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Synthesis and coordinating properties of 2-pyridyldimethylsilane

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Abstract

The reaction of 2-pyridyldimethylsilane with rhenium carbonyl yields 2-$C_5H_4NSi(CH_3)_2Re(CO)_4$ in which the ligand is bonded through N and Si donor atoms. The ligand also reacts with $Ir(CO)Cl(PPh_3)_2$ to give 2-$C_5H_4NSi(CH_3)_2Ir(CO)Cl(PPh_3)_2H$.

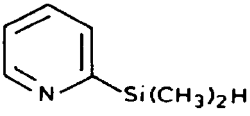
Introduction

As part of our continuing interest in the chemistry of organometallic compounds of transition metals containing ligands with nitrogen/phosphorus and silicon as donors [1–3], we report below the preparation and reactivity towards metal carbonyls of 2-pyridyldimethylsilane.

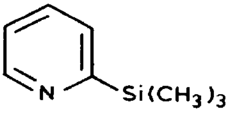
Results and discussion

The ligand 2-pyridyldimethylsilane, 2-$C_5H_4NSi(CH_3)_2H$ (I), was prepared by reaction between dimethylchlorosilane and the Grignard reagent, 2-C_5H_4NMgBr.

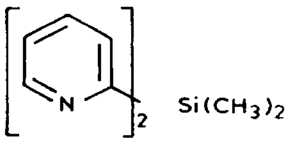
For purposes of comparison two related ligands 2-pyridyltrimethylsilane(II) and bis(2-pyridyl)dimethylsilane(III) were prepared.



(I)



(II)



(III)

All three ligands have been characterised by elemental analysis and infrared spectra. It is noteworthy that the number of Si–C stretch reduces from 2 to 1 as the

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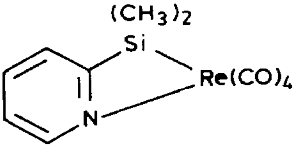
molecular symmetry increases from C_s for I to C_{3v} and C_{2v} for II and III, respectively [4].

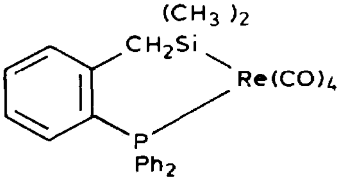
Of these three ligands only I reacts with the two metal carbonyls examined viz. rhenium carbonyl and $Ir(CO)(PPh_3)_2Cl$. The unreactivity of II and III towards the metal carbonyls is probably due to (a) steric hindrance and (b) the absence of a Si–H bond.

The reaction between the ligand I and rhenium carbonyl in cyclohexane required a temperature of 160 °C, and gave a yellow crystalline complex (m.p. 145–148 °C); it has previously been noted that reactions between triorganosilanes and rhenium carbonyl require elevated temperature [1]. The pale yellow complex obtained was formulated as $2C_5H_4NSi(CH_3)_2Re(CO)_4$ on the basis of its infrared spectrum and elemental analysis data. The disappearance of the Si–H stretch at 2130 cm^{-1} and the shifts of the 830 cm^{-1} (Si–C stretch) and 658 cm^{-1} (the metal-sensitive pyridine vibration) in I to 845 and 665 cm^{-1}, respectively, in the yellow complex IV suggests that bonding of I to the Re centre is through both N and Si donors IV [5,6,7].



(IV)

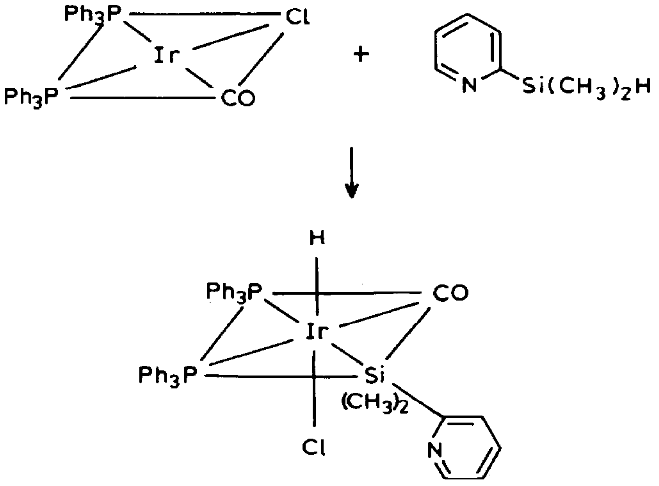
This mode of bonding is supported by the carbonyl stretching vibrations appearing as strong bands at 2050, 1995, 1940 and 1915 cm^{-1} which are similar to those reported for complex V obtained by reaction of (*o*-diphenylphosphinobenzyl)dimethylsilane with the rhenium carbonyl [1,8]:



(V)

The ligand I reacted with $Ir(CO)Cl(PPh_3)_2$ during 21 h at 80 °C to yield a light yellow crystalline product. The infrared spectra and elemental analysis suggest this reaction product is of 1/1 stoichiometry between I and $Ir(CO)Cl(PPh_3)_2$. Furthermore the infrared absorptions at 2290 cm^{-1} [9], characteristic of iridium-hydrogen stretch as well as the shift of the Si–C stretching to 850 cm^{-1} suggest that the complex contains both Ir–H and Ir–Si bonds, and can be formulated as $2\text{-}C_5H_4NSi(CH_3)_2Ir(CO)Cl(PPh_3)_2H$. Thus the reaction is essentially an oxidative addition [3].

A second possible structure in which the pyridyl nitrogen is also bonded to the Ir cannot be excluded. A weak band at 680 cm^{-1} suggests that the metal sensitive pyridine vibrations have been significantly affected upon reaction of I with the



iridium carbonyl. However, an X-ray structural analysis is necessary to establish the mode of bonding of I to the Ir centre unequivocally.

The reactions of 2-pyridyldimethylsilane with transition metal compounds occur much less readily than those of [*o*-(diphenylphosphino)benzyl]dimethylsilane, indicating that the phosphorus atom is a better donor than the pyridyl nitrogen.

Experimental

Synthesis of 2-pyridyldimethylsilane

A few iodine crystals and a little ethyl bromide were added to magnesium turnings (7.5 g, 0.31 mol) in dry ether (50 ml). When the iodine colour had been discharged, a solution of ethyl bromide (14.0 g, 0.12 mol) and 2-bromopyridine (69.8 g, 0.44 mol) in ether (50 ml) was added dropwise during 3 h. The mixture was refluxed for 3 h when cooled to room temperature. Dimethylchlorosilane (34.1 g, 0.36 mol) in dry ether (40 ml) was added during 2 h, and the mixture then refluxed for 4 h. The mixture was treated with saturated aqueous ammonium chloride. The ethereal layer was dried overnight over anhydrous sodium sulphate and distilled to yield 2-pyridyldimethylsilane (15.5 g) b.p. 175–178°C/758 mmHg (Found: C, 62.02; H, 7.86; $C_7H_{11}NSi$ calcd.: C, 61.31; H, 8.02%; IR (liquid film): 3080m, 3060sh, 3030m, 3000sh, 2960m, 2130m, 1600m, 1590s, 1490m, 1450s, 1260s, 1218m, 1148m, 1070-1045s,br, 1035s, 995m, 913s, 840sh, 830s, 803s, 773m, 750s, 710s, 658w, 630w, 605m cm^{-1}.

Reactions of 2-pyridyldimethylsilane with rhenium carbonyl

A mixture of rhenium carbonyl (0.569 g, 0.87 mmol), 2-pyridyldimethylsilane (0.365 g, 2.66 mmol) and cyclohexane (10 ml) was sealed in an evacuated tube and kept at 160°C for 10 h. The solution was then filtered and concentrated to half its volume under nitrogen, to yield a solid. Sublimation at 80°C/0.01 mmHg removed the unchanged rhenium carbonyl from the solid, which was then dissolved in ether. Yellow crystals (0.104 g) were obtained when petroleum ether (b.p. 40–60°C) was added. $(CH_3)_2SiC_5H_4NRe(CO)_4$ (m.p. 145–148°C) (Found: C, 29.75; H, 2.62. $C_{11}H_{10}SiNReO_4$ calcd.: C, 30.44; H, 2.30%) IR ($CHCl_3$ solution): 3020w, 2910w, 2050s, 1995s, 1940s, 1915s, 1605w, 1585w, 1450m, 1410w, 1260w, 1225m, 1195m, 1155w, 1100w, 1050w, 710w, 693w cm^{-1}.

Reactions of 2-pyridyldimethylsilane with $Ir(CO)Cl(PPh_3)_2$

A mixture of 2-pyridyldimethylsilane (0.112 g, 0.89 mmol), $Ir(CO)Cl(PPh_3)_2$ (0.180 g, 0.23 mmol) and benzene (10 ml) was sealed in an ampoule and kept at 80 °C for 21 h to yield a yellow solution. Yellow crystals were deposited upon cooling. The excess of 2-pyridyldimethylsilane and benzene was removed under reduced pressure. Fractional recrystallisation from ethanol yielded a solid (0.065 g), which displayed an IR band at 2150 cm^{-1} attributable to the Ir–H stretching vibration. The elemental analysis corresponded to that of the adduct $C_5H_4NSi(CH_3)_2Ir(CO)Cl(PPh_3)_2H$. (Found: C, 57.07; H, 4.33. $C_{44}H_{41}NSiP_2IrOCl$ calcd.: C, 57.57; H: 4.47%). IR: 3040w, 2920s, 2850s, 2290w, 2110s, 2065m, 2043m, 2010sh, 1990s, 1480s, 1460s, 1380m, 1160w, 1100s, 1073w cm^{-1}.

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