Preliminary communication

Methyltriphenylphosphonium[oxy(methylenetriphenylphosphorane)-carbene]pentacarbonylchromium(0): An ylide-carbene complex*

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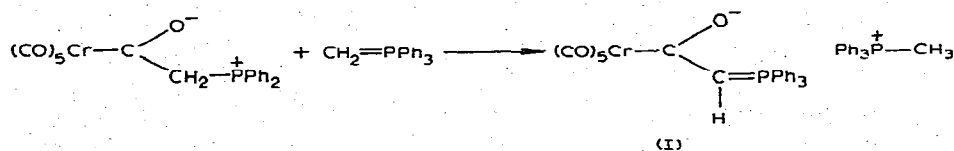*Department of Chemistry, University of California, Santa Barbara, California 93106 (U.S.A.)*

The addition of phosphorus ylides to transition metal carbonyl complexes gives ylide-carbene adducts in high yield. This facile addition to the metal coordinated carbon monoxide is in contrast to all previous reports which emphasize only substitution of carbon monoxide by the ylide carbon atom[1,2]. Thus, the interaction of alkali halide free methylenetriphenylphosphorane[3] with chromium hexacarbonyl in a 2/1 molar ratio respectively in THF gave a bright yellow addition product, $[(CO)_5Cr(O^-Ph_3PCH_3)^+_-CHPPh_3]$ (I) m.p. 115–126° (dec.) with satisfactory C, H, O, and P analyses (yield 0.3%). The 60 MHz NMR spectrum in pyridine showed two doublets at δ 4.65 ppm, J(PCH) 40 Hz and δ 3.05 ppm, J(PCH) 13 Hz in the ratio of 1/3 respectively. The same spectrum was obtained in DMSO-d_6. The absorption at δ 3.05 ppm was identified as $Ph_3PCH_3^+$ and the absorption at 4.65 ppm was assigned to the methynic proton of the complex, I.

An IR spectrum of the complex in THF solution showed four ν(CO) bands at 2015 w, 1985 m, 1890 vs, and 1859 m cm^{-1}. Ordinarily three IR active bands are observed for C_{4v} symmetry of pentacarbonyl adducts although an infrared inactive band of B_1 symmetry can often become allowed if the symmetry of the complex is distorted from idealized C_{4v} symmetry. Although the peak at 1985 cm^{-1} occurs at the same frequency as $Cr(CO)_6$, there was no evidence for $Cr(CO)_6$ as an impurity. After five recrystallizations from THF–pentane, the 1985 cm^{-1} band showed no diminution in intensity. The presence of THF could, however, induce slight decomposition of the complex. This has often been observed to be the case with carbene complexes[4]. These results are best described in terms of the following equation which has also been verified by a mass balance accounting of all the materials:

$$Ph_3P=CH_2 \ + \ Cr(CO)_6 \ \longrightarrow \ (CO)_5Cr-C \underset{CH_2-\overset{+}{P}Ph_3}{\overset{O^-}{<}}$$

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$$(CO)_5Cr-C\underset{CH_2-\overset{+}{P}Ph_2}{\overset{O^-}{\diagdown}} + CH_2=PPh_3 \longrightarrow (CO)_5Cr-C\underset{\underset{H}{\overset{|}{C}=PPh_3}}{\overset{O^-}{\diagdown}} \quad Ph_3\overset{+}{P}-CH_3$$
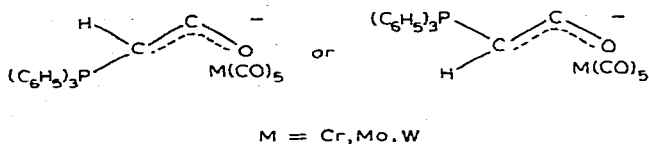
(I)

The initial carbonyl-ylide adduct does not eliminate triphenylphosphine oxide to give an olefin in the usual Wittig manner but rapidly undergoes transylidation[5] to give β-oxido ylide adducts of the type reported by Schlosser[6].
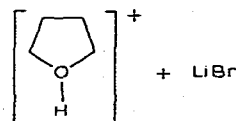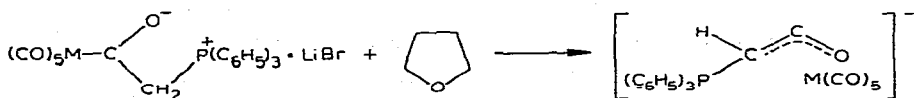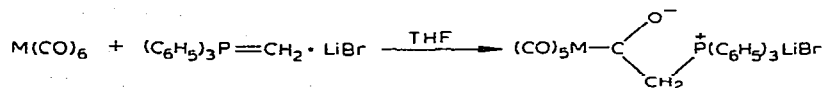
The chromium complex, suspended in toluene, can be methylated on the oxygen

atom with CH_3OSO_2F to give $(CO)_5Cr-C\underset{\underset{H}{\overset{|}{C}=PPh_3}}{\overset{OCH_3}{\diagdown}}$ and $Ph_3\overset{+}{P}CH_3\ OSO_2F^-$.

An NMR spectrum of the alkylated product in benzene showed a singlet at δ 3.50 ppm for the methyl group and a doublet at δ 5.40 ppm J(PCH) 33 Hz for the lone ylidic proton in a 3/1 ratio respectively. The methyltriphenylphosphonium fluorosulfonate was identified by comparison with an authentic sample.

Greco[2] has recently reported that equimolar amounts of Group VI transition metal carbonyls and methylenetriphenylphosphorane $[(C_6H_5)_3P=CH_2 \cdot LiBr]$ generated "*in situ*" give a 1/1 adduct instead of the 2/1 adduct reported here. A π-allylic structure

$$\underset{(C_6H_5)_3P}{\overset{H}{\diagdown}}C\overset{C}{\underset{M(CO)_5}{\diagdown\cdots O}}{}^- \quad or \quad \underset{H}{\overset{(C_6H_5)_3P}{\diagdown}}C\overset{C}{\underset{M(CO)_5}{\diagdown\cdots O}}{}^-$$

$$M = Cr, Mo. W$$

with a THF oxonium cation has been postulated. The following equation would describe the reaction:

$$M(CO)_6 + (C_6H_5)_3P=CH_2 \cdot LiBr \xrightarrow{THF} (CO)_5M-C\underset{CH_2}{\overset{O^-}{\diagdown}}\overset{+}{P}(C_6H_5)_3 LiBr$$

$$(CO)_5M-C\underset{CH_2}{\overset{O^-}{\diagdown}}\overset{+}{P}(C_6H_5)_3 \cdot LiBr + \underset{O}{\bigcirc} \longrightarrow \left[\underset{(C_6H_5)_3P}{\overset{H}{\diagdown}}C\overset{C}{\underset{M(CO)_5}{\diagdown\cdots O}} \right]^-$$

$$\left[\underset{\underset{H}{|}}{\overset{+}{\underset{O}{\bigcirc}}} \right]^+ + LiBr$$

Our studies with alkali halide free methylenetriphenylphosphorane and Group VI transition metal carbonyls in a 1/1 molar ratio in THF show the presence of two products. In the case of the tungsten complex, the NMR spectrum showed a set of three doublets at δ 4.70, J(PCH) 41.5 Hz; δ 3.35, J(PCH) 13.5 Hz; and δ 2.02, J(PCH) 13 Hz. The first two peaks at δ 4.7 and 3.35 were in the ratio of 1/3 respectively. The third peak was assigned to a 1/1 adduct and represented 30% of the reaction mixture:
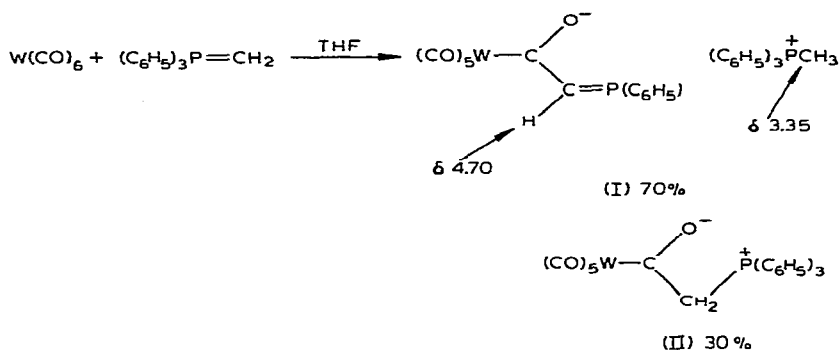
The addition of one molar equivalent of methylenetriphenylphosphorane to the mixture of I and II in THF results in the total disappearance of II and the formation of I. Thus the initial adduct in the reaction is II which subsequently loses a proton to methylenetriphenylphosphorane to form the salt I. The approximate pKa of THF in water[7] is −2.1, and the pKa of most conjugate acids of ylides range[8] from 5 to 7. Even though these values reflect determinations in water, it does not seem likely that THF is a strong enough base to remove a proton from II at equilibrium. Furthermore, as suggested by Greco[2], the postulate of a π-allylic structure for the ylide-pentacarbonyl complex I is also unnecessary since it implies that the structures have more electrons than the next inert gas configuration[9].

ACKNOWLEDGEMENT

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