Formation and Selective Trapping of 2,5-Dihydropyridine and Its Isopropylidene Derivative by Tungsten(0) Alkylidene Complexes. X-ray Structure of the 5-Isopropylidene-2,5-dihydropyridine Adduct

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Received September 11, 1997

A mixture of 1,2- and 2,5-dihydropyridines and 5-isopropylidene-2,5-dihydropyridine, obtained from 1-(methoxycarbonyl)-1,2-dihydropyridine and methyllithium followed by protonation, reacts with a series of pentacarbonyl tungsten(0) alkoxycarbene complexes to afford, besides the expected pyridinium ylide complexes **7**, the 2,5-dihydropyridinium ylide complexes **6** together with the 5-isopropylidene-2,5-dihydropyridinium ylide complexes **5**, which could be separated and fully characterized by X-ray analysis.

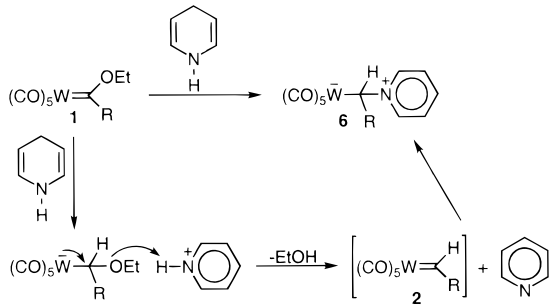
Introduction

Very recently we described the reduction of alkoxycarbene complexes of tungsten and chromium with 1,2- and 1,4-dihydropyridines, a reaction which opened the way to the synthesis and use as cyclopropanation and cycloaddition reagents of protected alkylidene complexes of W(0) and Cr(0) in the form of pyridinium ylides.[1,2]

A tentative mechanism explaining this transformation, which is akin to the dihydropyridine-induced reductions of carbonyl compounds in biological systems and involves a hydride transfer from dihydropyridine to the carbene carbon with formation of pyridinium, has been suggested. This transfer is probably followed by a pyridinium-induced elimination of alcohol and of a recoordination of the pyridine thus formed on the highly electrophilic intermediate alkylidene complex **2** (Scheme 1). The formation and isolation of a second complex, which could also be established as being an ylide of 2,5-dihydropyridine, was briefly mentioned, but its origin remained intriguing, since no 2,5-dihydropyridine was supposed to be formed upon reduction of pyridinium chloroformate by sodium borohydride.[3]

Herewith we provide evidence for the generality of the formation of 2,5-dihydropyridinium ylide complexes, starting from a series of ethoxycarbene complexes of tungsten, and demonstrate that indeed a mixture of 1,2- and 2,5-dihydropyridines is formed from the lithio amide of 1,2-dihydropyridine during the deprotection reaction of the 1-(methoxycarbonyl)-1,2-dihydropyridine precursor. The intermediate in this transformation could be trapped with acetone and isolated as a new isopropylidene-substituted 2,5-dihydropyridinium ylide complex of W(0).

Scheme 1



Results and Discussion

Formation of 2,5-Dihydropyridine and of 5-Isopropylidene-2,5-dihydropyridine from Protected 1,2-Dihydropyridine and Their Trapping by $(OC)_5W{=}C(CH_3)H$. When an excess of dihydropyridine, prepared according to the literature[3] from 1-(methoxycarbonyl)-1,2-dihydropyridine and methyllithium followed by protonation, was added to complex **1a**, a mixture of four complexes was obtained. Careful silica gel chromatography allowed their separation in the following order of elution: yellow $W(CO)_5$(pyridine) (**4**), the new orange complex **5a** (8.5%) having almost the same polarity as complex **4**, 2,5-dihydropyridinium ylide complex **6a** (20%), and the pyridinium ylide complex **7a** (50%) having almost the same polarity as complex **6a**.

^1H and ^{13}C NMR experiments on complex **5a** (R = Me) confirmed the presence of a CH_3CH group as for complexes **6a** and **7a**, giving respectively a quartet for one proton at δ 3.86 ppm and a doublet for three protons at δ 2.18 ppm in the ^1H NMR spectrum and signals at δ 52.6 and 30.1 ppm in the ^{13}C NMR spectrum.

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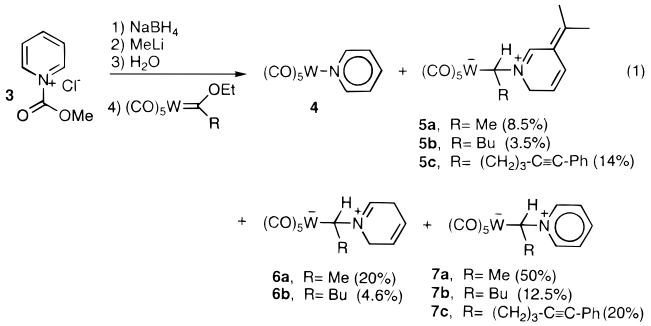
(1) Rudler, H.; Audouin, M.; Parlier, A.; Martín-Vaca, B.; Goumont, R.; Durand-Réville, T.; Vaissermann, J. *J. Am. Chem. Soc.* **1996**, *118*, 12045.

(2) Martín-Vaca, B.; Rudler, H. *J. Chem. Soc., Perkin Trans. 1* **1997**, 3119.

(3) Fowler, W. F. *J. Org. Chem.* **1972**, *37*, 1321.

S0276-7333(97)00807-8 CCC: $15.00
Publication on Web 01/07/1998

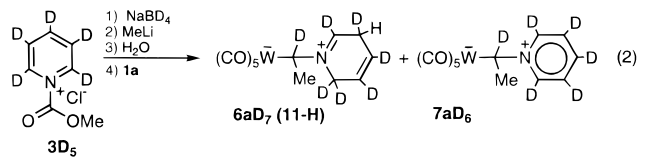


Moreover, signals for a methylene group at δ 53.0 ppm, three methine groups at δ 144.1, 120.9, and 120.6 ppm, two quaternary carbons at δ 147.7 and 121.8 ppm, and two methyl groups at δ 22.2 and 20.9 ppm were also observed. Altogether, these data suggested a structure such as **5a** (R = Me), which could indeed be confirmed by an X-ray analysis.

X-ray Crystal Structure of the 5-Isopropylidene-2,5-Dihydropyridinium Complex. The CAMERON drawing of the molecular structure of **5a** is shown in Figure 1. Interatomic distances and bond angles are listed in Tables 1 and 2; crystallographic data are given in Table 4. Noteworthy are the W(1)−C(1) and C(1)−N(1) single bonds (2.381(9) and 1.45(1) Å, respectively) which can be compared and are very close to those in complex **6a**, the carbon-carbon double bonds C(9)−C(10) (1.31(1) Å) and C(11)−C(13) (1.35(1) Å), and the carbon−nitrogen double bond N(1)−C(12) (1.29(1) Å); moreover, as for complex **6a**, the sum of the angles around N(1) is equal to 360°. The atoms of the pyridinium ring and C(1), C(13), and C(14) are in the same plane, with C(15) slightly above the mean plane. No appreciable differences in the bond distances of the coordinated carbonyl groups indicating a preferential delocalization of the negative charge from the metal to these groups have been detected however.

Origin of the New Dihydropyridines and of Their Complexes. An important observation, besides the fact that 1,2-dihydropyridine is able to reduce carbene complexes, is the fact that two unexpected 2,5-dihydropyridine complexes are also formed in this reaction. This means that 2,5-dihydropyridines are formed during the deprotection reaction and, moreover, that these dihydropyridines are stable enough to be trapped as such before their oxidation.

That complexes **5** and **6** had the same origin, the lithio amide of 1,2-dihydropyridine **9**, formed upon interaction of the protected dihydropyridine **8** and methyllithium, has been established in the following way. First, protected 1,2-dihydropyridine **8D$_6$** was prepared from perdeuterated pyridine and $NaBD_4$. After its deprotection as above (MeLi followed by protonation), it reacted with complex **1a** to give *inter alia* the new complex **6aD$_7$** (eq 2). According to its ^{1}H NMR spectrum, this complex



surprisingly bore hydrogen at C-11 (numbering scheme as in Figure 1 for the sake of simplicity). This indicates

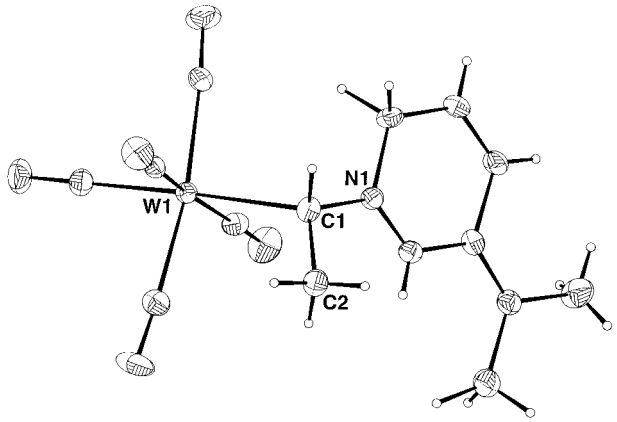


Figure 1. Molecular structure of $C_{15}H_{15}O_5NW$ showing the atomic numbering scheme.

Table 1. Interatomic Distances (Å) for [W(CO)$_5$(C$_{10}$H$_{15}$N)]

W(1)−C(1)	2.381(9)	W(1)−C(3)	2.03(1)
W(1)−C(4)	2.03(1)	W(1)−C(5)	1.98(1)
W(1)−C(6)	2.030(9)	W(1)−C(7)	2.055(9)
N(1)−C(1)	1.45(1)	N(1)−C(8)	1.48(1)
N(1)−C(12)	1.29(1)	O(3)−C(3)	1.13(1)
O(4)−C(4)	1.14(1)	O(5)−C(5)	1.15(1)
O(6)−C(6)	1.13(1)	O(7)−C(7)	1.12(1)
C(1)−C(2)	1.51(1)	C(8)−C(9)	1.47(1)
C(9)−C(10)	1.31(1)	C(10)−C(11)	1.47(1)
C(11)−C(12)	1.42(1)	C(11)−C(13)	1.35(1)
C(13)−C(14)	1.49(1)	C(13)−C(15)	1.48(1)

Table 2. Bond Angles (deg) for [W(CO)$_5$(C$_{10}$H$_{15}$N)]

C(1)−W(1)−C(3)	86.8(3)	C(1)−W(1)−C(4)	93.3(4)
C(3)−W(1)−C(4)	88.6(4)	C(1)−W(1)−C(5)	175.8(3)
C(3)−W(1)−C(5)	96.4(4)	C(4)−W(1)−C(5)	84.0(4)
C(1)−W(1)−C(6)	83.7(3)	C(3)−W(1)−C(6)	170.4(4)
C(4)−W(1)−C(6)	90.4(3)	C(5)−W(1)−C(6)	93.0(4)
C(1)−W(1)−C(7)	96.1(3)	C(3)−W(1)−C(7)	91.2(4)
C(4)−W(1)−C(7)	170.6(4)	C(5)−W(1)−C(7)	86.6(4)
C(6)−W(1)−C(7)	91.3(4)	C(1)−N(1)−C(8)	114.4(7)
C(1)−N(1)−C(12)	125.4(7)	C(8)−N(1)−C(12)	120.1(7)
W(1)−C(1)−N(1)	114.1(5)	W(1)−C(1)−C(2)	113.2(6)
N(1)−C(1)−C(2)	112.3(8)	W(1)−C(3)−O(3)	175.8(8)
W(1)−C(4)−O(4)	175.6(10)	W(1)−C(5)−O(5)	178.5(9)
W(1)−C(6)−O(6)	178.4(8)	W(1)−C(7)−O(7)	175.5(9)
N(1)−C(8)−C(9)	114.2(7)	C(8)−C(9)−C(10)	123.3(8)
C(9)−C(10)−C(11)	121.4(8)	C(10)−C(11)−C(12)	114.3(8)
C(10)−C(11)−C(13)	123.6(8)	C(12)−C(11)−C(13)	122.0(8)
N(1)−C(12)−C(11)	126.5(8)	C(11)−C(13)−C(14)	122.3(9)
C(11)−C(13)−C(15)	124.5(9)	C(14)−C(13)−C(15)	113.2(9)

that delocalization of the negative charge in the lithio amide **9** exists and that protonation can occur both at nitrogen and at carbon C-11: a mixture of 1,2- and 2,5-dihydropyridines **10** and **11** can thus be formed (Scheme 2). Whereas **10** can act as a reducing agent on complex **1** to give **7** as the expected complex, **11** could be trapped, at least in part, by the alkylidene complex **2** to give complex **6**. Second, the origin of complex **5a** and especially of the extra isopropylidene group can be explained in the following way: it is known that N,N-disubstituted carbamates react with 2 mol of an alkyllithium reagent to give symmetrical ketones in which both alkyl groups are derived from the organometallic compound.[4,5] Thus, during the reaction of 2 equiv of methyllithium with the protected dihydropyridine **8** acetone is formed together with the delocalized anion

(4) Michael, U.; Hörnfeldt, A. B. *Tetrahedron Lett.* **1970**, 5219.
(5) Scilly, N. F. *Synthesis* **1973**, 160.

Scheme 2

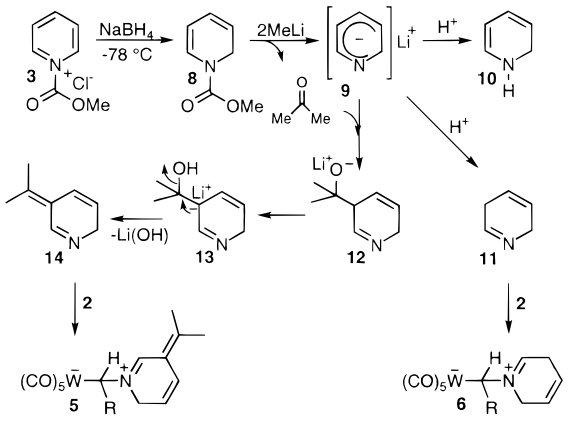
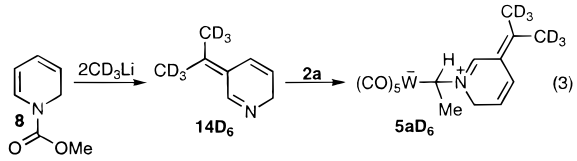


Table 3. H/D Ratio from NMR Labeling Experiments

position	complex					
	6aD$_2$	**7aD$_1$**	**6aD$_6$**	**7aD$_5$**	**6aD$_7$**	**7aD$_6$**
C-1	0.75/0.25	0.78/0.22	0.70/0.30	0.75/0.25	0.25/0.75	0.20/0.80
C-11	2.00/0		1.75/0.25		1.85/0.15	

9. Reaction of **9** with acetone (alkylation at C-11) can then lead to **12** and, after a proton shift via **13** followed by dehydration, can give the new isopropylidene-2,5-dihydropyridine **14**. Finally, the reaction of the latter with complex **2** might give complex **5** (Scheme 2).

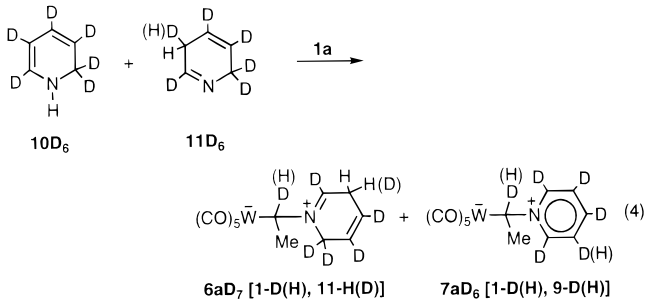
Confirmation of this assumption could be assessed by the use of perdeuterated methyllithium to carry out the deprotection reaction: in that case, the labeled complex **5aD$_6$** was obtained in addition to the other complexes.



The ^{1}H and ^{13}C NMR spectra clearly show the presence of deuterium at C-14 and C-15 with an almost complete disappearance of the signals at δ 2.09 and 2.06 ppm in the ^{1}H NMR spectrum and with broad but weak multiplets due to carbon−deuterium couplings at δ 22.2 and 20.9 in the ^{13}C NMR spectrum.

Utilization of more than 2 equiv of MeLi suppressed the formation of complex **5a**, acetone being transformed into tBuOH.

Kinetic Isotopic Effect during the Transformation of Alkoxycarbene Complexes into Pyridinium Ylide Complexes. As the first result of the labeling experiments (*vide supra*) we could establish the introduction of a hydrogen atom at C-11 upon deprotection of perdeuterated 1,2-dihydropyridine and thus demonstrate the formation of 2,5-dihydropyridine. However, this experiment led to several additional observations which warrant mention. First, in the new complex **6aD$_7$**, obtained from perdeuterated pyridine, $NaBD_4$, and complex **1a**, close to two hydrogen atoms are present at C-11, (Table 3, H/D = 1.85/0.15) where only one was expected: this means that both atoms at this position are exchangeable. This might occur either on 2,5-dihydropyridine during the deprotection process or within the complex **6aD$_7$** during the silica gel purification step, the hydrogen atoms at this position being rather labile. Second, the fact that, unexpectedly, several different dihydropyridines are formed from the protected 1,2-dihydropyridine **8** renders the analysis of the data obtained from labeled compounds more complicated, since both 1,2- and 2,5-dihydropyridines are able to reduce the alkoxycarbene complexes. This was experimentaly confirmed. Indeed, according to the ^{1}H and ^{2}H NMR spectra of the labeled complexes **6aD$_7$** and **7aD$_6$**, 20−25% of hydrogen is present at C-1, where only deuterium was expected in the case of the reduction due to 1,2-dihydropyridine **10D$_6$**. Since exchange at this position seems unlikely under the reaction conditions, it means that the alkylidene complex **2a**, which traps 1,2-dihydropyridine and pyridine to form **6aD$_7$** and **7aD$_6$**, is 20−25% **2a(1-H)** and results from the reduction of complex **1a** with the labeled 2,5-dihydropyridine **11D$_6$**[6] (eq 4).

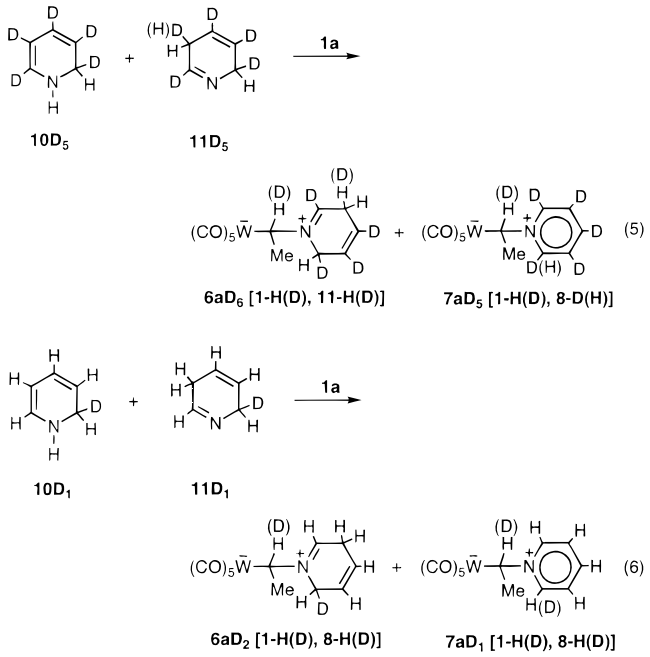


Information on the rate-determining step and on the nature of the transition state in the transformation of alkylalkoxycarbene complexes into pyridinium ylide complexes might be obtained by the determination of the kinetic isotopic effect by means of suitably labeled dihydropyridines. It is assumed (vide supra) that the key step in the transformation of carbene complexes into alkylidene complexes under the influence of dihydropyridines is the transfer of a hydride from dihydropyridine to the carbene carbon according to Scheme 1.

Preferential hydrogen over deuterium transfers during these transformations might be observed, as for the reduction of organic substrates with dihydropyridines and especially carbonyl compounds.[7] For that purpose, the two additional labeled and protected 1,2-dihydropyridines **8D$_5$** and **8D$_1$** were synthesized as above by using an excess of methyllithium in order to avoid the formation of complexes **5a**. Whereas **8D$_5$** led to **10D$_5$** and **11D$_5$**, **8D$_1$** led to **10D$_1$** and **11D$_1$**. At first glance, according to the results of eqs 5 and 6, an isotopic effect close to 3 is detected during the formation of complexes **6aD$_6$** and **7aD$_5$** and of **6aD$_2$** and **7aD$_1$**. However, and as already mentioned, the result of eq 4 indicates that around 20% of the transferred hydrogens is due to a secondary reaction, the oxidation of hydrogen-containing 2,5-dihydropyridine **11D$_6$** into pyridine with preferential transfer of hydrogen to the carbene complex **1a**. Thus, the overall isotopic effect is rather close to 2, a result

(6) According to theoretical calculations, 2,5-dihydropyridines are more stable (less oxidable) than 1,2 and 1,4-dihydropyridines, a result which explains why they survive in part and why they can be trapped by the alkylidene complexes (Hamon, L. Private communication).

(7) Verhoeven, J. W.; van Gerresheim, W.; Martens, F. M.; van der Kerk, S. M. *Tetrahedron* **1986**, *42*, 975.



which points toward the conclusions that the carbon−hydrogen bond rupture might be, as in the case of carbonyl compounds, the rate-determining step in these complex transformations of alkoxycarbene complexes of tungsten (and chromium) into pyridinium ylide complexes.

Extension of the Reduction Reaction to Other Carbene Complexes. The same types of complexes were isolated and characterized by starting from the alkylalkoxycarbene complexes **1b** (R = Bu) and **1c** (R = 5-phenylpent-4-ynyl) which contains a γ triple bond with respect to the carbene carbon. Thus, the reaction of complex **1b** with an excess of protected 1,2-dihydropyridine and 2 equiv of MeLi led to four new complexes. Besides $W(CO)_5Py$ (**4**), complexes **5b**, **6b**, and **7b** were isolated after silica gel chromatography in respectively 3.5, 4.6, and 12.8% yield and were characterized by their physical data (see the Experimental Section). Similarly, the reaction of the mixture of dihydropyridines with complex **1c** gave, under the same conditions as above, a mixture of complexes **4**, **6c**, and **7c** in 10, 14, and 20% yields. In this latter case, complex **5c**, formed in a too low yield, could not be obtained in a pure state.

Finally, it is important to notice that complexes **5** and **6** were not observed when the reduction of **1** was carried out with 1,4-dihydropyridine.

Conclusion

Although 2,5-dihydropyridine has been detected by NMR spectroscopy, together with 1,2- and 1,4-dihydropyridines, during the reduction of pyridine with $LiAlH_4$ followed by protonation,[8] to the best of our knowledge the results described herein constitute the first success in trapping it selectively. Complexes **5** and **6** are thus best described as the result of the reciprocal stabilization of two unstable species, 2,5-dihydropyridines and (pentacarbonyl)tungsten(0) alkylidene complexes.

(8) Tanner, D. D.; Yang, C.-M. *J. Org. Chem.* **1993**, *58*, 1840.

Experimental Section

General Methods. ^1H, ^2H, and ^{13}C NMR spectra were recorded on Bruker AC-200 or AMX-400 instruments. Column chromatography was performed with Merck silica gel (70−230 mesh) using various dichloromethane/light petroleum ether mixtures as eluent. All reagents were obtained from commercial suppliers and used as received. Reactions were performed under an argon atmosphere in carefully dried glassware. Solvents were dried by distillation from a drying agent: THF and Et_2O from Na/benzophenone; CH_2Cl_2 from CaH_2 and P_2O_5.

Carbene complexes **1a** and **1b** were prepared according to published methods.[9]

Synthesis of $(CO)_5W{=}C(OEt)(CH_2)_3C{\equiv}CPh$ (1c). This complex was obtained from $W(CO)_6$ (5.2 g, 14 mmol) in a mixture of pentane (135 mL) and diethyl ether (90 mL) and $PhC{\equiv}C(CH_2)_3Li$ (from the corresponding iodide (4 g, 14.8 mmol) and tBuLi in hexanes (18 mL, 31.1 mmol)) as a yellow oil (4.0 g, 55%) after filtration on silica gel with petroleum ether as eluent. Spectral data: ^1H NMR ($CDCl_3$) δ 7.46−7.32 (m, 5H, Ar), 4.94 (q, 2H, J = 7.1 Hz, OCH_2), 3.44 (m, 2H, $=CCH_2$), 2.50 (t, 2H, J = 6.9 Hz, $\equiv CCH_2$), 1.86 (m, 2H, CH_2), 1.66 (t, 3H, J = 7.1 Hz, CH_3); ^{13}C NMR ($CDCl_3$) δ 332.80 (W=C), 203.41, 197.40 (CO), 131.69, 128.38, 127.91 (Ar), 88.66 (C≡C), 82.00 (OC), 80.92 (≡CPh), 64.28 ($\equiv CCH_2$), 25.27 (2 CH_2), 14.85 (CH_3). MS (EI 70 eV; *m/e*) 524. Anal. Calcd for $C_{19}H_{16}O_6W$: C, 43.52; H, 3.05. Found: C, 43.57; H, 3.09.

General Procedure for the Reaction of Carbene Complexes with the Mixtures of Dihydropyridines: Reaction of $(CO)_5W{=}C(CH_3)OEt$ (1a). Freshly prepared dihydropyridines (obtained from 1-carbomethoxy dihydropyridine (24.6 mmol) and methyllithium (50 mmol) in diethyl ether (100 mL)) were added at room temperature to the carbene complex **1a** (3.6 g, 8.22 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) (**4**).[1] Elution with dichloromethane/petroleum ether (25/75) gave complex **5a** (0.33 g, 8.5%), mp 112 °C. Elution with dichloromethane/petroleum ether (30/70) gave complex **6a** (0.7 g, 20%). Elution with dichloromethane/petroleum ether (40/60) gave complex **7a** (1.75 g, 50%). Spectral data for **5a** (R = Me): ^1H NMR ($CDCl_3$) δ 8.21 (br s, 1 H, 12-H), 6.59 (ddd, 1H, J = 10.6, 3.9, and 1.9 Hz, 10-H), 5.91 (ddd, 1H, J = 10.6, 3.5, and 3.5 Hz, 9-H), 5.43 (br d, 1H, J = 22.7 Hz, 8-H), 4.43 (br d, 1H, J = 22.7 Hz, 8-H), 3.86 (q, 1H, J = 6.6 Hz, 1-H), 2.18 (d, 3H, J = 6.6 Hz, 2-H_3), 2.09 and 2.06 (2 s, 3H, 14- and 15-H_3); ^{13}C NMR ($CDCl_3$) δ 204.1 (CO trans), 202.41 (CO cis), 147.7 (C-11), 144.1 (C-12), 121.8 (C-13), 120.9 and 120.6 (C-9, C-10), 53.0 (C-8), 52.6 (C-1), 30.1 (C-2), 22.2 and 20.9 ($=CMe_2$). Anal. Calcd for $C_{15}H_{15}O_5NW$: C, 38.08; H, 3.20; N, 2.96. Found: C, 38.16; H, 3.20; N, 2.97.

Reaction of $(CO)_5W{=}C(Bu)OEt$ (1b) with Dihydropyridines. Under the same conditions as above, complex **1b** gave a mixture of complexes **5b** (0.15 g, 3.5%; mp 125 °C), **6b** (0.18 g, 4.6%; mp 85 °C), and **7b** (0.5 g, 12.8%). Spectral data for **5b** (R = Bu): ^1H NMR ($CDCl_3$) δ 8.25 (br s, 1H, C-12 H), 6.56 (m, 1H, 10-H), 5.87 (m, 1H, 9-H), 4.85 (br d, 1H, J = 23.0 Hz, 8-H), 4.46 (br d, 1H, J = 23 Hz, 8-H), 3.79 (m, 1H, 1-H), 2.30 (m, 2H, 2-H_2), 2.05 and 2.00 (s, 3H, 14- and 15-H_3), 1.40−1.15 (m, 4H, $2CH_2$), 0.90 (t, 2H, J = 6.7 Hz, 2-H_3); ^{13}C NMR ($CDCl_3$) δ 204.1 (CO), 202.5 (CO), 148.2 (C-11), 145.7 (C-12), 121.7 (C-13), 120.7 and 121.0 (C-10 and C-9), 60.6 (C-1), 52.1 (C-8), 42.34 (C-2), 31.05 (C-16), 22.4 (C-17), 20.9 and 22.3 (C-14 and C-15), 14.2 (C-18); MS (EI 70 eV; *m/e*) 516. Spectral data for **6b** (R = Bu): ^1H NMR ($CDCl_3$) δ 7.85 (br s, 1H, 12-H),

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5.98−5.83 (m, 2H, 10-H, 9-H), 4.72 (m, 1H, 8-H), 4.22 (m, 1H, 8-H), 3.76 (m, 1H, 1-H), 3.40−3.05 (m, 2H, 11-H_2), 2.30 (m, 2H, 2-H_2), 1.40−1.15 (m, 4H, 2CH_2), 0.91 (t, J = 6.6 Hz, 15-H_3); ^{13}C NMR ($CDCl_3$) δ 203.8 (CO), 202.5 (CO), 151.5 (C-12), 120.9 and 119.1 (C-9 and C-10), 61.2 (C-1), 51.3 (C-8), 42.5 (C-2), 30.8 (C-11), 28.6 and 22.3 (2 CH_2), 14.12 (CH_3); MS (EI 70 eV, *m*/*e*) 476. Spectral data for **7b** (R = Bu): ^{1}H NMR ($CDCl_3$) δ 8.50 (m, 2H, H ortho Py), 7.83 (m, 1H, H para Py), 7.61 (m, 2H, H meta Py), 4.65 (dd, 1H, J = 9.8 and 5.4 Hz, 1-H), 2.55 (m, 2H, 2-H_2), 1.45−1.10 (m, 4H, 13-H_2 and 14-H_2), 0.85 (t, 3H, J = 7.0 Hz, 15-H_3); ^{13}C NMR ($CDCl_3$) δ 204.9 (CO), 202.2 (CO), 140.2, 136.8, and 127.0 (Py), 64.5 (C-1), 43.9 (C-2), 31.9 (C-13), 22.3 (C-14), 14.2 (C-15). Anal. Calcd for $C_{15}H_{15}O_5NW$: C, 38.08; H, 3.20; N, 2.96. Found: C, 38.15; H, 3.17; N, 2.96.

Reaction of $(CO)_5W{=}C(CH_2CH_2CH_2C{\equiv}CPh)OEt$ (1c) with Dihydropyridines. Under the same conditions as above, complex **1c** gave a mixture of complexes **5c** (0.75 g, 14%) and **7c** (0.92 g, 20%). Spectral data for **5c** (R = 5-phenyl-4-pentynyl): ^{1}H NMR ($CDCl_3$) δ 8.31 (br s, 1H, 12-H), 7.35 (m, 5H, Ar), 6.54 (m, 1H, 10-H), 5.85 (m, 1H, 9-H), 4.86 (br d, 1H, J = 23.0 Hz, 8-H), 4.45 (br d, 1H, J = 23.0 Hz, 8-H), 3.90 (br s, 1H, 1-H), 2.66 and 2.46 (m, 4H, 2-H_2 and 17-H_2), 1.95 (br s, 6H, 2CH_3), 1.57 (m, 2H, 16-H_2); ^{13}C NMR ($CDCl_3$) δ 204.0 (CO), 202.3 (CO), 148.8 (C-11), 145.9 (C-12), 131.6, 128.3, 127.8, and 123.7 (Ar), 121.6 (C-13), 120.8 and 120.5 (C-9 and C-10), 89.7 and 81.3 (C-18 and C-19), 59.7 (C-1), 52.0 (C-8), 41.5 (C-2), 27.6 (C-17), 22.2 and 20.7 (Me), 18.9 (C-16); MS (EI, 70 eV; *m*/*e*) 587. Spectral data for **7c** (R = 5-phenyl-4-pentynyl): ^{1}H NMR ($CDCl_3$) δ 8.51 (m, 2H, H ortho Py), 7.81 (m, 2H, H para Py), 7.55 (m, 2H, H meta Py), 7.30 (m, 5H, Ar), 4.73 (dd, 1H, J = 10.3, 5.4 Hz, 1-H), 2.72 (m, 2H, 2-H_2), 2.43 (t, 2H, J = 6.0 Hz, 14-H_2), 1.49 (m, 2H, 13-H_2); ^{13}C NMR ($CDCl_3$) δ 204.6 (CO), 201.9 (CO), 140.0, 136.9, and 131.6 (Py), 127.8, 126.9, and 123.8 (Ar), 89.7 and 81.3 (C-15 and C-16), 63.4 (C-1), 43.2 (C-2), 28.4 (C-14), 16.9 (C-13H); MS (EI, 70 eV; *m*/*e*) 559. Anal. Calcd for $C_{22}H_{17}O_5NW$: C, 47.24; H, 3.04; N, 2.50. Found: C, 47.27; H, 3.11; N, 2.51.

Reaction of the Carbene Complex $(CO)_5W{=}C(CH_3)OEt$ (1a) with Mixtures of Deuterated Dihydropyridines. Reaction with Monodeuterated Dihydropyridines. Under the same conditions as above, complex **1a** reacts with a mixture of monodeuterated dihydropyridines (prepared from pyridine, methyl chloroformate, $NaBD_4$, methyllithium, and H_2O) to give the complexes **6aD$_2$** (20%) and **7aD$_1$** (49%). Spectral data for **6aD$_2$**: ^{1}H NMR ($CDCl_3$) δ 7.82 (br s, 1H, 12-H), 5.91 (m, 2H, 9-H/10-H), 4.87 (m, 0.6H, 8-H), 4.19 (m, 0.6H, 8-H), 3.81 (m, 0.75H, 1-H), 3.21 (m, 2H, 11-H), 2.11 (d, 3H, J = 6.5Hz, CH_3); ^{2}H NMR ($CHCl_3$) δ 4.87 (br s, 0.4D, C-8D), 4.19 (br s, 0.4D, C-8D). Spectral data for **7aD$_1$**: ^{1}H NMR ($CDCl_3$) δ 8.55 (d, 1.6H, J = 6.0Hz, H ortho Py), 7.82 (m, 1H, H para Py), 7.59 (m, 2H, H meta Py), 4.90 (q, 0.78H, J = 7.0Hz, C-1H), 2.35 (d, 3H, J = 7.0Hz, C-2H_3); ^{2}H NMR ($CHCl_3$) δ 8.5 (br s, 0.4D, D ortho Py), 4.90 (br s, 0.22D, C-1D).

Reaction with Pentadeuterated Dihydropyridines. Under the same conditions as above, complex **1a** reacts with a mixture of pentadeuterated dihydropyridines (prepared from pyridine-d_5, methyl chloroformate, $NaBH_4$, methyllithium, and H_2O) to give complexes **6aD$_6$** (7%) and **7aD$_5$** (27%). Spectral data for **6aD$_6$**: ^{1}H NMR ($CDCl_3$) δ 4.87 (m, 0.45H, 8-H), 4.19 (m, 0.5H, 8-H), 3.81 (m, 0.7H, 1-H), 3.21 (m, 1.75H, 11-H), 2.11 (d, 3H, J = 6.5Hz, 2-H_3); ^{2}H NMR ($CHCl_3$) δ 7.82 (br s, 1D, 12-D), 5.90 (m, 2D, 9-D/10-D), 4.87 (m, 0.5D, 8-D), 4.19 (m, 0.5D, 8-D), 3.81 (m, 0.3D, 1-D), 3.21 (m, 0.3D, 11-D). Spectral data for **7aD$_5$**: ^{1}H NMR ($CDCl_3$) δ 8.55 (s, 0.25H, H ortho Py), 4.90 (q, 0.75H, J = 7.0Hz, 1-H), 2.35 (d, 3H, J = 7.0Hz, 2-H_3); ^{2}H NMR ($CHCl_3$) δ 8.5 (br s, 1.7D, ortho Py), 7.82 (br s, 1D, D para Py), 7.59 (br s, 2D, D meta Py), 4.90 (br s, 0.25D, 1-D).

Reaction with Hexadeuterated Dihydropyridines. Under the same conditions as above, complex **1a** reacts with a mixture of hexadeuterated dihydropyridines (prepared from pyridine-d_5, methyl chloroformate, $NaBD_4$, methyllithium, and H_2O) to give complexes **6aD$_7$** (4%) and **7aD$_6$** (18%). Spectral data for **6aD$_7$**: ^{1}H NMR ($CDCl_3$) δ 4.87 (m, 0.1H, 8-H), 4.19 (m, 0.1H, 8-H), 3.81 (m, 0.25H, 1-H), 3.21 (m, 1.85H, 11-H), 2.11 (d, 3H, J = 6.5Hz, 2-H_3); ^{2}H NMR ($CHCl_3$) δ 7.82 (br s, 1D, 12-D), 5.90 (m, 2D, 9-D/10-D), 4.87 (m, 0.9D, 8-D), 4.19 (m, 0.9D, 8-D), 3.81 (m, 0.75D, 1-D), 3.21 (m, 0.15D, 11-D). Spectral data for **7aD$_6$**: ^{1}H NMR ($CDCl_3$) δ 8.53 (s, 0.1H, H ortho Py), 4.90 (q, 0.2H, J = 7.0Hz, 1-H), 2.35 (d, 3H, J = 7.0Hz, 2-H_3); ^{2}H NMR ($CHCl_3$) δ 8.5 (sl, 1.9D, ortho Py), 7.82 (br s, 1D, D para Py), 7.59 (br s, 2D, D meta Py), 4.90 (br s, 0.8D, 1-D).

Reaction of $(CO)_5W{=}C(CH_3)OEt$ (1a) with a Mixture of Dihydropyridines Prepared with CD_3Li. Freshly prepared dihydropyridines (obtained from 1-carbomethoxy dihydropyridine and perdeuterated methyllithium (2 equiv) in diethyl ether (20 mL)) was added at room temperature to the carbene **1a** (1 g, 2.7 mmol) in diethyl ether (10 mL). The solution was worked up as above to give, besides complexes **6a** and **7a**, **5aD$_6$**. Spectral data for **5aD$_6$**: ^{1}H NMR ($CDCl_3$) δ 8.21 (br s, 1 H, C-12H), 6.59 (ddd, 1H, J = 10.6, 3.9, and 1.9Hz, C-10H), 5.91 (ddd, 1H, J = 10.6, 3.5, and 3.5Hz, C-9H), 5.43 (br d, 1H, J = 22.7Hz, C-8H), 4.43 (br d, 1H, J = 22.7Hz, C-8H), 3.86 (q, 1H, J = 6.6Hz, C-1H), 2.18 (d, 3H, J = 6.6Hz, C-2H_3); ^{13}C NMR ($CDCl_3$) δ 204.1 (CO trans), 202.41 (CO cis), 147.7 (C-11), 144.1 (C-12), 121.8 (C-13), 120.9 and 120.6 (C-9, C-10), 53.0 (C-8), 52.6 (C-1), 30.1 (C-2), 22.2 and 20.9 (m, =C(CD_3)$_2$).

Table 4. Crystal Data for $C_{15}H_{15}O_5NW$

fw	473.1
a (Å)	6.809(2)
b (Å)	20.928(12)
c (Å)	11.611(4)
α (deg)	90
β (deg)	100.93(3)
γ (deg)	90
V (Å^3)	1625(9)
Z	4
cryst syst	monoclinic
space group	$P2_1/n$
linear abs coeff μ (cm^{-1})	72.8
density ρ (g cm^{-3})	1.93
diffractometer	CAD4 Enraf-Nonius
radiation	Mo Kα (λ = 0.710 69 Å)
scan type	$\omega/2\theta$
scan range (deg)	0.8 + 0.345 tan θ
θ limits (deg)	1−25
temp of measurement	room temp
octants collected	0−8; 0−24; −13 to 13
no. of data collected	3208
no. of unique data collected	2851
no. of unique data used for refinement	2150 ($(F_o)^2 > 3\sigma(F_o)^2$)
R(int)	0.0487
R (=$\Sigma\|\|F_o\| - \|F_c\|\|/\Sigma\|F_o\|$	0.0299
Rw = $[\Sigma w(\|F_o\| - \|F_c\|)^2/\Sigma wF_o^2]^{1/2}$	0.0328 (w = 1.0)
abs cor	DIFABS (min 0.86, max 1.33)
extinction param	none
no. of variables	245
$\Delta\rho_{min}$ (e Å^{-3})	−1.11
$\Delta\rho_{max}$ (e Å^{-3})	0.75

X-ray Structure Determination. X-ray-quality crystals were obtained by slow evaporation of dichloromethane from a solution of complex **4a** (R = Me) in a mixture of dichloromethane and hexane. Data were collected at room temperature on a Nonius CAD4 diffractometer (Table 4). Empirical absorption correction using DIFABS (minimum 0.86, maximum 1.33) was applied. Anomalous dispersion terms were applied, there was no correction of secondary extinction. The structure was solved by standard Patterson-Fourier techniques and refined by least-squares analysis using anisotropic

thermal parameters for all non-hydrogen atoms. H atoms were located on a difference Fourier map, and their coordinates were refined with an overall isotropic thermal parameter. A total of 2851 reflections, with $I > 3\sigma(I)$, were used to solve and refine the structure to $R = 0.0299$ and $R_W = 0.0328$ (unit weights; 245 least-squares parameters). The programs used were Crystals and Cameron.[10,11]

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(11) Watkin, D. J.; Prout, C. K.; Pearce, L. J. Cameron; Chemical Crystallography Laboratory; University of Oxford, Oxford, U.K., 1996.

Acknowledgment. This research was supported by the Ministerio de Educación y Cultura (Spain) (postdoctoral grant to B.M.-V.), the Centre National de la Recherche Scientifique, and the Ministère de l'Enseignement Supérieur et de la Recherche Scientifique. We thank the Laboratoires des Douanes for ^{2}H NMR facilities.

Supporting Information Available: Tables of atomic positional and thermal parameters (2 pages). Ordering information is given on any current masthead page.

OM9708079