.49−3.46 (m, 1H, C(7)-H), 3.03−3.00 (m, 1H, C(7)-H), 2.07−1.68 (m, 3H, C(2)-H_2, C(3)-H_2, C(4)-H_2, C(5)-H), 0.93 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 139.1, 128.9, 128.2, 127.7 (Ar), 75.3 (C(1)), 64.1 (C(7)), 31.6 (C(6)), 29.9 (C(5)), 28.7 (C(2)), 24.9 (C(4)), 22.3 (C(3)), 15.8 (C(8)); HRMS calcd (obsd) for $C_{14}H_{18}O^+$ 202.1357 (202.1357).

2-[(Trimethylsilyl)oxy]-3-phenyltricyclo(3.2.1.0^{2,4})octane (28c) was obtained from complex **17** (0.30 g, 0.6 mmol) and 2-[(trimethylsilyl)-oxy]bicyclo(2.2.1)hept-2-ene (4.9 mmol)[50] in dichloromethane at room temperature for 24 h. Workup as above gave **28c** as an oil (0.16 g,

98%). Spectral data for **28c** (2.5:1 mixture of two isomers): ^{1}H NMR ($CDCl_3$) δ 7.28−7.09 (m, 5H, Ar), 2.50−2.20 (m, 2H, C(1)-H and C(5)-H), 2.18 (d, 1H, J = 3.7 Hz, CHPh), 2.00−1.00 (m, 6H, $3CH_2$), 0.9−0.5 (m, 1H, C(4)-H), 0.25 and −0.16 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_*$) δ 140.5, 139.74, 128.85, 126.03, 125.41 (Ar), 67.78 and 65.80 (C(2)), 43.13 and 42.32 (C(1)), 37.13 and 36.89 (C(5)), 33.07 and 31.68 (C(8)), 30.75 and 30.44 (C(6)), 29.12 and 28.90 (C(7)), 25.66, 25.23, 25.12, 1.34 and 0.7 ($SiMe_3$); MS calcd (obsd) for $C_{17}H_{24}OSi^+$ 272 (272).

1-Methyl-1-acetoxy-3-phenylcyclopropane (28d) was obtained from complex **17** (0.20 g, 0.4 mmol) and isopropenyl acetate (10 mL) at room temperature for 12 h. Workup as above gave **28d** as an oil (0.050 g, 63%). Spectral data for **28d** (cis/trans = 73/27): ^{1}H NMR ($CDCl_3$) δ (cis) 7.28 (m, 5H, Ar), 2.37 (dd, J = 7.5 and 2.7 Hz, CHPh), 1.74 (s, 3H, CH_3CO), 1.66 (s, 3H, CH_3), 1.36−1.03 (m, 2H, CH_2); (trans) 7.30−7.12 (m, 5H, Ar), 2.16−2.09 (m, 1H, CHPh), 2.03 (s, 3H, CH_3CO), 1.36−1.03 (m, 2H, CH_2), 1.21 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ (cis) 170.43 (CO), 137.09, 127.89, 127.80, 126.01 (Ar), 61.00 (C-O), 29.23 (CH_3C═O), 22.20 (CH_3), 20.91 (CHPh), 18.42 (CH_2); HRMS calcd (obsd) for $C_{12}H_{14}O_2^+$ 190.0993 (190.0993).

2-[(Trimethylsilyl)oxy]-3-methyltricyclo(3.2.1.0^{2,4})octane (28e) was obtained from complex **7a** (0.50 g, 1.16 mmol) and 2-[(trimethylsilyl)oxy]bicyclo(2.2.1)hept-2-ene (1.65 g, 9 mmol) in reluxing benzene for 12 h. Workup as above gave compound **28e** (0.11 g, 28%). Spectral data for **28e** (1/4 mixture of *endo*/*exo*-cyclopropyl-*endo*-methyl isomers): ^{1}H NMR ($CDCl_3$) δ (endo) 2.31−2.30 (1H, m, C(1)-H), 2.17−2.16 (m, 1H, C(5)-H), 1.97−1.90 (m, 2H, C(7)-H_2), 1.55−0.98 (m, 4H, C(6)-H_2 and C(8)-H_2), 0.98 ((s, 3H, CH_3), 0.98−0.80 (m, 1H, C(4)-H), 0.74−0.68 (dd, 1H, C(3)-H), 0.13 (s, 9H, $SiMe_3$); (exo) 2.33−2.32 (m, 1H, C(1)-H), 2.30−2.19 (m, 1H, C(5)-H), 1.97−1.90 (m, 2H, C(7)-H_2), 1.55−0.9 (m, 4H, C(6)-H_2 and C(8)-H_2), 0.98−0.80 (m, 1H, C(4)-H), 0.74−0.68 (dd, 1H, C(3)-H), 0.23 (s, 3H, CH_3), 0.13 (s, 9H, $SiMe_3$); ^{13}C NMR ($CDCl_3$) δ 65.5 (C(2)), 42.5 (C(1)), 36.4 (C(5)), 29.2 (C(4)), 28.6 (C(6)), 24.7 (C(7)), 19.9 (C(3)), 12.0 (C(3)), 1.0 ($SiMe_3$); HRMS calcd (obsd) for $C_{12}H_{22}OSi^+$ 210.1439 (210.1430).

1-Ethoxy-1-phenyl-2-methylcyclopropane (28f) was obtained from complex **7a** (0.50 g, 1.16 mmol) and acetophenone ethyl enol ether (0.45 g, 2.3 mmol) in benzene at 50 °C for 3 days. Workup as above gave **28f** as an oil (0.065 g, 31%). Spectral data for **28f** (2.2:1 mixture of isomers): ^{1}H NMR ($CDCl_3$) δ 7.33−7.29 (m, 5H, Ar), 3.58−3.32 (m, 2H, OCH_2), 1.31 and 1.29 (2s, 6H, $2CH_3$), 1.20−1.16 (t, 6H, $2OCH_2CH_3$), 0.93−0.82 (m, 1H, *CH*CH_3), 0.78−0.70 (m, 1H, C*H*CH_3); HRMS calcd (obsd) for $C_{12}H_{16}O^+$ 176.1201 (176.1181).

(1-Ethoxy-3-phenylprop-2-enylidene)pentacarbonyltungsten(0) (29) was obtained upon stirring complex **17** (0.3 g, 0.6 mmol) with ethoxyacetylene (0.5 g, 50% by weight in hexane, 3.6 mmol) in methylene chloride (10 mL) for 1 h at room temperature. Evaporation of the solvent followed by silica gel chromatography gave with petroleum ether as the eluent complex **29** (0.017 g, 6%) as a red solid. Its physical data were in all respect identical with those of an authentic sample prepared in the laboratory. The same result was obtained by carrying out the reaction at −78 °C.

(1-Ethoxy-2-benzylhex-5-enylidene)pentacarbonyltungsten(0) (30b). Complex **30a** (9.0 g, 2×10^{-2} mol) in THF (160 mL) was cooled to −78 °C. A solution of BuLi (13.8 mL, 1.6 M) in hexanes was then slowly added followed by benzyl bromide (2.6 mL, 2.2×10^{-2} mol). The solution was then warmed to room temperature over 1 h. Evaporation of the solvents followed by the addition of silica gel (15 g) gave a slurry which was put on a column of silica gel. Elution with petroleum ether first gave the unreacted starting complex **30b** contaminated with benzyl bromide (3.31 g). Elution with petroleum ether/methylene chloride (95/5) gave complex **30b** as a yellow oil (3.63 g, 33.6%). Spectral data for **30b**: ^{1}H NMR (CDCl) δ 7.31−7.05 (m, 5H, Ar), 5.78−5.61 (m, 1H, CH═CH_2), 5.01−4.85 (m, 4H, CH═CH_2, OCH_2), 4.21 (dt, J = 6.4 Hz, W═C−CH), 2.92 (dd, 1H, Ph−CH), 2.44 (dd, 1H, PhCH), 2.03 (m, 2H, CH_2CH═), 1.64 (m, 1H, −CH−C*H*H), 1.62 (t, 3H, CH_3), 1.40 (m, 1H, CH−CH*H*); ^{13}C NMR ($CDCl_3$) δ 339.44 (W═C), 203.10 (CO), 197.31 (CO), 139.02, 138.13, 129.31, 128.53, 128.40, 126.50, 115.18 (Ar, C═C), 80.60 (OCH_2), 75.65 (═C−CH), 37.81, 31.73, 31.18, 14.67; HRMS calcd (obsd) for $C_{20}H_{20}OW^+$ 540.0769 (540.0767).

(1α,2β,5α)-2-Benzylbicyclo(3.1.0)hexane (31b), 2-Benzyl-hexa-1,5-diene (32b), and 5-Benzylhex-1-ene (33b). A mixture of 1,2- and 1,4-dihydropyridines prepared from *N*-carbomethoxydihydropyridines (2.78 g, 2×10^{-2} mol) in diethyl ether (50 mL) as above was slowly added to a solution of complex **30b** (3.60 g, 6.66×10^{-3} mol) in diethyl ether (50 mL) at 0 °C. The solution turned to dark orange and was kept at room temperature for 10 h. Evaporation of the solvent followed by silica gel chromatography of the residue gave with petroleum ether as the eluent first a mixture of **32b** and **31b** (0.79 g) and then the diene **32b** (0.20 g, 18%). Chromatography on silver nitrate impregnated silica gel of the first fraction gave pure **31b** as a liquid (0.5 g, 44%), then the olefin **33b** (0.06 g), and finally the diene **32b**. Spectral data for **32b**: ^{1}H NMR ($CDCl_3$) δ 7.36−7.21 (m, 5H, Ar), 5.85−5.77 (m, 1H, C*H*═CH_2), 5.85 (d, 1H, J = 6.6 Hz, CH═CH*H*), 5.01 (d, 1H, J = 1.6 Hz, CH═C*H*H), 4.88 (br s, 1H, C═CH), 4.81 (br s, 1H, C═CH*h*), 3.38 (s, 2H, $PhCH_2$), 2.23 (m, 2H), 2.1 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 148.43, 139.81, 138.44, 129.13, 128.41, 126.20, 114.70, 111.54 (Ar, CH═CH_2), 43.20 (PhC), 34.83, 32.00; MS calcd (obsd) for $C_{13}H_{16}^+$ 172 (172). Spectra data for **33b**: ^{1}H NMR ($CDCl_3$) δ 7.32−7.12 (m, 5H, Ar), 5.86−5.73 (m, 1H, C*H*═CH_2), 5.04 (m, 1H, CH═C*H*H), 4.90 (m, 1H), 2.65 (dd, 1H, J = 13.4 and 6 Hz, CH*H*Ph), 2.33 (dd, 1H, J = 13.4 and 8 Hz, C*H*HPh), 2.10 (m, 2H, CH_2C═), 1.73 (m, 1H, C*H*CH_3), 1.48 (m, 1H, CHCH*H*), 1.26 (m, 1H, CHC*H*H), 0.85 (d, 3H, J = 6.8 Hz, CHCH_3); ^{13}C NMR ($CDCl_3$) δ 141.48, 139.14, 129.23, 128.13, 125.68, 114.25, (Ar, CH═CH_2), 43.63 ($^+$PhC), 35.88 (CH_2), 34.53 (CH), 31.45 (CH_2), 19.32 (CH_3); HRMS calcd (obsd) for $C_{13}H_{10}^+$ 174.14085 (174.14078). Spectral data for **31b** (1/1 mixture of isomers): ^{1}H NMR ($CDCl_3$) δ 7.15−7.01 (m, 10H, Ar), 2.50−2.12 (m, 6H), 1.59−1.51 (m, 5H), 1.18−1.02 (m, 6H), 0.64−0.56 (m, 1H), 0.16−0.011 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 142.0, 141.8, 129.24, 128.87, 125.72, 125.62 (Ar), 42.30, 41.77, 40.20, 27.46, 26.72, 25.18, 21.81, 20.68, 16.70, 16.10, 6.66, 3.29; HRMS calcd (obsd) for $C_{13}H_{16}^+$ 172.1252 (172.1252).

(1-Ethoxy-2-cinnamylhex-5-enylidene)pentacarbonyltungsten-(0) (30c) was obtained as above from complex **30a** (4.5 g, 10 mmol) and cinnamyl bromide (2.22 mL, 15 mmol) as an orange oil (2.55 g, 45%): ^{1}H NMR ($CDCl_3$) δ 7.33−7.31 (m, 5H, Ar), 6.37 (d, 1H, J = 15.8 Hz, CHPh), 6.17 (dt, 1H, J = 15.8 and 17.6 Hz), 5.78 (m, 1H, C*H*═CPh), 4.98−5.06 (m, 2H, C═C*H*2), 4.94 (q, 2H, OCH_2), 4.16 (m, 1H, CH), 2.46 (m, 1H CH*H*), 2.22 (m, 2H, CH_2), 2.06 (m, 1H, C*H*H), 1.70 (m, 1H, CH*H*), 1.62 (t, 3H, CH_3), 1.46 (m, 1H, C*H*H); ^{13}C NMR ($CDCl_3$) δ 339.02 (W═C), 203.21 and 197.41 (CO), 138.11, 137.26, 132.54, 128.58, 127.32, 126.92; 126.11, 115.24 (CH═CH, Ar), 80.65 (OCH_2), 71.9 (W═C*C*), 35.54, 31.77, 31.14 ($3CH_2$), 14.74 (CH_3); HRMS calcd (obsd) for $C_{22}H_{23}WO_6^+$ 566.0925 (566.0924).

(1α,2β,5α)-2-(3-Phenyl-2-propenyl)bicyclo(3.1.0)hexane (31c) and 2-(3-phenyl-2-propenyl)-1,5-hexadiene (32c) were obtained from complex **30c** (2.2 g, 3.88 mmol) and *N*-carbethoxydihydropyridine (3 equiv) as above in diethyl ether (30 mL) first at 0 °C and then at room temperature for 22 h. Evaporation of the solvent under vacuum followed by silica gel chromatography gave first with petroleum ether as eluent a mixture of **31c** and **32c** and then with the same eluent the starting complex **30c** (0.24 g). Chromatography on silver nitrate impregnated silica gel first gave **31c** as an oil (0.30 g, 40%), then **31c** and **32c** (0.1 g), and finally **32c** as an oil (0.060 g, 8%). Spectral data for **31c** (1/1 mixture of isomers): NMR ($CDCl_3$) δ 7.77−7.18 (m, 10H, Ar), 6.45−6.18 (m, 4H, CH═CH), 2.30−0.79 (m, 18H), 0.34−0.12 (m, 4H, CH_2 cyclopropane); ^{13}C NMR ($CDCl_3$) δ 138.06, 137.93, 130.74, 130.65, 129.96, 128.50, 126.83, 126.77, 125.98 (Ar, C═C), 40.45 and 40.06 (2CH), 39.27 and 37.39 ($2CH_2$), 27.50, 26.53, 25.44, 25.38 (CH_2), 21.89 and 20.77 (CH cyclopropane), 16.58 and 16.28 (CH cyclopropane), 6.82 and 3.40 (CH_2); HRMS calcd for $C_{15}H_{18}$ 198.1408 (M^+), measd 198.1408. Spectral data for **32c**: ^{1}H NMR ($CDCl_3$) δ 7.35−7.25 (m, 5H, Ar), 6.42 (d, 1H, J = 15.7 Hz, ═CHPh), 6.28−6.14 (m, 1H, C*H*═CHPh), 5.90−5.73 (m, 1H, C*H*═CH_2), 5.08−4.94 (m, 2H, CH═CH_2), 4.83 (m, 2H, C═CH_2), 2.92 (d, 2H, J = 6.9 Hz, CCH_2C═), 2.19 (m, 4H, $2CH_2$); ^{13}C NMR ($CDCl_3$) δ 147.77 (*C*═CH_2), 138.42 (*C*H═CH_2), 137.74 (Ar), 131.59 (═*C*HPh), 128.60 (Ar), 128.33 (*C*H═CHPh), 127.12 (Ar), 126.17 (Ar), 114.72 (CH═CH_2), 110.67 (C═CH_2), 40.09, 35.45, 32.02 ($3CH_2$); HRMS calcd for $C_{15}H_{18}^+$ 198.1408 (198.1408).

(1α,5α,6α)-6-Pentylbicyclo(3.1.0)hexane (31d) was obtained from complex **30d** (1.5 g, 2.88 mmol) and dihydropyridine obtained from *N*-carbethoxydihydropyridine (3 equiv) first at 0 °C, then at room temperature for 24 h, and finally at the reflux temperature of diethyl ether for 1 h. Evaporation of the solvent followed by silica gel chromatography first gave **31d** (0.3 g, 70%) and then the starting complex **30d** (0.28 g). Spectral data for **31d**: ^{1}H NMR ($CDCl_3$) δ 1.75−1.60 (m, 4H, C(2)-H_2 and C(4)-H_2), 1.53 (m, 1H, C(3)-H), 1.34−1.28 (m, 6H, C(8)-H_2, C(9)-H_2 and C(10)-H_2), 1.15 (m, 2H, C(7)-H_2), 1.10 (m, 1H, C(3)-H), 0.95 (m, 2H, C(1)-H and C(5)-H), 0.91 (t, 3H, CH_3), 0.44 (hep, 1H, J = 3.1 and 6.2 Hz, C(6)-H); ^{13}C NMR ($CDCl_3$) δ 33.83 (C(7)), 31.88 and 29.40 (C(8) and C(9)), 27.66 (C(2) and C(4)), 24.39 (C(1) and C(5)), 22.69 (C(10)), 21.70 (C(3)), 19.16 (C(6)), 14.13 (CH_3); HRMS calcd (obsd) for $C_{11}H_{20}^+$ 152.1565 (152.1565).

(1α,2α,5α,6α)-6-Pentyl-2-benzylbicyclo(3.1.0)hexane (31e) and 2-benzylundec-1,5-diene (32e) were obtained as above from complex **30e** (1.2 g, 2 mmol) and dihydropyridine (3 equiv) as above first at 0 °C then at room temperature for 12 h. Workup and purification as above gave starting carbene complex **30e** (0.25 g), compound **31e** (0.185 g, 40%) as an oil, and the diene **32e** (0.070 g). Spectral data for **31e**: ^{1}H NMR ($CDCl_3$) δ 7.32−7.20 (m, 5H, Ar), 2.64 (d, 1H, J = 3.6 Hz, C*H*HPh), 2.35 (m, 1H, H-2), 1.74 (m, 1H, H-4′), 1.67 (m, 1H, H-4), 1.53 (m, 1H, H-3), 1.39−1.27 (m, 6H, 3CH_2-8,9,10), 1.19 (m, 1H, H-7), 1.11 (m, 1H, H-7′), 0.95 (m, 1H, H-5), 0.92 (m, 3H, CH_3), 0.89 (m, 1H, H-1), 0.84 (m, 1H, H-3′), 0.62 (m, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ 132.90, 128.45, 127.72, 125.12 (Ar), 42.27 (C(2)), 39.80 (CH_2Ph), 32.32 (C(7)), 31.43, 29.07 (2CH_2), 28.00 and 27.95 (C(3) and C(5)), 27.22 (C(4)), 24.14 (C(1)), 22.38 (CH_2), 16.30 (C(6)), 13.77 (CH_3); HRMS calcd for $C_{18}H_{26}$ 242.2034 (M^+), measd 242.2034. Spectral data for **32e**: ^{1}H NMR ($CDCl_3$) δ 7.33−7.20 (m, 5H, Ar), 5.43−5.38 (m, 2H, CH═CH), 4.76 (s, 1H, C═CH*H*), 3.36 (s, 2H, CH_2Ph), 2.14 (m, 2H, CH_2C═C), 2.06 (m, 2H, CH_2C═), 1.87 (m, 2H, CH_2C═), 1.37−1.25 (m, 6H, 3 CH_2), 0.90 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 148.72 (*C*═CH_2), 139.86 (Ar), 130.91 (═CH), 129.52 (═CH), 129.10 (Ar), 128.31 (Ar), 126.09 (Ar), 11.30 (C═*C*H_2), 43.20 (CH_2Ph), 35.50, 32.62, 31.47 (3 *C*H_2C═), 30.83, 29.34, 22.64 (3CH_2), 14.18 (CH_3); HRMS calcd (obsd) for $C_{18}H_{26}^+$ 242.2034 (242.2034).

(1-Ethoxyundec-5-enylidene)pentacarbonyltungsten(0) (30d) was obtained as above from the corresponding iodide (5.8 g, 22 mmol), tBuLi (25.9 mL, 44 mmol), and $W(CO)_6$ (7.75 g, 22 mmol) as a yellow oil (4.5 g, 40%): ^{1}H NMR ($CDCl_3$) δ 5.50−5.35 (m, 2H, CH═CH), 4.87 (q, 2H, OCH_2), 3.17 (m, 2H, W═CCH_2), 2.02−1.91 (m, 4H, CH_2-CH═CHCH_2), 1.60 (t, 3H, CH_3), 1.61−1.50 (m, 2H, CH_2), 1.36−1.22 (m, 6H, 3CH_2), 0.86 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 334.21 (W═C), 203.58 and 197.42 (CO), 132.06, 128.85 (2C═C), 80.68 (OCH_2), 64.57 (W═CC), 32.60, 32.04 (CC═CC), 31.47, 29.26, 26.28, 22.59 (3CH_2), 14.84 (OCH_2*C*H_3), 14.15 (CH_3); HRMS calcd (obsd) for $C_{18}H_{24}O_6W^+$ 520.1082 (520.1081).

(1-Ethoxy-2-benzylundec-5-enylidene)pentacarbonyltungsten-(0) (30e) was obtained as above by alkylation of complex **30d** (3 g, 5.77 mmol) with benzyl bromide (1.03 mL, 8.65 mmol) in the presence of BuLi as a yellow oil (1.9 g, 55%): ^{1}H NMR ($CDCl_3$) δ 7.33−7.10 (m, 5H, Ar), 5.45−5.25 (m, 2H, CH═CH), 4.90 (q, 2H, OCH_2), 4.23 (m, 1H, W═CCH), 2.90 (dd, 1H, J = 13.3 and 6.6 Hz, C*H*HPh), 2.48 (dd, 1H, J = 13.3 and 7.4 Hz, CH*H*Ph), 2.07−1.89 (m, 4H, CH_2CH═CHCH_2), 1.71−1.50 (m, 5H, CH_2 and CH_3), 1.41−1.18 (m, 6H, 3CH_2), 0.89 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 332.98 (W═C), 203.32 and 197.34 (CO), 139.18, 131.67, 129.34, 128.54, 126.48, 126.04 (C═C and Ph), 80.62 (OCH_2), 73.61 (CH), 37.82 (CH_2Ph), 32.64, 31.87, 31.54, 30.63, 29.33, 22.66 (6CH_2), 14.80 (CH_2*C*H_3), 14.18 (CH_3); MS calcd (obsd) for $C_{25}H_{30}O_6W^+$ 610.1551 (610.1550).

(1-Ethoxy-2-cinnamylundec-5-enylidene)pentacarbonyltungsten-(0) (30f) was obtained as above from complex **30d** (3.7 g, 7.9 mmol) and cinnamyl bromide (1.6 g, 7.9 mmol) in the presence of BuLi as a yellow oil (2.4 g, 50%): ^{1}H NMR ($CDCl_3$) δ 7.30−7.23 (m, 5H, Ar), 6.37 (d, J = 16 Hz, PhC═C*H*), 5.37 (m, 2H, C*H*═C*H*), 4.90 (q, 2H, OCH_2), 4.13 (m, 1H, W═CC*H*), 2.46 and 2.22 (m, 2H, CH_2Ph), 1.95 (m, 4H, CH_2C═CCH_2), 1.62 (t, 3H, OCH_2CH_3), 1.17 (m, 6H, 3CH_2), 8.87 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 333.0 (W═C), 203.2 and 197.4 (CO), 137.1, 128.6, 127.3, 126.1 (Ar), 132.2, 129.1, 127.1, 127.0 (C═C), 80.5 (OCH_2), 71.7 (W═C*C*), 35.3, 32.5, 31.7, 31.4, 30.5, 20.1, 22.5 (CH_2), 14.7 (OC*C*H_3), 14.0 (CH_3); HRMS calcd (obsd) for $C_{27}H_{32}O_6W^+$ 636.1708 (636.1708).

[1-Ethoxy-2-(methoxymethyl)undec-5-enylidene]pentacarbonyltungsten(0) (30g) was obtained as above by alkylation of complex **30d** (1.8 g, 3.46 mmol) with chloromethyl methyl ether (2.4 mL, 3.8 mmol) in the presence of BuLi: yellow oil (0.7 g, 35%); ^{1}H NMR ($CDCl_3$) δ 5.41−5.32 (m, 2H, CH═CH), 4.89 (q, 2H, OCH_2), 4.28 (m, 1H, CH), 3.50 (dd, 1H, J = 9.3 and 7.5 Hz, OCH*H*), 3.30 (dd, 1H, J = 9.3 and 5.5 Hz, OC*H*H), 3.26 (s, 3H, OCH_3), 2.07−1.90 (m, 4H, ═CCH_2), 1.58 (t, 3H, CH_3), 1.38−1.19 (m, 8H, 4CH_2), 0.86 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 337.74 (W═C), 200.51 and 197.35 (CO), 131.72 and 129.10 (CH═CH), 80.62 (OCH_2), 73.75 (OCH_2), 59.17 (OCH_3), 32.57, 31.45, 30.63, 29.95, 29.22, 22.58 (CH_2), 14.72, 14.09 (CH_3); MS calcd (obsd) for $C_{13}H_{28}O_6W$ (M − CO)$^+$ 536.1395 (536.1395).

(1α,2α,5α,6α)-6-Pentyl-2-(3-phenyl-2-propenyl)bicyclo(3.1.0)-hexane (31f) and 2-(3-phenyl-2-propenyl)undec-1,5-diene (32f) were obtained as above from complex **30f** (1.8 g, 2.8 mmol) and dihydropyridine (2 equiv). Workup followed by silica gel chromatography gave **31f** as an oil (0.27 g, 35%) and then **32f** (0.05 g, 7%). Spectral data for **31f**: ^{1}H NMR ($CDCl_3$) δ 7.40−7.20 (m, 5H, Ar), 6.42 (1H, d, J = 16 Hz, ═CHPh), 6.35−6.27 (1H, m, ═C*H*CH_2), 2.27−2.21 (m, 3H, CH_2 and H-2), 1.75−1.69 (m, 2H, H-4, H-4′), 1.63−1.60 (m, 1H, H-3), 1.32−1.25 (m, 7H, H-7, H_2-8,9,10), 1.03−1.00 (m, 3H, H-7′, H-1, H-5), 0.94−0.90 (m, 3H, CH_3), 0.87−0.79 (m, 1H, H-3′), 0.61−0.56 (m, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ 138.14, 130.83 (CH_2CH═), 130.04 (PhCH═), 128.54 (Ar), 126.78, 125.97 (Ar), 40.76 (C(2)), 37.51 (CH_2C═), 32.75 (C(7)), 31.86 (CH_2), 29.54 (CH_2), 28.59 (C(5)), 28.26 (C(3)), 27.72 (C(4)), 24.54 (C(1)), 22.83 (CH_2), 16.90 (C(6)), 14.23 (CH_3); HRMS calcd (obsd) for $C_{20}H_{28}^+$ 268.2191 (268.2191). Spectral data for **32f**: ^{1}H NMR ($CDCl_3$) δ 7.28 (m, 5H, Ar), 6.42 (d, 1H, J = 16 Hz, ═CHPh), 6.24 (m, 1H, CH═CPh), 5.44 (m, 2H), 4.84 (m, 2H), 2.94 (m, 2H), 2.17 (m, 4H), 1.99 (m, 2H), 1.33 (m, 6H), 0.87 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 137.2, 132.4, 130.9, 128.6, 127.9, 127.8, 127.1, 126.4, 125.2, 39.4, 35.5, 32.0, 30.2, 28.7, 22.0, 18.9, 13.5; HRMS calcd (obsd) for $C_{20}H_{28}^+$ 268.2191 (268.2191).

(1α,2α,5α,6α)-(6-Pentyl-2-methylmethoxy)bicyclo(3.1.0)hexane (31g) and 2-(methylmethoxy)undec-1,5-diene (32g) was obtained as above from complex **30g** (0.6 g, 1.06 mmol) and dihydropyridine at room temperature for 4 h. Workup as usual gave first **32g** (0.065 g, 33%) as an oil. Spectral data of **31g**: ^{1}H NMR ($CDCl_3$) δ 3.37 (s, 3H, OCH_3), 3.35−3.31 (m, 2H, OC*H*H), 2.39−2.34 (m, 1H, H-2), 1.74−1.69 (m, 2H, H-4,4′), 1.61−1.58 (m, 1H, H-3), 1.36−1.23 (m, 6H, CH_2-8,9,10), 1.22 (m, 1H, H-7), 1.02 (m, 2H, H-1, H-5), 0.89 (m, 3H, CH_3), 0.79−0.70 (m, 1H, H-3′), 0.54−0.49 (m, 1H, H-6); ^{13}C NMR ($CDCl_3$) δ 76.64 (OCH_2), 58.97 (OCH_3), 40.50 (C(2)), 31.53 and 31.74 (C(7), C(8)), 29.40 (C(9)), 27.43 (C(4)), 26.84 and 24.37 (C(1), C(5)), 25.65 (C(3)), 22.79 (C(10)), 16.88 (C(6)), 14.18 (CH_3); MS calcd (obsd) for $C_{13}H_{24}O^+$ 196 (196). Spectral data for **32g**: 0.020 g, 10%, oil; ^{1}H NMR ($CDCl_3$) δ 5.50−5.39 (m, 2H, CH═CH), 5.00 and 4.92 (br s, 2H, ═CH_2), 3.85 (s, 2H, OCH_2), 3.32 (s, 3H, OCH_3), 2.12 (m, 2H, CH_2), 1.96 (m, 4H, 2═CCH_2), 1.30−1.25 (m, 6H, 3CH_2), 0.88 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 145.77 (═C), 131.09 and 129.54 (2═CH), 111.72 (═CH_2), 75.78 (OCH_2), 57.99 (OCH_3), 33.21, 32.66, 31.51, 30.84, 29.39, 22.69 (CH_2), 14.20 (CH_3); MS calcd (obsd) for $C_{13}H_{24}O^+$ 196 (196).

(1-Ethoxy-2-benzylpentylidene)pentacarbonyltungsten(0) (34) was obtained as above from (1-ethoxypentylidene)pentacarbonyltungsten-(0) (2.5 g, 5.75 mmol) and benzyl bromide (1.0 mL, 8.6 mmol), in the presence of BuLi, as a yellow oil (1.4 g, 46%): ^{1}H NMR ($CDCl_3$) δ 7.40−7.10 (m, 5H, Ar), 4.92 (q, 2H, OCH_2), 4.22 (m, 1H, CH), 2.90 (dd, 1H, J = 13.3 and 7.1 Hz, CH*H*Ph), 2.43 (dd, 1H, J = 13.3 and 7.8 Hz, CH*H*Ph), 1.62 (t, 3H, CH_3), 1.60−1.15 (m, 4H, 2CH_2), 0.85 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 340.12 (W═C), 203.95 and 197.39 (CO), 139.27, 129.25, 128.55, 128.46, 126.03 (Ar), 80.65 (OCH_2), 74.26 (CH), 38.00 (CH_2Ph), 34.35 and 21.02 (CH_2), 14.81 (2CH_3); HRMS calcd (obsd) for $C_{19}H_{20}O_6W^+$ 528.0769 (528.0767).

2-Benzylpent-2-ene (36) was obtained from complex **34** (1 g, 1.9 mmol) and dihydropyridine (2 equiv) at room temperature. Evaporation of the solvent followed by chromatography gave with petroleum ether as the eluent the olefin **36** (0.060 g, 33%) and then with the same eluent complex **34** (0.4 g). Spectra data for **36**: ^{1}H NMR ($CDCl_3$) δ 7.33−

7.20 (m, 5H, Ar), 4.84 and 4.75 (s, 1H, C═CHH), 3.35 (s, 2H, CH_2-Ph), 1.96 (t, 2H, J = 7.5 Hz, CH_2C═), 1.48 (m, 2H, CH_2), 0.90 (t, 3H, CH_3); ^{13}C NMR ($CDCl_3$) δ 149.08 (C═CH_2), 140.01, 129.09, 128.33, 126.07 (Ar), 43.10 (CH_2Ph), 37.64 (CH_2C═C), 20.81 (CH_2), 13.90 (CH_3); HRMS calcd (obsd) for $C_{12}H_{16}^+$ 160.1252 (160.1252).

(1-Ethoxyundec-5(*E*)-enylidene)pentacarbonyltungsten(0) (30d′) was obtained as **30d** from the corresponding iodide as a yellow oil (35%): ^{1}H NMR ($CDCl_3$) δ 5.50−5.30 (m, 2H, HC═CH), 4.89 (q, 2H, J = 7.1 Hz, OCH_2), 3.20 (m, 2H, W═CCH_2), 2.10−1.95 (m, 4H, 2═CCH_2), 1.61 (t, 3H, J = 7.1 Hz, CH_3), 1.60−1.45 (m, 2H, CH_2), 1.40−1.20 (m, 6H, 3CH_2), 0.80 (t, 3H, J = 6.9 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 334.04 (W═C), 203.37 and 197.39 (CO), 131.41 and 128.26 (C═C), 80.69 (OCH_2), 64.70 (W═CC), 31.55, 29.44, 27.28, 26.65, 22.61 (CH_2), 14.79 and 14.11 (CH_3); HRMS calcd (obsd) for $C_{18}H_{24}O_6W^+$ 520.1082 (520.1081).

(1α,5α,6*β*)-6-Pentylbicyclo(3.1.0)hexane (31d′) was obtained as above from complex **30d′** (0.7 g) and dihydropyridines (3 equiv) as an oil (0.120 g, 60%): ^{1}H NMR ($CDCl_3$) δ 1.90−1.80 (m, 2H, H-4 and H-2), 1.80−1.75 (m, 1H, H-3), 1.60−1.53 (m, 2H, H-4 and H-2), 1.43−1.25 (m, 9H, H-1,3,5,8,9,10), 1.17 (dt, J = 7.1 Hz, CH_2-7), 0.90 (t, 3H, J = 6.9 Hz, CH_3), 0.67 (dddd, 1H, J = 7.12 Hz, H-6); ^{13}C NMR ($CDCl_3$) δ 32.27 (C(10)), 30.46 (C(9)), 27.56 (C(3)), 25.45 (C(3)), 25.45 (C(2), C(4)), 23.90 (C(7)), 23.11 (C(8)), 22.59 (C(1), C(5)), 21.66 (C(6)), 14.48 (C(11)); HRMS calcd (obsd) for $C_{11}H_{20}^+$ 152.1565 (152.1564).

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Supporting Information Available: Tables of fractional parameters and anisotropic thermal parameters for complexes **7a** and **8a** (4 pages). See any current masthead page for ordering and Internet access instructions.

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