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METAL COMPLEXES OF UNSATURATED TERTIARY PHOSPHINES AND ARSINES
V*. CARBONYL COMPLEXES OF GROUP VI METALS WITH *o*-STYRYLDIPHENYLPHOSPHINE

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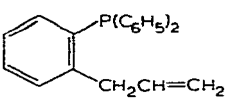
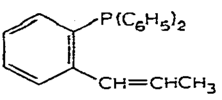
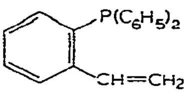
The preparation of (2-allylphenyl)diphenylphosphine (AP) and its coordination complexes with zero-valent Group VI metals has been described by Interrante, Bennett and Nyholm[1,2]. It was found that during coordination the ligand isomerises and that in these complexes the coordinated olefin, (2-*cis*-propenylphenyl)diphenylphosphine (PP), is present.



AP



PP



SP

We now report the preparation of the Group VI complexes of the parent ligand, *o*-styryldiphenylphosphine (SP).

EXPERIMENTAL

o-Styryldiphenylphosphine (SP)

This compound was prepared by treating the Grignard reagent of *o*-bromostyrene with chlorodiphenylphosphine[3]. The product was recrystallized from a large volume of petroleum spirits (40–60° fraction) and an approximately 70% yield of white crystals was obtained.

Chromium and molybdenum complexes $[M(CO)_4SP]$

(*a*) *Via (norbornadiene)*$M(CO)_4$. The procedure used was analogous to that of Interrante *et al.*[2] and in each case, recrystallization from hexane gave air-stable, yellow crystals of the chromium or molybdenum complex in a yield of 50–70%.

(*b*) *Directly from* $M(CO)_6$. The ligand was refluxed in methylcyclohexane or toluene under nitrogen with an equimolar amount of $M(CO)_6$ until no more carbon monoxide was evolved (up to 20 h). The solvent was then removed under vacuum and the residue recrystallized twice from hexane. The yields obtained were quite

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* Part IV: M. A. BENNETT, G. J. ERSKINE AND R. S. NYHOLM, *J. Chem. Soc.*, (1967) in press.

low (20–30%) and it is perhaps noteworthy that the use of toluene as solvent (rather than methylcyclohexane) appeared to give a faster reaction and better yields (*cf.* data in ref. 4). The reaction of $Cr(CO)_6$ with the ligand in benzene is very much slower than that of $Mo(CO)_6$.

Tungsten complex $[W(CO)_4SP]$

Since the norbornadiene complex of tungsten is difficult to prepare directly[5], an acetonitrile tungsten carbonyl complex has been used as an alternative intermediate. The use of the compound $(CH_3CN)_3W(CO)_3$ as a means of preparing olefinic and acetylenic derivatives of tungsten has recently been discussed by King and Fronzaglia[6]. Hence, following Strohmeier and Schönauer[7], $W(CO)_6$ (0.02 mole) was refluxed under nitrogen in acetonitrile until 0.04 mole of carbon monoxide were evolved (~24 h). Excess acetonitrile was removed under vacuum. 0.58 g (0.02 mole) of *o*-styryldiphenylphosphine, dissolved in dry benzene (25 ml), was added and the solution was refluxed under nitrogen for 3 h. The benzene was removed under vacuum and the residue was extracted with 20 ml of dry pentane at −78°. The solid remaining was twice recrystallized from hexane giving stable, yellow crystals in a yield of 50%.

The acetonitrile complex $(CH_3CN)_3Mo(CO)_3$, prepared by the method of Tate, Knipple and Augl[8], is also a satisfactory intermediate in the preparation of $Mo(CO)_4SP$, using a method similar to that given above for $W(CO)_4SP$. No product corresponding to $Mo(CO)_4(SP)_2$, $Mo(CO)_3(SP)_2$ or $Mo(CO)_2(SP)_2$ could be isolated from this or any other reaction mixture.

Measurements

Infrared spectra were obtained in the solid state as Nujol and hexachlorobutadiene mulls using a Perkin–Elmer 337 spectrometer. The NMR spectra were recorded at 60Mc/sec. on a Perkin–Elmer R10 instrument. Molecular weights were determined in benzene solution with a Mechrolab Vapour Pressure Osmometer. Microanalyses were performed by the microanalytical laboratories of Oxford and

TABLE 1

ANALYTICAL DATA AND PHYSICAL PROPERTIES

Compound		*C (%)*	*H (%)*	*P (%)*	*Decomp. point*	*Mol.wt.*
SP	Calcd.	83.3	5.94	10.7	100°[a]	
	Found	83.0	6.05	10.8		
$Cr(CO)_4SP$	Calcd.	63.7	3.79	6.85	165–175°	452
	Found	63.7	3.91	6.95		447
$Mo(CO)_4SP$	Calcd.	58.1	3.45	6.24	155–165°	496
	Found	58.2	3.50	6.40		508
$W(CO)_4SP$	Calcd.	49.3	2.93	5.30	160–175°	584
	Found	49.0	2.93	5.35		577

[a] Melting point.

University College London. Results of the analytical and molecular weight measurements are summarized in Table 1.

RESULTS AND DISCUSSION

Infrared spectra

By analogy with the Group VI compounds of (2-propenylphenyl)diphenylphosphine[1,2], it seems clear that *o*-styryldiphenylphosphine is acting as a bidentate ligand (I). Coordination of the olefinic bond to the metal should result in a lowering of the C=C stretching frequency in the complex compared with that in the free ligand. Unfortunately the C=C stretching band is very weak in the free phosphine but an absorption at 1625 cm^{-1} can be attributed to this vibration. This absorption is absent in the spectra of the three complexes and additional weak bands or shoulders at 1505, 1505 and 1490 cm^{-1} for the Cr(0), Mo(0) and W(0) complexes respectively, can probably be assigned to the coordinated double bond stretching frequency. The $\Delta\nu$(C=C) values thus obtained (120, 120 and 135 cm^{-1} respectively for the Cr, Mo and W complexes) are close to those observed for (2-*cis*-propenylphenyl)diphenylphosphine[2], in which the C=C absorption is more intense. However, it should be remembered that a lowering of the C=C stretching frequency is a qualitative measure only of the strength of the metal–olefin bond[9].

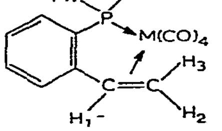
In the carbonyl region (~2000 cm^{-1}) each complex shows four absorptions as expected for a *cis*-disubstituted octahedral carbonyl complex[10]. The following is a complete list of infrared absorption frequencies (cm^{-1}; w, weak; m, medium; s, strong; sh, shoulder; br, broad).

SP: 422w, 430m, 467m, 491m, 511m, 524m, 533m, 546m, 580w br, 697s, 723m, 744s, 753m, 775s, 790m, 847w br, 927s, 939w, 991m, 1000m, 1027m, 1070w, 1090w br, 1121m br, 1161w br, 1179w, 1196m, 1307w, 1325w, 1405w, 1435s, 1460m, 1480m, 1580m, 1625w, 2855w, 2925m br, 3010w, 3050m br.

Cr(CO)$_4$SP: 431w, 459w br, 489m, 510s, 527m, 537w, 584w, 633s, 641s sh, 671s, 690w, 703s, 740m, 747m, 773m, 793w, 937w, 955w, 998m, 1075m, 1094m, 1135w, 1188w, 1245w, 1256w, 1390w, 1435s, 1470m, 1480m, 1505w br, 1885s, 1905s, 1930s, 2015s, 2850w br, 2925w br, 3005w br, 3065w.

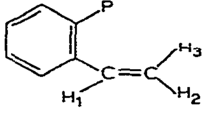
Mo(CO)$_4$SP: 425m, 441m sh, 461m, 484m, 499s, 509s, 521s, 538m, 572s, 587s, 601m, 615s, 676w, 696s, 725m, 746s, 769m, 790w, 849w, 920w, 947w, 970w, 999m, 1028w, 1074m br, 1095m, 1130w br, 1157w, 1167w, 1185m, 1246w, 1306w, 1330w, 1385w, 1435m, 1475m, 1485m, 1505w, 1585w, 1885s, 1910s, 1950s, 2035s, 2850w br, 2920w, 3010w, 3070m br.

W(CO)$_4$SP: 410w, 430w, 446m, 468m, 489m sh, 499s, 514s, 523m, 539w, 549w, 566m, 585m, 592w, 601s, 678w, 694s, 702w, 745s, 753s sh, 774m, 790w, 848w, 919w, 943w, 998m, 1027w, 1071w br, 1095m, 1129w br, 1157w, 1167w, 1184m, 1236w, 1247w, 1305w, 1330w, 1380w, 1430m, 1474m, 1480m, 1490w sh, 1585w, 1880s, 1910s, 1945s, 2030s, 2850w br, 2930w br, 3015w, 3070 m br.



(M = Cr, Mo, W)

(I)



(II)

Proton magnetic resonance spectra

The chemical shift and coupling constant data for *o*-styryldiphenylphosphine and its complexes are given in Table 2. In all four compounds the aromatic protons give rise to a complex band in the range 7.0–8.0 ppm downfield from tetramethylsilane.

TABLE 2

NUCLEAR MAGNETIC RESONANCE DATA IN DEUTERIOCHLOROFORM

Compound	*Chemical shift values*[a]			*H–H spin–spin coupling constants (cps)*		
	δ_3	δ_2	δ_1	$\lvert J_{13}\rvert$	$\lvert J_{12}\rvert$	$\lvert J_{23}\rvert$
SP	5.76	5.37	[b]	17.5	11.0	1.3
$Cr(CO)_4SP$	3.08	3.64	5.63	13.5	9.0	5.0
$Mo(CO)_4SP$	3.48	3.91	5.98	14.5	9.5	2.5
$W(CO)_4SP$	3.23	3.75	5.64	14.0	9.0	3.0

[a] In ppm from Me_4Si; all values negative with respect to Me_4Si. Protons 2 and 3 are assigned such that $J_{13} > J_{12}$ (*i.e.* $J_{trans} > J_{cis}$) in each case. [b] Obscured by the aromatic protons.

Chemical shift values. The large upfield shift of the vinyl group proton resonances, when the double bond is involved in bonding to the metal atom, can be qualitatively explained by changes in the shielding effects of π-electrons[5]. The fact that the shift of H_3 is considerably greater than that of H_2, can be attributed to an unsymmetrical positioning of the metal atom in relation to the double bond (*i.e.* the olefin–metal axis is not perpendicular to the olefin group); this situation is observed in the crystal structure of $[(styrene)PdCl_2]_2$[11]. Thus the shielding field of the "magnetic point dipole" of the C=C bond will be different for H_2 and H_3. Qualitatively the situation is similar for (2-propenylphenyl)diphenylphosphine and its complexes[2], although the upfield shifts are not as great, presumably due to the steric and other effects of the methyl group.

Spin-spin coupling constants. The analysis of geminal H–H coupling constants has been discussed by a number of workers[12–15] and possible correlations have been deduced between $J(H\text{–}H)_{gem}$ and the HCH angle involved. For example, in styrene and styrene oxide, the geminal coupling constants are 1.1 and 5.4 cps respectively, while the HCH bond angles are ~120° and 116.3° respectively[12,15]. The present case is more complex and the actual sign of the geminal coupling constant is not known, but the increase in $|J_{gem}|$ upon coordination could be due, at least in part, to a small decrease in the HCH bond angle of the methylene group. The greater deviation observed for the chromium compound could be attributed to the closer approach of the smaller chromium atom to the vinyl group.

Both the *trans* and *cis* coupling constants ($|J_{13}|$ and $|J_{12}|$ respectively) are reduced upon formation of the metal–olefin bond, and the reductions are approximately equal for all three metals. Decreases of the same order of magnitude were observed for *cis*- and *trans*-(2-propenylphenyl)diphenylphosphine and their complexes[2]. However, there are much larger changes in the case of styrene and styrene oxide: J_{13} decreases from 17.5 to 2.6 cps and J_{12} from 10.9 to 4.0 cps respectively[12,15]. This is due to the formation of an eclipsed, ethane-type model of styrene oxide, in which the carbon and hydrogen atoms are well out of plane. Thus the present coupling constants indicate that in these chromium, molybdenum and tungsten complexes, the vinyl group is still nearly planar and that in the carbon–carbon bond there is no extensive loss of double bond character.

Reactions of the complexes $M(CO)_4SP$

A. With acids. Davison *et al.*[16] have shown that transition metal carbonyl complexes, in strongly acid media, may form cationic species containing metal–hydrogen bonds *e.g.* $[HFe(CO)_4PPh_3]^+$. Alternatively, in the case of olefin-containing ligands, a proton may add to the double bond to give a type of "carbonium ion" stabilised by the carbonyl metal portion. However, the proton magnetic resonance spectra of $Mo(CO)_4SP$ in concentrated sulphuric acid and in trifluoroacetic acid failed to give any evidence of protonation, as decomposition appeared to occur quite rapidly.

B. With antimony pentachloride. Oxidation of the Mo and W complexes was attempted using $SbCl_5$ in chloroform at temperatures down to $-60°$ but decomposition occurs. Snow and Stiddard[17] have found that tricarbonylhexamethylbenzenetungsten, $(HMB)W(CO)_3$ precipitates $[(HMB)W(CO)_3Cl]SbCl_6$ under these conditions.

C. With bromine. The addition of halogens to these compounds is of interest since there is a possibility that a metal–carbon σ-bond may be formed[3,18]. When a solution of bromine in carbon tetrachloride is added dropwise with stirring to a solution of the chromium, molybdenum or tungsten complex in the same solvent, there is an obvious reaction marked by several colour changes both at room temperature and at $\sim -20°$. In particular, when equimolar quantities of complex and bromine are used, an insoluble coloured precipitate is finally formed. The chromium product is light green, that of molybdenum is brown, while the solid obtained from the tungsten complex is bluish-green. However infrared spectra indicate that in each case this major product, or mixture of products, no longer contains any carbonyl groups and analyses show that in the formation of this precipitate more than one molecule of bromine has reacted with each molecule of complex. As yet it has not been possible to isolate any carbonyl intermediates which may contain metal to carbon bonds.

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SUMMARY

The preparation of the compounds $M(CO)_4SP$, where $M = Cr$, Mo or W and SP = *o*-styryldiphenylphosphine, is described. IR and NMR data are recorded for these complexes and briefly discussed in relation to the nature of the metal–olefin bond.

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