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THE REACTION OF METAL CARBONYLS WITH PHOSPHORUS METHYLENE AND ALLYLIDENE YLIDES: ALLYLIDENE(TRIPHENYLPHOSPHORANE)TETRACARBONYLMOLYBDENUM AND -TUNGSTEN A NON-CLASSICAL ALLYLIC SYSTEM

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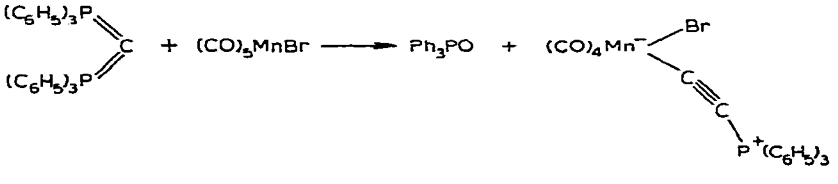
SUMMARY

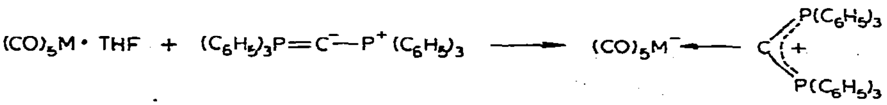
The carbonyls $Mo(CO)_6$, $W(CO)_6$, $Fe(CO)_5$ react with methylenetriphenylphosphorane in tetrahydrofuran to give tris(tetrahydrofuranate) of 1/1 metal carbonyl–phosphorus ylide adducts, which are thought to be oxonium salts. Allylidenetriphenylphosphorane reacts with $Mo(CO)_6$ or $W(CO)_6$ in boiling tetrahydrofuran to yield $(CO)_4M[(C_6H_5)_3P{=}CH{-}CH{=}CH_2]$. Preliminary X-ray analysis of the molybdenum complex has revealed the presence of a non-classical allylic system on the metal. The complex reacts with triphenylphosphine with displacement of one carbonyl group, to give $(CO)_3Mo[P(C_6H_5)_3][(C_6H_5)_3P{=}CH{-}CH{=}CH_2]$.

INTRODUCTION

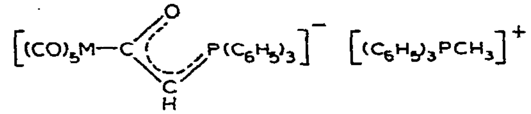
Organometallic phosphorus ylide complexes of transition metals have recently been described by Kaska and coworkers[1-3], who succeeded in applying the Wittig reaction to transition metal carbonyls. The reaction between carbobis(triphenylphosphorane) and pentacarbonylmanganese bromide[1] led to oxygen abstraction from a complexed carbon monoxide and to the formation of a crystalline complex, to which an acetylenic structure was attributed[2]:



On the other hand, carbobis(triphenylphosphorane), in another resonance form, reacted with pentacarbonyltungsten (or -chromium) to a 1/1 adduct as follows[3]:



However, a very different behaviour was reported for methylenetriphenylphosphorane when treated with $M(CO)_6$ (M=W, Mo or Cr). Kaska and Mitchell[3] attributed the following phosphonium salt structure to the resulting 2/1 adducts:

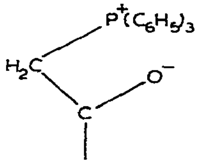


In these adducts the ketene ylide is formed by the addition of the methylene group of methylenetriphenylphosphorane to one complexed carbon monoxide.

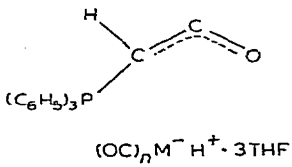
We describe below a study of the reaction of methylenetriphenylphosphorane with several carbonyl transition metal compounds in tetrahydrofuran; the results differ from those reported by Kaska's group. The very different behaviour of allylidene triphenylphosphorane towards the same carbonyl transition metal compounds is also described.

RESULTS AND DISCUSSION

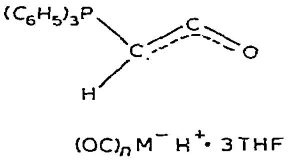
By treating methylenetriphenylphosphorane "*in situ*" with an equimolecular amount of carbonyl compounds of Mo, W or Fe in tetrahydrofuran, we succeeded in isolating crystalline tris(tetrahydrofuranate) of 1/1 adducts, which like the 2/1 adducts described by Kaska, probably originated from the attack of one metal-bonded carbonyl group by phosphorus ylide, as indicated by structures (I), (II) and (III). All these 1/1 adducts are not very stable in the solid state at room temperature, and are even less stable in (benzene) solution. They are readily oxidized in air. Treatment with ethanol gives the original metal carbonyls again. These facts suggest that there is only a very weak bond between the ylide and the carbonyl.



(Ia),(IIa),(IIIa)

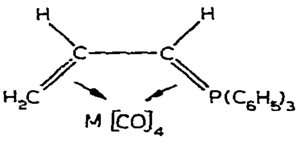


(Ib),(IIb),(IIIb)

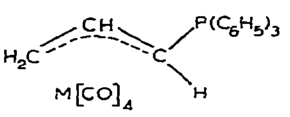


(Ic),(IIc),(IIIc)

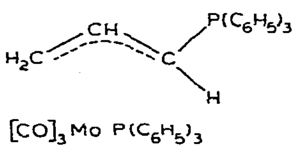
(I), M=Mo n=5; (II), M=W n=5; (III), M=Fe n=4



(IVa),(Va)



(IVb),(Vb)



(VI)

(IV), M=Mo; (V), M=W

The IR spectra of (I) and (II) show carbonyl bands at 2035 m, 1988 m, 1895 vs, and 1854 vs cm^{-1}; (III) at 2000 s and 1880 vs(br) cm^{-1}. The ^1H NMR spectra of (I), (II) and (III) are almost identical. Signals are observed at τ 9.0 (m, 12 H, β protons of THF), 6.9 (m, 12 H, α protons of THF), 5.7 and 5.1 [d, 1 H, methynic protons, $J(^{31}P-H)$ 60 Hz], 3.3 and 2.8 (two m, 15 H, aromatic protons). In addition to these signals, the NMR spectra of (I) and (II) show another doublet of lower intensity at τ 4.53 and 4.15 [$J(^{31}P-H)$ 38 Hz], which suggests either that an impurity or an isomeric form is present as considered below.

Low solubility and non-volatility prevented mol.wt. determination. Nevertheless the absence of CO bridges and the spectral multiplicity of the CO bands (IR spectra) permit the assignment of a highly asymmetric, monomeric structure. On the basis of such observations and of elemental analyses, one betainic and two different allylic structures, shown above, may be assumed. However, none of the structures fully explains all the experimental findings.

The betainic structures [(Ia), (IIa) and (IIIa)] are not consistent with the presence in the NMR spectra of only one methynic proton adjacent to phosphorus. Allylic structures (Ib), (IIb), (IIIb), (Ic), (IIc) and (IIIc) are consistent with the presence of only one methynic proton. Although we could not find any evidence for the second proton, we have assumed an oxonium salt structure, formed by the shift of one proton from the ylide group to tetrahydrofuran; it is well known that methylene hydrogens can be easily withdrawn from β-ketocarboxylic acids, diketones, etc.

The two different allylic structures take into account the possible isomerism implied by two different doublets in the NMR spectra of the Mo and W complexes. The doublet downfield must be attributed to the least shielded hydrogen; hence structures (Ib), (IIb) and (IIIb) may be assigned to the minor isomer and structures (Ic), (IIc) and (IIIc) to the major one. This interpretation is similar to that given by Kaska for the 2/1 adducts; the main difference is that the second methynic proton appears as methyl group of the phosphonium cation.

In order to further elucidate the structure of these adducts, we tried the same reaction with allylidenetriphenylphosphorane, which was expected to yield more stable products. However, the products had different structures. Thus the reaction "*in situ*" of allylidenetriphenylphosphorane with hexacarbonyls of Mo and W in refluxing tetrahydrofuran proceeded with evolution of carbon monoxide to yield the two new complexes (IV) and (V) corresponding to the formula $(CO)_4M[(C_6H_5)_3P{=}CH{-}CH{=}CH_2]$. The IR spectra of cyclohexane solutions of both complexes show four bands in the CO stretching region at 2012 s, 1905 vs, 1890 vs, and 1860 s cm^{-1} and 1995 s, 1897 vs, 1884 vs and 1860 s cm^{-1} [for (IV) and (V), respectively], in agreement with a *cis* C_{2v} octahedral symmetry[4]. The NMR spectra of both complexes reveal signals at τ 2.4 (m, 15 H, aromatic protons), 5.0 (m, 1 H, head proton of the allylic system), 7.1–7.7 (complex m, 3 H, allylic protons). The four allylidenic protons formed a rather complicated ABCX system; an additional difficulty is caused by the coupling with ^{31}P. It follows that the structure of the complexed allylidene group is not easily interpreted.

On the basis of the above results and of cryoscopy in benzene, which indicated monomeric structures, formulas (IVa), (Va) and (IVb), (Vb) seemed plausible. However a preliminary X-ray examination of (IV) revealed that (IVb) is the true structure, with three carbon atoms centred on the metal in an allylic system, the quaternary phosphorus, bonded to one of them, projecting outside[5]. Since (IV) and (V) are diamagnetic, one of the two electrons of the carbon–phosphorus double bond of the starting ylide probably contributes to the formation of an allylic system, whereas the other one is digested by the electronic shell of the metal. In this sense, the structures of (IV) and (V) may be considered analogous to those proposed for (I), (II) and (III), with the difference that, in the latter, oxygen replaces one carbon atom of the allylic group. Isoelectronic structures similar to those described were found in triphenylphosphonium tricarbonylcyclopentadienylides of Mo and W[6].

(IV) reacts in hot benzene with an excess of triphenylphosphine to yield a complex, in which one of the carbonyls is replaced by the phosphine (VI). Consistently, three bands were found in the carbonyl stretching frequencies of the IR spectrum (CCl_4) at 2030 s, 1932 vs, 1914 vs cm^{-1}, consistent with a *cis* trigonal bipyramid[7]. An additional band is observed in the C–H bending region at 1485 cm^{-1} due to the unchanged allylidene system.

EXPERIMENTAL

All experiments were carried out under nitrogen. Solvents were purified in standard ways. ^1H NMR spectra were recorded on C-60 HL Jeol spectrometer, and IR spectra with a Perkin–Elmer 221 spectrophotometer, on Nujol or hexachlorobutadiene mulls unless otherwise stated.

Reaction of methylenetriphenylphosphorane

(*a*). *With* $Mo(CO)_6$. $(C_6H_5)_3PCH_3Br$ (2 g, 5.7 mmoles) in THF (60 ml) at room temperature was treated with C_4H_9Li (7.3 mmoles) in hexane solution (5 ml). The suspension was stirred for 30 min until the solid had disappeared. $Mo(CO)_6$ (1.32 g, 5.0 mmoles) was added, and stirring was continued for 30 min more. The solution turned from red to orange. Some white solid was filtered off, and the filtrate left at $-5°$ overnight. Yellow crystals of (I) separated (0.6 g, yield 15%) m.p. 110° dec. (Found: C, 58.2; H, 5.1; Mo, 13.3; P, 3.9 for $C_{37}H_{41}MoO_9P$ calcd.: C, 58.7; H, 5.4; Mo, 12.8; P, 4.1%.) ν_{max}: 3080 w, 2990 m, 2890 m, 2035 m (CO), 1988 m (CO), 1895 vs (CO), 1854 vs (CO), 1588 w, 1576 w, 1463 w, 1440 w, 1380 s, 1340 w, 1317 w, 1285 s, 1184 w, 1112 w, 1091 s, 1055 s, 998 w, 915 w, 896 m, 843 m, 754 w, 746 s, 713 w, 708 m, 692 s. $\tau(C_6D_6)$: 9.0 m (12 H), 6.9 m (12 H), 5.7 and 5.1 [d, 1 H, $J(^{31}P\text{–}H)$ 60 Hz], 3.3 and 2.8 (two m, 15 H). Another doublet was detected at 4.5 and 4.1 with a 20% intensity compared with that of the 5.7–5.1 doublet $J(^{31}P\text{–}H)$ 40 Hz; this is attributed to the methynic proton of the coexistent isomer.

(*b*). *With* $W(CO)_6$. The reaction was carried out following the procedure described for molybdenum hexacarbonyl. From $(C_6H_5)_3PCH_3Br$ (2 g, 5.7 mmoles) and $W(CO)_6$ (1.8 g, 5.1 mmoles) (II) was obtained in the form of yellow crystals (1.1 g, yield 26%), m.p. 110° dec. (Found: C, 51.8; H, 4.7; P, 3.9; W, 21.6. $C_{37}H_{41}O_9PW$ calcd.: C, 52.6; H, 4.9; P, 3.7; W, 21.8%.) ν_{max}: 2035 m (CO), 1892 m (CO), 1890 vs (CO), 1850 vs (CO). Apart from the slight differences in the CO frequencies, IR and NMR spectra were identical with those of (I).

(*c*). *With* $Fe(CO)_5$. By the same method (III) was obtained in the form of white shining plates (0.9 g, yield 25%) m.p. 110° dec. (Found: C, 63.3; H, 5.8; Fe, 8.0; P, 4.7. $C_{36}H_{41}FeO_8$ calcd.: C, 63.0; H, 5.9; Fe, 8.1; P, 4.5%.) ν_{max}: 2000 s (CO), 1880 vs (br) (CO). The IR and NMR spectra were very similar to those of (I) and hence are omitted.

Reaction of (I), (II), (III) with ethanol

Decomposition took place immediately when (I), (II) or (III) was treated with ethanol; $Mo(CO)_6$, $W(CO)_6$ and $Fe(CO)_5$ were recovered from the solutions in 80% yield by sublimation under vacuum.

Reaction of allylidenetriphenylphosphorane

(*a*). *With $Mo(CO)_6$*. A stirred suspension of $[(C_6H_5)_3P–CH_2CH=CH_2]Br$ (2 g, 5.2 mmoles) in THF (60 ml) was treated with C_4H_9Li in hexane, (5 ml, 7.3 mmoles). When the solid was completely dissolved, $Mo(CO)_6$ (1.3 g, 4.9 mmoles) was added and the solution was refluxed for 70 min. Then the solvent was removed under vacuum and the oily residue was redissolved in benzene (5 ml) and partially reprecipitated with light petroleum (5 ml). The suspension obtained was evaporated under vacuum, and the residue extracted with five 20 ml portions of benzene at 0°. Each portion was filtered and, after addition of petroleum ether, left at $-5°$ overnight. A yellow solid crystallized from the three last fractions; it was recrystallized from benzene/pentane to give pure (IV), as yellow prisms (0.65 g, yield 26%) m.p. 168–170. Correct analyses were obtained on samples by drying (IV) and (V) at 50° under high vacuum. (Found: C, 58.5; H, 3.6; Mo, 18.6; P, 6.0; mol.wt. cryoscopic in benzene, 540 ± 20. $C_{25}H_{19}MoO_4P$ calcd.: C, 58.8; H, 3.7; Mo, 18.8; P, 6.1%; mol.wt., 510.) ν_{max}: 3090 w, 3080 w, 2012 s (CO), 1905 vs (CO), 1890 vs (CO), 1860 s (CO), 1590 w, 1576 w, 1504 w, 1482 m, 1450 m, 1440 m, 1418 w, 1393 w, 1246 w, 1215 w, 1185 w, 1173 m, 1107 s, 1033 w, 1026 w, 997 w, 986 m, 848 w, 837 w, 823 m, 753 m, 720 s, 683 s. τ (acetone-d_6): 2.4 (m, 15 H, aromatic protons of the arylphosphine), 5.0 (m, 1 H, head proton of the allyl system), 7.2–7.5 (complex multiplet, the remaining three allylic protons).

(*b*). *$W(CO)_6$*. With the same amounts of reagents as were used for (IV), the THF solution was boiled for 40 min then treated as above. From the first three fractions a yellow product was obtained mixed with reddish oil. Recrystallization from benzene/pentane gave pure yellow crystals of (V) (0.35 g, yield 15%) m.p. 160–162, dec. (Found: C, 50.5; H, 3.1; P, 5.0; W, 30.6. $C_{25}H_{19}O_4PW$ calcd.: C, 50.2; H, 3.2; P, 5.1; W, 30.8%.) ν_{max}: 1995 s (CO), 1897 vs (CO), 1884 vs (CO), 1860 vs (CO). The other data are omitted since the IR and NMR spectra of (IV) and (V) are identical.

Reaction of triphenylphosphine with (IV)

When an excess of triphenylphosphine (0.5 g, 1.9 mmoles) was heated with (IV) (0.2 g, 0.39 mmoles) in benzene (5 ml) at 70° for 3 min, the solution turned from yellow to orange. After cooling, pentane was added, to give pale yellow crystals of (VI) (0.25 g; yield 85%) m.p. 265–267, dec. (Found: C, 68.2; H, 4.5; Mo, 12.7; P, 8.5. $C_{42}H_{34}O_3P_2W$ calcd.: C, 67.8; H, 4.6; Mo, 12.8 P, 8.3%.) ν_{max}: 3080 w, 3060 w, 2030 s (CO), 1932 vs (CO), 1914 vs (CO), 1590 w, 1575 w, 1483 m, 1450 m, 1437 s, 1307 w, 1190 w, 1184 w, 1160 w, 1093 m, 1038 w, 1000 w, 976 w, 747 s, 738 m, 694 s.

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