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Preliminary communication

Vinylmetallics as Ligands. V.*
Bis(triphenylphosphine)(vinyltrimethylsilane)platinum(0)

John W. Fitch and Joseph A. Froelich

Department of Chemistry
Southwest Texas State University
San Marcos, Texas 78666

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Summary

The preparation and some reactions of the compound, bis(triphenylphosphine)(vinyltrimethylsilane)platinum(0) are reported.

Both alkenes and alkynes are known to form platinum(0) complexes of the type, $[Pt(Ph_3P)_2(un)]$ (un = alkene, alkyne).[1-3] In general the alkyne complexes are more stable, with stability being greatest among electron deficient alkynes.[4] Although examples are limited, a similar pattern appears to be followed in alkene complexes since those derived from alkenes containing electron withdrawing groups also appear to be the most stable in this series.[5-7]

Since the trimethylsilyl group has been shown to exert a net electron withdrawing effect when attached to a carbon-carbon double bond,[8] it should activate vinylsilanes toward coordination to low-valent transition metals such as platinum(0). We now wish to report

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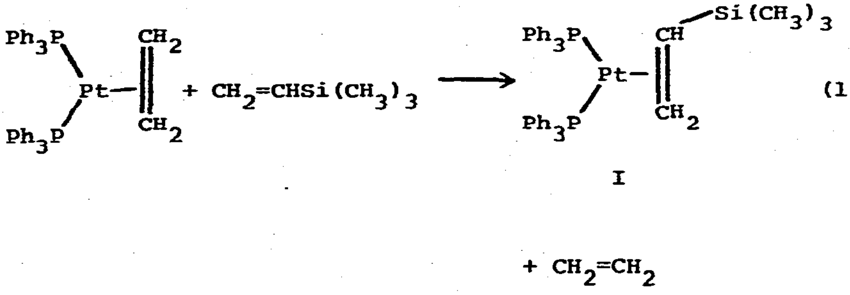
*For Part IV, see ref. 14.

the preparation and characterization of bis(triphenylphosphine)(vinyltrimethylsilane)platinum(O) (Compound I), the first example of a vinylsilane-platinum(O) complex (eq. 1).



(1)

I

In a typical preparation vinyltrimethylsilane (27 mmol) was added to a stirred solution of bis(triphenylphosphine)-(ethylene)platinum(O) (1.3 mmol) in benzene (20 ml). The reaction mixture was stirred for 10 minutes then frozen and partially evacuated. When thawed, the reaction mixture was stirred under partial vacuum for 15 minutes. The freezing, pumping, thawing and stirring procedure was repeated twice after which the solvent and excess ligand were removed <u>in vacuo</u> to leave I, a white powder, which was washed with hexane and dried in vacuo (79% yield). I is stable for hours in air and for days under argon. It is moderately soluble in benzene, toluene and chloroform (with reaction) and melts at 136-8°d. (in air or in vacuo). (Found: C, 60.27; H, 5.13; Mol. Wt., 803 (in benzene). $C_{41}H_{42}P_2PtSi$ calcd.; C, 60.06; H, 5.16%; Mol. Wt., 819).

The infrared spectrum of I (KBr pellet) is very similar to that of $(Ph_3P)_2Pt(CH_2{=}CH_2)$. Unique bands do occur at 1262, 1245 (sh), 1235, 883, 835, 819 and 744 (sh) cm^{-1}. Compounds containing the trimethylsilyl group normally have bands at 1280-1255, 840 and 765 cm^{-1} associated with methyl group vibrations and the Si-C stretching modes.[9]

The ^1H NMR spectrum of I, obtained in benzene-d_6 solution, shows peaks at $\delta7.7$ and $\delta7.1$ (30 H, aromatic protons) a very broad and poorly resolved resonance centered at $\delta2.7$ (3 H, vinyl group), and a very sharp resonance at $\delta0.1$ (9 H, trimethylsilyl group). The chemical shift of the vinylic protons of I is very close to that reported for the ethylenic protons ($\delta2.59$) in bis(triphenylphosphine)-(ethylene)platinum(O).[10] It is shifted upfield from that of the free ligand ($\delta5.37$-6.49) and the platinum(II) complex, $K[PtCl_3(CH_3)_3SiCH=CH_2]$, (Compound II) ($\delta3.96$-$4.40$ in acetone-d_6).[11]

The chemistry of I is that expected for a platinum(O)-olefin complex. ^1H NMR spectroscopy indicates that the vinyltrimethylsilane ligand does not remain coordinated to platinum in the solvents CS_2 and $CDCl_3$. Both alkyl halides and carbon disulfide are reported to react with platinum(O)-phosphine complexes.[12] On the other hand the Si-C bond in I is not subject to hydrolysis as has been observed for $K[PtCl_3(CH_3)_3SiCH=CH_2]$[11] since the ^1H NMR spectrum of a wet acetone-d_6 solution of I shows no change in any signal intensities during a 24 hour period. The vinyltrimethylsilane ligand can, however, be readily displaced from I by excess triphenylphosphine to form $[(Ph_3P)_4Pt]$ (40% yield, mp 132-4°, IR identical to known sample).

Finally, thermal decomposition of I occurs with the initial loss of vinyltrimethylsilane (TGA shows 11.2% wt. loss at 144° (under N_2), loss of the vinyltrimethylsilane ligand corresponds to a 12.2% weight loss). These data were confirmed by pyrolysis of I at 180-200° for 0.5 hour to liberate only benzene and vinyltrimethylsilane (both isolated and characterized by GLC). This behaviour should be contrasted to that observed when $K[PtCl_3(CH_3)_3SiCH=CH_2]$ is pyrolyzed to yield chlorotrimethylsilane[13] resulting from cleavage of the silicon to vinylic carbon bond.

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