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SYNTHESIS AND COORDINATING PROPERTIES OF (*o*-DIPHENYLPHOSPHINOBENZYL)DIMETHYLSILANE

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Summary

The reactions of (*o*-diphenylphosphinobenzyl)dimethylsilane with manganese and rhenium carbonyl afford *o*-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2Mn(CO)_4$ (M = Mn, Re), in which the ligand behaves as a chelate. Similar reactions occur with π-cyclopentadienemolybdenum tricarbonyl dimer to give *o*-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2Mo(\pi\text{-}C_5H_5)(CO)_2$. However, photolysis of a mixture of the ligand with manganese carbonyl yielded *o*-$(C_6H_5)_2PC_6H_4CH_2Si(H)(CH_3)_2Mn_2(CO)_9$.

Introduction

The chemistry of organometallic compounds of transition metals containing ligands bonded through phosphorus or silicon has attracted much interest. We report below the synthesis and coordinating properties of a new type of organometallic ligand containing both phosphorus and silicon as coordinating atoms, namely (*o*-diphenylphosphinobenzyl)dimethylsilane [1,2].

Results and discussion

The ligand (*o*-diphenylphosphinobenzyl)dimethylsilane, *o*-$Ph_2PC_6H_4CH_2Si(CH_3)_2H$ (I), was prepared by a two-step synthesis. The first step involved the reaction between *o*-bromobenzyl bromide with magnesium in ether to give *o*-bromobenzylmagnesium bromide, which was then treated with dimethylchlorosilane:

$$o\text{-}BrC_6H_4CH_2Br + Mg \rightarrow o\text{-}BrC_6H_4CH_2MgBr \xrightarrow{(CH_3)_2SiHCl} o\text{-}BrC_6H_4CH_2Si(CH_3)_2H + MgBrCl$$

The yield was about 47%. The Grignard reagent, *o*-$BrMgC_6H_4CH_2Si(CH_3)_2H$

was then made, and treated with diphenylchlorophosphine:

$$o\text{-}BrC_6H_4CH_2Si(CH_3)_2H + Mg \rightarrow o\text{-}BrMgC_6H_4CH_2Si(CH_3)_2H \xrightarrow{(C_6H_5)_2PCl}$$

$$o\text{-}(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2H$$

(I)

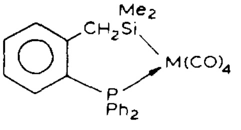
The reaction between diphenylchlorophosphine and the Grignard reagent at 0°C gave the product in 30% yield. When it was carried out at room temperature the yield was only 15–18% and substantial amounts of $[Ph_2P]_2$ and $Ph_2P(O)OH$ were isolated.

The ligand I is a heavy liquid, which is converted into the corresponding phosphine oxide $o\text{-}(C_6H_5)_2P(O)C_6H_4CH_2Si(CH_3)_2H$ (m.p. 189–190°C) on exposure to air.

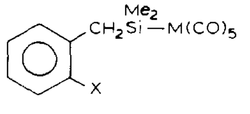
The reactions between the ligand I and manganese carbonyl in an evacuated ampoule proceeded at temperatures as low as 50°C in benzene, to give a yellow crystalline solid which can be formulated as $o\text{-}(Ph_2PC_6H_4CH_2Si(CH_3)_2Mn(CO)_4$ (II) on the basis of its infrared data and elemental analysis. When the reaction mixture was kept at 125°C for 24 h the yields increased to 37%. The complex can be assigned structure II, in which the ligand is coordinated to the central manganese atom through the silicon and phosphorus atoms. It undergoes some decomposition when exposed to air for 24 h, but there is no apparent decomposition when the crystals are kept under dry nitrogen for several weeks. It melts with decomposition at 158–159°C.

In a comparative study, it was found that *o*-bromobenzyldimethylsilane also reacted with manganese carbonyl at 50°C in benzene to give $o\text{-}BrC_6H_5CH_2\text{-}Si(CH_3)_2Mn(CO)_5$ in low yield. When the reactions were carried out in the presence of triphenylphosphine at the same temperature the yield was increased from about 5 to 20%. These results show that the presence of a phosphorus ligand promotes facile cleavage of the Si–H band and facilitates the formation of the silicon-manganese compounds; formation of such compounds has previously been reported to require much higher temperatures [3–5].

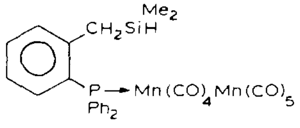
The reactions with rhenium carbonyl in benzene proceeded only at about 150°C to give an off-white complex (m.p. 169–171°C), which has the structure II with M = Re, similar to that of the manganese complex. The need to use elevated temperatures is general for reactions between triorganosilanes and rhenium carbonyl. However, *o*-bromobenzyldimethylsilane did not react with rhenium carbonyl even at elevated temperatures.



(II; M = Mn, Re)



(III, X = PPh2, Br ; M = Mn, Re)



(IV)

The carbonyl stretching vibrations of the *cis*-disubstituted complexes II (where M = Mn, Re), appear as four relatively strong bands, as shown in Table 1. The *trans* complexes reported elsewhere give only 2 strong bands [3]. Moreover, the complexes we obtained show no Si–H stretching vibration. On the basis of infrared and analytical data, structure III (where M = Mn, Re; and X = PPh_2) can be eliminated. On the other hand, the complex derived from *o*-bromobenzyldimethylsilane and manganese carbonyl had structure III (M = Mn; X = Br), and its infrared spectrum showed three strong bands at 2045, 2010 and 1980 cm^{-1}, as expected for a manganese pentacarbonyl complex [3,4].

Comparison of the carbonyl stretching vibration of a number of Si–Mn complexes (see Table 1) reveals that the disubstituted complexes have absorption bands at lower wave numbers than those of monosubstituted complexes. The *trans* complex, *trans*-$(CH_3)_3SiMn(CO)_4PF_3$, shows only two bands at 2074 and 1990 cm^{-1}. Thus, the complex $(C_6H_5)_3SiMn(CO)_4P(C_6H_5)_3$ reported by Schrieke and West must have the silyl and phosphine groups in the *cis* positions [4].

When a mixture of *o*-diphenylphosphinobenzyldimethylsilane and manganese carbonyl in benzene was irradiated with ultraviolet light for 30 h, the reaction proceeded differently, to afford compound IV, in which only one CO ligand of the manganese carbonyl has been displaced by the phosphine. There was no cleavage of the silicon–hydrogen or the manganese–manganese bonds, and bonding occurs only through the phosphorus atom. This type of asymmetrical structure has been obtained before, either by heating or photolysing a mixture of triphenylphosphine and manganese carbonyl [7,8]. Compound IV is a pale yellow crystalline solid which melts at 118–120°C with decomposition. Its infrared spectrum shows a peak at 2130 cm^{-1} which can be attributed to the silicon–hydrogen stretching vibration. Bands located at 2047, 2015, 1970, 1955 and 1915 cm^{-1} due to the carbonyl stretching vibrations are comparable to those for $(C_6H_5)_3PMn_2(CO)_9$ as reported by Wawersik and Basolo [7], (see Table 1).

The ligand I did not react with Group VI metal carbonyls even at elevated temperatures. However, reactions with π-cyclopentadienemolybdenum tricarbonyl

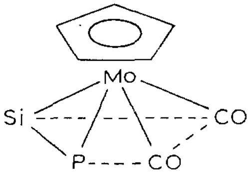
TABLE 1

INFRARED DATA FOR SOME RELEVANT METAL CARBONYL COMPLEXES

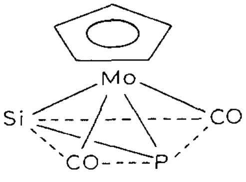
Complex	$\nu(CO)(cm^{-1})$			Reference
$(CH_3)_3SiMn(CO)_5$	2094	2000	1993	3
$(C_6H_5)_3SiMn(CO)_5$	2098	2030	2003	6
o-$BrC_6H_4CH_2Si(CH_3)_2Mn(CO)_5$	2045vs	2010vs	1980s	This work [a]
o-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2Mn(CO)_4$	2047m	2018m	1980sh, w	This work [a]
	1958s	1920s		
o-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2Re(CO)_4$	2060	1985m	1945s	This work [a]
	1925s			
trans-$(CH_3)_3SiMn(CO)_4PF_3$	2074w	1990vs		3
$(C_6H_5)_3SiMn(CO)_4P(C_6H_5)_3$	2047w	1990w	1950vs	6
	1910sh, w			
o-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2(H)$-$Mn_2(CO)_9$	2047vs	2015vs	1970s	This work [a]
	1955sh, s	1915m		
$(C_6H_5)_3PMn_2(CO)_9$	2098s	2015s	1997vs	7
	1969w	1837s		
o-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2$-$Mo(CO)_2(\pi$-$C_5H_5)$	1965s	1950sh, m	1920s	This work [a]
	1890s			

[a] Infrared data measured in chloroform.

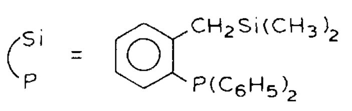
dimer, [π-$(C_5H_5)Mo(CO)_3]_2$, in benzene at 120°C for 24 h gave a red complex, m.p. is 168–170°C. On the basis of its elemental analysis it can be formulated as *o*-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2Mo(\eta$-$C_5H_5)(CO)_2$, in which means the ligand acts as a chelate by bonding through the phosphorus and silicon atoms. Its infrared spectrum did not show any silicon–hydrogen stretching vibrations. On the other hand, the infrared spectrum in chloroform showed four bands at 1965, 1950, 1920 and 1890 cm^{-1}, which can be attributed to C–O stretching vibrations, and these may come from an isomeric mixture of the complex which can be represented as follows:



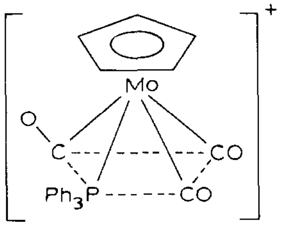
cis



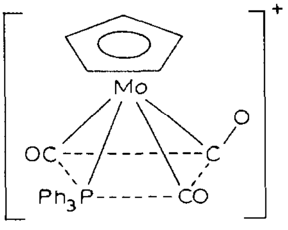
trans



Attempts to resolve the isomeric mixture by recrystallization or chromatography on silica gel or alumina columns were unsuccessful. The complexes are similar to the charged species reported by Cotton and Lukehart [5], shown below:



cis



trans

The infrared spectrum in dichloromethane of the *cis* complex gave peaks due to the carbonyl stretching vibration at 1980 and 1910 cm^{-1}, whereas for the *trans* complex the peaks are at 1985 and 1910 cm^{-1}.

Experimental

The infrared spectra of solids, as KBr pellets, were recorded on a Perkin–Elmer Model 337 infrared spectrophotometer. The IR spectra of metal carbonyl complexes in the carbonyl region were recorded on chloroform solutions.

Synthesis of o-bromobenzyldimethylsilane

Some iodine crystals and methyl iodide were added to magnesium turnings (7.5 g, 0.31 mol) and ether (100 ml). When the iodine colour had been discharged a solution of *o*-bromobenzyl bromide (77.7 g, 0.31 mol) in ether (30 ml) was added dropwise during 1.5 h. Stirring was then continued until the solution had cooled to room temperature. A mixture of dimethylchlorosilane (29.6 g, 0.31 mol) and ether (25 ml) was then added during a period of 1 h. The mixture was stirred for another 1.5 h then treated with saturated aqueous ammonium chloride. The organic layer was separated and dried (Na_2SO_4), and the ether was removed. Vacuum distillation of the residue gave *o*-bromobenzyldimethylsilane (34.5 g, 48.3 mol) b.p. 56–58°C/0.01 mmHg, (Found: C, 47.96; H, 5.86; Br, 35.80; $C_9H_{13}SiBr$ calcd.: C, 47.81; H, 5.70; Br, 34.69%); IR (liquid film): 3050m, 3000w, 2950s, 2890s, 2800w, 2140s, 1585m, 1565m, 1470s, 1440s, 1415s, 1290m, 1280m, 1260sh, 1250vs, 1205s, 1155s, 1140m, 1080w, 1045m, 1020vs, 995m, 850vs, 770s, 745vs, 720m, 695m, 655m, 600 m cm^{-1}.

The dibenzyl species $(o\text{-}BrC_6H_4CH_2)_2$ (2.50 g) was also obtained; m.p. 80–82°C. (Found: C, 49.81; H, 3.90; Br, 47.13; $C_{14}H_{12}Br_2$ calcd.: C, 49.70; 3.55; Br, 46.75%).

Synthesis of (o-diphenylphosphinobenzyl)dimethylsilane

o-Bromobenzyldimethylsilane (17.0 g, 0.07 mol) in ether (20 ml) was added dropwise to magnesium filings (1.8 g, 0.07 mol) covered with ether (50 ml). The mixture was allowed to reflux at 50°C until most of the magnesium had disappeared, then cooled to 0°C and a mixture of diphenylchlorophosphine (16.1 g, 0.07 mol) and ether (20 ml) was added dropwise. After 8 h of reflux the mixture was treated with saturated ammonium chloride solution (150 ml). Some white solid appeared in the aqueous layer, and after separation of the aqueous layer from the ethereal layer (A) the white solid was filtered off. It was washed with water to remove undissolved magnesium halides, and recrystallized from chloroform to yield a white solid, m.p. 120–123°C. Its elemental analysis and melting point corresponded to that of $[(C_6H_5)_2P]_2$. (Found: C, 77.56; H, 5.07; $C_{24}H_{20}P_2$ calcd.: C, 77.83; H, 5.40%.)

The ethereal fraction (A) was dried overnight over anhydrous sodium sulphate and was then distilled under nitrogen to remove the ether. The residue was subjected to bulb-to-bulb distillation at 0.01 mmHg pressure to give (*o*-diphenylphosphinobenzyl)dimethylsilane) (7.94 g) at 175–180°C (external temperature). Found: C, 75.98; H, 6.68; $C_{21}H_{23}SiP$ calcd.: C, 75.44; H, 6.88%. IR (liquid film): 3050s, 3000w, 2950m, 2895w, 2130s, 1950w, 1880w, 1810w, 1590s, 1560w, 1495s, 1420vs, 1320w, 1395w, 1250s, 1195m, 1155m, 1110m, 1095sh, 1070m, 1028m, 1000w, 945w, 885vs, 840s, 778s, 740vs, 698vs, 645w, 630w cm^{-1}.

On cooling the residue left in the end bulb became a very viscous yellow liquid. Acetone was added, and a white solid separated during 6 d. This was recrystallized from ethanol to give white crystals m.p. 195–198°C. Its elemental analysis corresponded to the compound $(C_6H_5)_2P(O)OH$. (Found: C, 65.87; H, 5.23; $C_{12}H_{11}PO_2$ calcd.: C, 66.05; H, 5.04%.)

Reactions of (o-bromobenzyl)dimethylsilane with manganese carbonyl

A mixture of manganese carbonyl (0.429 g, 1.10 mmol), (*o*-bromobenzyl)dimethylsilane (0.322 g, 1.41 mmol) and benzene (10 ml) was sealed in an evacuated tube which was kept in an oven at 50°C for 15 h. An orange solution was obtained, and this was transferred to a pear-shaped flask and concentrated to half its volume under nitrogen. The orange crystals formed were triturated, and sublimation at 50°C/0.01 mmHg removed the parent carbonyl. The yellow crystals (0.016 h) left behind melted over a range (130–145°C) because of decomposition before melting. It was formulated as *o*-$BrC_6H_4CH_2Si(CH_3)_2Mn(CO)_5$. (Found: C, 38.66; H, 2.38; Br, 18.57; $C_{14}H_{12}BrSiMnO_5$ calcd.: C, 39.81; H, 2.84; Br, 18.72%). IR: 3030w, 2950w, 2870w, 2045vs, 2010vs, 1980s, 1725m, 1690m, 1440s, 1280sh, 1260m, 1160s, 1120s, 1100m, 1070m, 1043m, 1023, 998w, 830m, 795m, 750m, 723m, 695s, 635w cm^{-1}.

Reactions of (o-bromobenzyl)dimethylsilane and triphenylphosphine with manganese carbonyl

A mixture of (*o*-bromobenzyl)dimethylsilane (0.121 g, 0.53 mmol), manganese carbonyl (0.172 g, 0.44 mmol), triphenylphosphine (0.150 g, 0.57 mmol) and benzene (10 ml) was sealed in a Carius tube under vacuum. The tube was kept in an oven at 50°C, for 18 h then the solution was removed and concentrated under nitrogen. Orange crystals were obtained. Sublimation under vacuum (0.01 mmHg) at 50°C removed the unreacted manganese carbonyl, and the residue was recrystallized from petroleum ether (b.p. 40–60°C) to give the pale yellow complex *o*-BrC_6H_4-$CH_2Si(CH_3)_2Mn(CO)_5$, (0.103 g); this began to decompose around 100°C and eventually melted to a brown liquid at 148°C. (Found: C, 39.54; H, 2.47; $C_{14}H_{12}BrSiMnO_5$ calcd.: C, 39.81; H, 2.84%). Its infrared spectrum is similar to that reported above.

Reactions of (o-diphenylphosphinobenzyl)dimethylsilane with manganese carbonyl

(a) A mixture of (*o*-diphenylphosphinobenzyl)dimethylsilane (0.349 g, 1.04 mmol), manganese carbonyl (0.396 g, 1.01 mmol) and benzene (10 ml) was sealed in an evacuated tube. Bubbling was observed when the tube warmed to room temperature. After several hours the bubbling slowed down and the tube was left overnight in the oven at 50°C. On removal of the tube from the oven and standing at room temperature for 30 h, crystals appeared. These were filtered off under nitrogen, and sublimation under vacuum (0.01 mmHg) at 60°C removed any unreacted manganese carbonyl (0.301 g). The yellow residue was recrystallised from benzene to yield pale yellow crystals of *o*-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2Mn(CO)_4$ (0.034 g, 6.5%) which decomposed on melting at 158–159°C. (Found: C, 59.86; H, 4.50; $C_{25}H_{22}SiPO_4Mn$ calcd.: C, 60.00; H, 4.40%).

In other experiment, a reaction involving this ligand (0.312 g, 0.93 mmol), manganese carbonyl (0.401 g, 1.02 mmol) and benzene (10 ml) was similarly carried out at 125°C. The same complex, *o*-$(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2Mn(CO)_4$, was obtained in higher yield, (0.188 g, 37.2%); IR: 3040w, 2940s, 2920s, 2860sh, 2850s, 2050m, 2018vs, 1980sh, 1958s, 1920s, 1580w, 1570w, 1480m, 1455m, 1430m, 1370m, 1360sh, 1305w, 1290w, 1260w, 1253w, 1180w, 1108m, 1093m, 1000w, 840sh, 830s, 805m, 775m, 750m, 740m, 695m, 680m, 668s, 638m cm^{-1}.

(b) A mixture of (*o*-diphenylphosphino)dimethylsilane (0.405 g, 1.21 mmol), manganese carbonyl (0.504 g, 1.29 mmol), and cyclohexane (10 ml) was sealed in a Carius tube and irradiated for 30 h with an ultraviolet lamp. Removal and concentration of the solution under nitrogen left a viscous reddish solution and some starting manganese carbonyl (0.095 g). Addition of petroleum ether (b.p. 40–60°C) gave a yellow precipitate which was filtered off and subjected to vacuum sublimation at 50°C to remove the manganese carbonyl (0.383 g). The residue was recrystallized from cyclohexane to give pale yellow crystals (0.192 g) which melted with decomposition at 118–120°C. This compound was identified as o-$(C_6H_5)_2PC_6H_4CH_2$-$Si(CH_3)_2(H)Mn(CO)_4Mn(CO)_5$, (Found: C, 54.71; H, 3.55; $C_{30}H_{23}SiPMn_2O_9$ calcd.: C, 54.54; H, 3.48%). IR: 3050w, 2960w, 2870w, 2120m, 2047vs, 2015vs, 1970s, 1955sh, 1915m, 1720m, 1590w, 1460s, 1280sh, 1260s, 1160s, 1120s, 1070m, 1045m, 1025m, 1000w, 820m, 795m, 750m, 723m, 695s, 638w cm^{-1}.

Reactions of (o-diphenylphosphinobenzyl)dimethylsilane with rhenium carbonyl

A mixture of (o-diphenylphosphinobenzyl)dimethylsilane (0.310 g, 0.92 mmol), rhenium carbonyl (0.510 g, 1.09 mmol) and benzene (10 ml) were kept in a Carius tube at 150°C for 12 h. Removal of the benzene left sticky, yellowish residue. Cyclohexane was then added and the resulting solution was concentrated under nitrogen and allowed to stand overnight. White crystals were deposited. These were recrystallized from cyclohexane to give off-white crystals (0.230 g) which melted with decomposition at 169–171°C. The compound was identified as o-$(C_6H_5)_2$-$PC_6H_4CH_2Si(CH_3)_2Re(CO)_4$ on the basis of its IR and elemental analysis. (Found: C, 47.98; H, 3.54; $C_{25}H_{22}PSiReO_4$ calcd.: C, 47.54; H, 3.48%). IR: 3040w, 2930w, 2090w, 2060s, 1995m, 1945s, 1925s, 1580w, 1560w, 1475m, 1430s, 1410m, 1320w, 1265w, 1238m, 1178w, 1105m, 1093m, 1025w, 998w, 875w, 843m, 825s, 803s, 778s, 755sh, 748s, 738s, 700m, 693s, 675m, 638m cm^{-1}.

Reactions of (o-diphenylphosphinobenzyl)dimethylsilane and -cyclopentadienemolybdenum tricarbonyl dimer

A mixture of cyclopentadienemolybdenum tricarbonyl dimer (0.723 g, 1.46 mmol), o-diphenylphosphinobenzyldimethylsilane (0.495 g, 1.46 mmol) and benzene (10 ml) was kept in a Carius tube at 120°C for 24 h. The solution was then filtered and the filtrate concentrated under nitrogen. The reddish-brown solid which formed was filtered off and recrystallized from ether to give red crystals (0.360 g) which melted at 168–170°C with decomposition. On the basis of the elemental analyses, the complex can be formulated as $(C_6H_5)_2PC_6H_4CH_2Si(CH_3)_2Mo(\pi\text{-}C_5H_5)(CO)_2$. (Found: C, 61.73; H, 5.29; $C_{28}H_{27}PSiMoCoO_2$ calcd.: C, 61.09; H, 4.91%). IR: 3020w, 2940s, 2910s, 2845s, 2070w, 1965s, 1950sh, 1920s, 1890s, 1465m, 1395m, 1380w, 1255w, 1120w, 1070w, 1015w, 850sh, 840m, 828s, 800w, 745w, 725w, 698, 610w cm^{-1}.

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