Variable Temperature NMR study of compounds 7 and 5a.

The $^{31}P\{^{1}H\}$ NMR spectrum of **7** recorded at room temperature exhibits just one broad signal at 18.0 ppm. When the solution is cooled, further broadening occurs and then the resonance splits into two doublets of the same intensity below 258 K, in agreement with the solid state structure. The spectrum remains unchanged down to the freezing temperature of the solvent except for changes in the linewidths. The above observations are consistent with changes detected in the ^{1}H NMR spectra. In fact, the spectrum of **7** at room temperature shows a single signal for either the methylenic protons or the Cp groups, whereas at 188 K both signals have splitted into two resonances of the same intensity respectively (the methyl resonance remains virtually unchanged at all temperatures). From the coalescence temperature of the Cp resonances we have obtained an estimation[32] of the free energy of activation for the dynamic process involved (Table 2). The resulting figure (*ca.* 44 $KJmol^{-1}$) is identical within experimental error to that one calculated from the coalescence of the ^{31}P resonances. This suggests the existence of just one dynamic process in the solutions of compound **7**, which in a simultaneous fashion results in the equivalence of both phosphorus atoms, both cyclopentadienyl groups and both methylenic protons in the molecule.

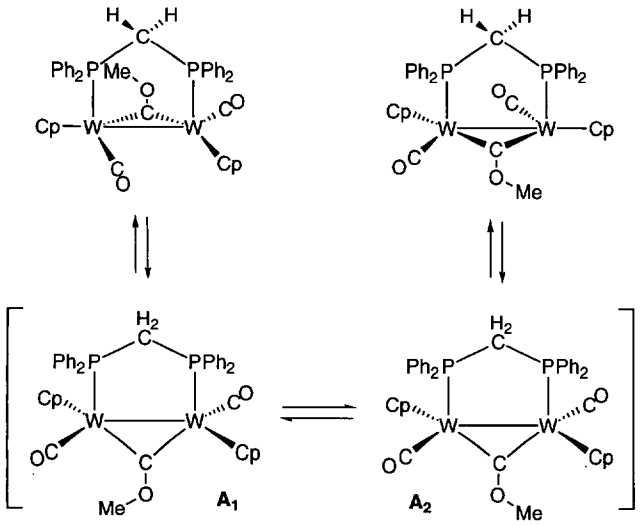
The above data allow us to propose for compound **7** the dynamic process depicted in the Figure. Essentially, the process involves rotation of the methoxycarbyne bridge around the W-W bond so as to reach an equivalent position at the other side of the pseudoplane defined by the metallic atoms and the diphosphine bridge. This rearrangement implies structure **A** as an intermediate step; in this structure, which is similar to that of hydrides **3**, the carbyne ligand is placed in a *transoid* arrangement with respect to the phosphorus atoms of the diphosphine and there are two possible orientations of the methyl group ($\mathbf{A_1}$ and $\mathbf{A_2}$) which are isoenergetic. Conversion between $\mathbf{A_1}$ and $\mathbf{A_2}$ would be accomplished through rotation around the C-O bond, a well known process,[29,30,33] and this would require less energy than in the ground

geometry, because in structure **A** the methoxycarbyne group is placed further away from the bulky groups of the molecule.

The $^{13}C\{^1H\}$ NMR spectra of hydroxycarbyne **5a** are similar to those of **7**. At room temperature the μ-COH group gives rise to a resonance at 356.9 ppm, and only one signal is found for the Cp groups and CO ligands respectively. The spectrum recorded at 198 K shows two singlets for the carbonyl groups and another two ones for the Cp ligands. All this suggests a similar situation to that found for the methoxycarbyne compound **7**. However, the $^{31}P\{^1H\}$ NMR data for **5a** indicate a more complex behavior. The broad resonance at 18.4 ppm observed for **5a** at room temperature splits into two doublets below 248 K, as observed for compound **7**. The free energy of activation calculated from the coalescence is virtually identical to that for **7**, suggesting that the responsible processes are similar in both cases. However, at lower temperatures, the spectrum of **5a** experiences a further change; the lower-field resonance splits into two signals with relative intensities 2:3 while the higher field one just broadens significantly. This is indicative of the presence of two isomers with very similar energies ($\Delta G^0 \leq 1$ KJ mol^{-1} at 172 K). From the coalescence data and ignoring the small population difference, we can estimate an average free energy of activation of 32 KJ mol^{-1} for the conversion between isomers, a value substantially smaller than that obtained for the first coalescence. Unfortunately, it was not possible to check the above calculations against ^1H NMR data, because both the Cp groups and the methylenic protons as well as the proton of the hydroxy group showed only one chemical environment respectively at all temperatures studied. This can be due merely to the existence of very small differences in the proton shifts involved.

The data just discussed clearly reveal that compound **5a** experiences in solution two independent dynamic processes. That one with the smaller activation energy (32 KJmol^{-1}) is obviously an isomerization, whereas the process with the higher activation energy (44 KJ mol^{-1}) is a fluxional process similar to that one detected for the methoxycarbyne **7**. The fastest reorganization is just the rotation of the OH group

around the C–O bond of the carbyne ligand, a process not observed for compound **7** but detected in other carbynes,[29,30,33] for which steric rather than electronic effects seem to be responsible for the rotation barriers[29] or the ratio of isomers observed.[33] For **5a** it is sensible to assume that the major isomer (δ_P = 20.8 ppm) should correspond to that one with the OH group pointing away from the nearest CO ligand. With regard to the slower dynamic process, it should be similar to that proposed for **7** except that the interconversion $\mathbf{A_1/A_2}$ is not longer required once that rotation of the OH group can occur fast enough in the ground structures.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