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REACTIONS OF DI-3-BUTENYLPHENYLPHOSPHINE WITH OCTACARBONYLDICOBALT AND HYDRIDOTETRACARBONYLCOBALT

T. J. BAILLIE, B. L. BOOTH and C. A. McAULIFFE

Department of Chemistry, University of Manchester Institute of Science and Technology, Manchester M60 1QD (Great Britain)

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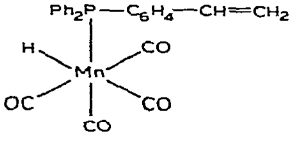
SUMMARY

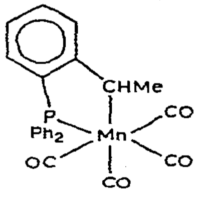
The alkenylphosphine, $C_6H_5P(CH_2CH_2CH{=}CH_2)_2$ (L), has been shown to react with $CoH(CO)_4$ at low temperatures to give mainly the hydride $CoH(CO)_3L$, which decomposes above 0° to afford the non-bridged dimer $[Co(CO)_3L]_2$. Under similar conditions reaction between $Co_2(CO)_8$ and L gives the ionic compound $[Co(CO)_3L_2]^+[Co(CO)_4]^-$, which forms a tetraphenylborate derivative, and which gives the same dimer $[Co(CO)_3L]_2$ on heating. In none of these reactions was any evidence obtained for coordination of the olefinic bond to the metal atom.

INTRODUCTION

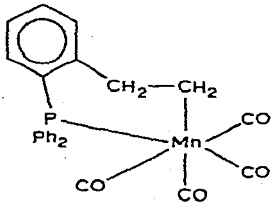
There has been considerable interest recently in the preparation and reactions of chelating ligands containing one, two, or three olefin groups attached to a good σ-donor, such as tertiary arsine or phosphine atoms[1]. One such ligand, (*o*-vinylphenyl)diphenylphosphine, has recently been shown to react with $MnH(CO)_5$ to give the monosubstituted complex (I) initially, and this, on heating, undergoes an olefin insertion reaction to afford the mixed σ-alkyl complexes (IIa) and (IIb), with the former as the major product[2]. Surprisingly the similar reaction of $ReH(CO)_5$



(I)

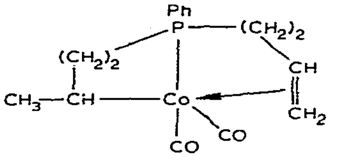


(IIa)



(IIb)

apparently gives only the anti-Markovnikov product analogous to (IIb)[3]. We now report some reactions of the new di-olefin chelating ligand, di-3-butenylphenylphosphine, with $CoH(CO)_4$, and the preparation of several cobalt carbonyl derivatives of this ligand. These reactions were attempted in the hope that with the more reactive cobalt hydride the substitution and olefin insertion reactions would occur under much milder conditions perhaps to give complexes of type (IIIa) or (IIIb) and their isomers, and hence a system which may have caused catalysis of olefin or diene oligomerisation reactions.



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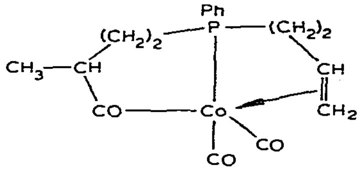

(IIIb)

RESULTS AND DISCUSSION

Di-3-butenylphenylphosphine (IV) was prepared in moderate yield by the reaction of 3-butenylmagnesium chloride and one-half molar equivalent of dichlorophenylphosphine in ether at room temperature. It is important to use the minimum amount of magnesium in this reaction, since the initially formed product (3-butenyl)chlorophenylphosphine apparently reacts more readily with any excess magnesium metal than with the Grignard reagent. Under these conditions the major product after hydrolysis is 3-butenylphenylphosphine. The IR spectrum of (IV) shows strong bands at 1638 cm^{-1} [ν(C=C)], 992 cm^{-1} [=CHR out-of-plane deformation] and 990 cm^{-1} [$=CH_2$ in-plane deformation], and the ^1H NMR spectrum is also in good agreement with that expected for the assigned structure, and is very similar to that of the previously reported ligand, tri-3-butenylphosphine[4].

The equimolar reaction between (IV) and $CoH(CO)_4$ in hexane at $-30°$ afforded a sticky, orange solid. On warming above 0° this solid decomposed rapidly with gas evolution to give a red solid from which could be isolated deep red crystals of bis[(di-3-butenylphenylphosphine)tricarbonylcobalt] (V) identified by comparison with an authentic sample (*vide infra*). The IR spectrum of the unstable orange solid showed four terminal metal carbonyl bands at 2070 w, 2030 m–s, 1985 s and 1945 m, and a medium–strong band at 1875 cm^{-1} attributed to the ν(CO) band of $[Co(CO)_4]^-$ anion[5]. The spectrum also shows strong bands at 1640, 995 and 918 cm^{-1} for an unco-ordinated olefinic group, whereas strong bands at ca. 1500 and 800–900 cm^{-1} expected for a co-ordinated olefin[4] are absent. The IR data suggest that the orange solid is a mixture of an ionic complex, possibly $\{Co(CO)_3[PhP(C_4H_7)_2]\}^+[Co(CO)_4]^-$ (VI) and an unstable compound, which is possibly $CoH(CO)_3[PhP(C_4H_7)_2]$. Mono-phosphine substituted derivatives of $CoH(CO)_4$ are known to be unstable at room temperature or even below, and to decompose to the corresponding derivatives of $Co_2(CO)_8$[6,7]. Unfortunately the composition of this orange solid mixture could not be confirmed by NMR spectroscopy as the solid was not sufficiently soluble in any suitable solvent at low temperatures.

The ionic complex (VI) has been obtained in 90% yield from reaction between (IV) and $Co_2(CO)_8$ in hexane at $-5°$. This orange-red solid, which is stable indefinitely at room temperature, has a molar conductivity $\Lambda_M = 114.6\ S \cdot cm^2 \cdot mol^{-1}$ in good agreement with the values obtained for similar complexes[5]. A plot of $\Lambda_0 - \Lambda_c$ versus $c^{\frac{1}{2}}$ according to the method of Feltham and Hayter[8] gives a straight line of slope 302 as expected for a 1/1 electrolyte. The IR spectrum of (VI) shows a band at 1874 cm^{-1} for the anion, and four bands in the terminal metal carbonyl region at 2060 w, 1998 s, 1989 sh and 1963 m–s cm^{-1}. The two bands at 1998 and 1989 cm^{-1} can only be resolved with difficulty using a dilute mull. If it is assumed that these two bands are unresolved in the spectrum of the unstable orange solid from $CoH(CO)_4$ then there is reasonable agreement between the two spectra except for a strong band at 2030 cm^{-1} which is absent in the spectrum of (VI). This latter band is therefore assigned to $CoH(CO)_3[PhP(C_4H_7)_2]$, which, if it has a similar structure to its analogue $CoH(CO)_3PPh_3$[6], should approximate to C_{3v} symmetry and exhibit only one weak and one strong band in the metal carbonyl region. Although an NMR spectrum of compound (VI) could not be obtained the compound has been adequately characterised by preparation of its tetraphenylborate derivative (VII) in 63% yield by reaction with an excess of $NaBPh_4$ in acetone at room temperature. Neither (VI) nor its derivative (VII) show any evidence in their IR spectra for co-ordination of the ligand olefinic bond to the cobalt atom.

When compound (VI) was refluxed in hexane for two hours deep red crystals of $\{Co(CO)_3[PhP(C_4H_7)_2]\}_2$ (V) were obtained in 88% yield. The IR and ^1H NMR spectra of this compound were identical to those of the compound obtained on decomposition of the unstable orange solid from $CoH(CO)_4$. The IR spectrum shows four bands at 2025 w, 1980 m–s, 1950 vs and 1890 msh cm^{-1} in the metal carbonyl region, and the position and intensities of these bands are similar to those observed for analogous compounds[9]. There is no indication in the IR spectrum that the olefinic group is co-ordinated to the metal atom, and the ^1H NMR spectrum is essentially identical to that of the free ligand with no indication of any shift of the olefinic protons as expected[4] for a co-ordinated double bond. It is also apparent from the NMR spectrum that no isomerisation of the double bond occurs either during the formation of (V) from (VI) or, more importantly, during the formation of (V) obtained by decomposition of the unstable orange mixture. This must imply that at no stage during the reaction of (IV) with $CoH(CO)_4$ does the olefin co-ordinate to the metal atom, since it is reasonable to assume that even if co-ordination had occurred for a relatively short time then some isomerisation of the olefinic bond would be apparent both in the spectrum of $CoH(CO)_3[PhP(C_4H_7)_2]$ and particularly in the sample of (V) obtained from this hydride. Furthermore, as the ionic complex (VI) is quite stable at room temperature the formation of (V) as the major product from decomposition of the orange solid mixture from $CoH(CO)_4$ must imply that $CoH(CO)_3$-$[PhP(C_4H_7)_2]$ is the major component of this mixture. The presence of (VI) in this mixture probably arises from reaction of (IV) with a small amount of $Co_2(CO)_8$ perhaps formed during the preparation of $CoH(CO)_4$ by acidification of the salt $[Co(DMF)_6]^{2+}2[Co(CO)_4]^-$[10] (where DMF = dimethylformamide).

These results show quite clearly that unlike $MnH(CO)_5$ or $ReH(CO)_5$ the rate of decomposition of the monophosphine substituted complex $CoH(CO)_3PR_3$ is much faster than the rate of insertion of the olefin into the Co–H bond.

EXPERIMENTAL

IR spectra were recorded on a Perkin–Elmer 621 instrument and ^{1}H NMR spectra were recorded on a Varian HA 100 instrument on solutions in $CDCl_3$. Molar conductivity measurements were carried out on a Cambridge Instruments Ltd. conductivity bridge. Except where stated all reactions were carried out under an atmosphere of dry nitrogen.

Preparation of di-3-butenylphenylphosphine

A solution of 4-chloro-1-butene[11] (25.7 g, 0.28 mole) in ether (50 ml) was added slowly with vigorous stirring to magnesium turnings (7.0 g, 0.29 g-atom) in ether (50 ml), which had been previously activated with iodomethane (1 ml). After complete addition the mixture was refluxed for 30 min, then cooled in ice before adding dropwise a solution of dichlorophenylphosphine (25.2 g, 0.14 mole) in ether (30 ml). A vigorous reaction ensued and when the addition was complete the mixture was refluxed for 20 min. The flask was then cooled in ice and an aqueous solution of ammonium chloride (90 g/l) was added slowly until two layers formed. The upper ethereal layer was separated, and after further extraction of the aqueous layer with ether (3 × 50 ml), the ether was then removed from the combined extracts by distillation. Fractional distillation of the residue gave fractions b.p. 48–72° (1.70 g) and b.p. 74–80° (1.88 g) which were discarded, and a third fraction b.p. 81–85° (9.46 g, 43 mmole, 31%) which was shown by IR and NMR spectroscopy to be di-3-butenylphenylphosphine (IV). Its IR spectrum showed bands at 3075 s, 3000 m–s, 2975 s, 2925 s, 2895 s, 2845 m–w, 1820 w, 1638 s, 1585 w, 1570 w, 1540 w, 1475 m–s, 1442 m–s, 1435 s, 1415 m–s, 1320 m–w, 1302 m–w, 1295 m–w, 1270 w, 1200 m–w, 1157 w, 1096 m, 1070 m, 1028 m, 992 s, 910 s, 790 m–w, 740 s, 697 s, 615 m, 553 w, 483 m and 400 w cm^{-1}. The ^{1}H NMR spectrum of $C_6(H^f)_5{-}P[C(H^a)_2{-}C(H^b)_2{-}C(H^c){=}C(cis H^d)(trans H^e)]_2$ showed bands at τ 2.6 (multiplet, 5H, H^f), 4.05 (a doublet of doublets further split into triplets, 2H, H^c; J_{ec} 175 Hz; J_{cd} 9.6 Hz; J_{cb} 6.0 Hz), 4.96 (doublet, 2H, H^e), 5.0 (doublet, 2H, H^d) and 8.05 (complex multiplet, 8H, H^a and H^b).

When this reaction was attempted using 4-chloro-1-butene (25.2 g, 0.27 mole), dichlorophenylphosphine (25.3 g, 0.15 mole) and an excess of magnesium turnings (10.2 g, 0.35 g-atom) the major product was 3-butenylphenylphosphine (6.3 g, 34.8 mmole, 25%) which showed major IR bands at 3060 s, 2950 m–s, 2890 m–s, 2270 s and 1637 s cm^{-1}.

Reaction of di-3-butenylphenylphosphine

(*a*). *With hydridotetracarbonylcobalt.* A cold solution (−70°) of hydridotetracarbonylcobalt [1.72 g, 10 mmole based on a quantitative conversion of $Co_2(CO)_8$] in hexane (15 ml), prepared from $Co_2(CO)_8$ (2.64 g, 7.7 mmole) by a previously reported procedure[10], was added dropwise to a stirred solution of the phosphine (2.18 g, 10 mmole) in hexane (15 ml) cooled to −30°. Reaction occurred immediately with gas evolution (90.0 gas ml at STP, 4.0 mmole) and the precipitation of a sticky orange-red solid. The red hexane solution was decanted and the orange solid (2.60 g) was washed with hexane before drying under vacuum (4 h) at −30°. This compound only solidified completely below −30° and on warming above 0° it decomposed to give a deep red solid, which on recrystallisation from benzene gave bis[(di-3-butenylphenylphosphine)tricarbonylcobalt] (V). (Found: C, 56.4; H, 5.2. $C_{34}H_{38}Co_2O_6P_2$ calcd.: C, 56.5; H, 5.3 %.) Its IR spectrum showed bands at 3080 m, 3060 m, 3003 w, 2980 m, 2960 m, 2920 m–s, 2850 w, 2025 w, 1980 s, 1950 vs, 1890 m–w, 1640 m–s, 1587 w, 1573 w, 1482 w, 1460 w, 1433 m–s, 1410 m–w, 1300 w, 1260 m–s, 1210 w, 1096 m–s, 1070 msh, 1020 m, 995 m, 913 s, 840 w, 800 s, 740 s, 720 m, 692 s. The ^1H NMR spectrum showed bands at τ 2.5 (5 H), 4.31 (2H, H^c; J_{cd} 10.0 Hz, J_{ce} 17.2 Hz, $J_{cb} \approx 6.0$ Hz), 5.29 (doublet 2H, H^e), 5.43 (doublet, 2H, H^d) and 8.10 (multiplet, 8H, H^a and H^b).

(*b*). *With octacarbonyldicobalt.* A cold solution of octacarbonyldicobalt (2.80 g, 8.0 mmole) in hexane (15 ml) was rapidly added dropwise to a stirred solution of the phosphine (1.88 g, 8.6 mmole) in hexane (15 ml) cooled at −5°. Carbon monoxide (78 gas ml at STP, 3.5 mmole) was evolved and an orange solid precipitated. The solvent was decanted and the solid was washed with cold hexane (8 ml) before being dried under vacuum to give bis(di-3-butenylphosphine)tricarbonylcobalt(I) tetracarbonylcobaltate(−I) (VI) (2.9 g, 3.86 mmole, 90%) as an orange-red powder. (Found: C, 56.4; H, 5.2. $C_{35}H_{38}Co_2O_7P_2$ calcd.: C, 56.3; H, 5.1 %.) Its IR spectrum showed bands at 3080 m–s, 3060 m, 3010 m, 2980 m, 2920 m–s, 2900 m–s, 2860 w, 2850 w, 2060 w, 1998 ssh, 1989 ssh, 1963 m–s, 1874 sbr, 1637 s, 1582 w, 1569 w, 1483 w, 1450 w, 1445 w, 1433 ssh, 1414 w, 1407 m, 1302 m–w, 1276 m–w, 1217 m, 1188 m, 1160 w, 1140 w, 1096 ssh, 1065 w, 997 m–s, 991 m–s, 980 m–s, 986 m–s, 949 w, 918 s, 845 w, 780 m, 748 s, 740 s, 734 s, 688 s, 620 m–s, 550 s, 490 s, 448 m, 390 m–w.

Addition of a solution of sodium tetraphenylborate (1.0 g, 2.9 mmole) in acetone (15 ml) to (VI) (1.45 g, 1.9 mmole) gave a yellow solution which, after filtration to remove a small amount of black solid and removal of the solvent under vacuum, gave a pale yellow solid. This was washed with a 1/1 mixture of acetone/hexane (2×5 ml) and then dried *in vacuo* for several hours to afford the tetraphenylborate derivative (VII) (1.0 g, 1.2 mmole, 63%). (Found: C, 74.0; H, 6.9. $C_{55}H_{58}BCoO_3P_2$ calcd.: C, 75.8; H, 7.1 %.)

Action of heat on compound (VI)

When a solution of (VI) (1.40 g, 1.87 mmol) in hexane (25 ml) was stirred under reflux for 2 h the orange solid slowly dissolved to give a dark red solution, which, after removal of the solvent, and washing with hexane (3 ml), gave (V) (1.19 g, 1.65 mmole, 88%) identified by analysis, IR and ^1H NMR spectroscopy.

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