

## THE PREPARATION OF OPTICALLY ACTIVE GERMANYL- AND SILYL-PLATINUM COMPLEXES

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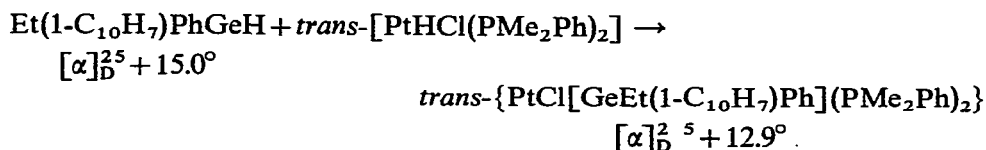
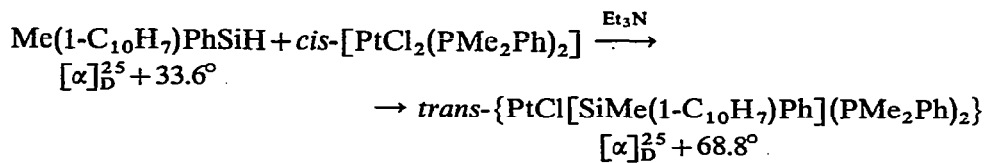
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### SUMMARY

The compounds (+)-*trans*-{PtCl[SiMe(1-C<sub>10</sub>H<sub>7</sub>)Ph](PMe<sub>2</sub>Ph)<sub>2</sub>}, [α]<sub>D</sub><sup>25</sup> + 68.8° (benzene), and (+)-*trans*-{PtCl[GeEt(1-C<sub>10</sub>H<sub>7</sub>)Ph](PMe<sub>2</sub>Ph)<sub>2</sub>}, [α]<sub>D</sub><sup>25</sup> + 12.9° (benzene), have been prepared from the hydrides (+)-Me(1-C<sub>10</sub>H<sub>7</sub>)PhSiH and (+)-Et(1-C<sub>10</sub>H<sub>7</sub>)PhGeH. There appears to be little loss of optical activity during the formation of the silicon-platinum compound, but possibly a substantial loss occurs during the formation of the germanium-platinum compound.

We describe below the preparations of the first compounds in which an optically-active silicon or germanium atom is bonded to platinum. These were made by established general procedures<sup>1</sup>, as shown in the following equations:



The large optical rotation of the hydride Me(1-C<sub>10</sub>H<sub>7</sub>)PhSiH (*viz.* [α]<sub>D</sub><sup>25</sup> + 29.1°) regenerated by lithium aluminium hydride reduction of the silicon-platinum compound shows that there can have been little loss of activity during the synthesis. This is consistent with the high degree of stereospecificity associated with hydrosilylation catalysed by platinum complexes<sup>2</sup>. On the other hand, the smallness of the rotation of the germanium-platinum compound in comparison with that of the silicon-platinum compound suggests that substantial loss of activity has occurred during preparation of the former, which would not be surprising in view of the fact that the hydride (+)-Et(1-C<sub>10</sub>H<sub>7</sub>)PhGeH racemizes when heated alone.

It is likely that the predominant stereochemistry is retention of configuration

at the silicon and germanium centres in both preparations, and experiments are in hand to establish this. It is known that the formation of a Si-Co bond occurs with retention at silicon<sup>3</sup>.

*(+)-trans-Chloro[methyl(1-naphthyl)phenylsilyl]bis(dimethylphenylphosphine)-platinum(II).*

A mixture of (+)-Me(1-C<sub>10</sub>H<sub>7</sub>)PhSiH (0.69 g, 2.8 mmole)<sup>4</sup>,  $[\alpha]_D^{25} + 33.6^\circ$  (c, 3.08 in cyclohexane), *cis*-[PtCl<sub>2</sub>(PMe<sub>2</sub>Ph)<sub>2</sub>] (1.5 g, 2.8 mmole), toluene (20 ml), and triethylamine (10 ml) was boiled under reflux for 65 h. During this time, the platinum complex dissolved, and a white solid separated. The mixture was subsequently cooled and triethylamine hydrochloride was removed by filtration. The filtrate was concentrated to give an oil, which was washed with light petroleum (10 ml, b.p. 60–80°) to leave a tacky solid. Recrystallization from toluene–light petroleum gave somewhat impure material (1.35 g, 65%),  $[\alpha]_D^{25} + 53.5^\circ$  (c, 1.74 in benzene), which was recrystallized from chloroform–pentane to give a sample of pure (+)-*trans*-{PtCl[SiMe(1-C<sub>10</sub>H<sub>7</sub>)Ph](PMe<sub>2</sub>Ph)<sub>2</sub>} (nc), m.p. 158–160°,  $[\alpha]_D^{25} + 68.8^\circ$  (c, 0.65 in benzene) (Found: C, 52.6; H, 5.0. C<sub>33</sub>H<sub>37</sub>ClP<sub>2</sub>PtSi calcd.: C, 52.6; H, 4.9%).

*(+)-trans-Chloro[ethyl(1-naphthyl)phenylgermyl]bis(dimethylphenylphosphine)-platinum(II)*

(+)-Et(1-C<sub>10</sub>H<sub>7</sub>)PhGeH (0.36 g, 1.18 mmole)<sup>6</sup>,  $[\alpha]_D^{25} + 15.0^\circ$  (c, 2.01 in benzene), and *trans*-[PtHCl(PMe<sub>2</sub>Ph)<sub>2</sub>] (0.60 g, 1.18 mmole) were mixed under oxygen-free dry nitrogen in an open Schlenk tube and the tube was maintained at 70° for 8 h with a slow current of nitrogen flowing through to remove evolved hydrogen. The mixture was then cooled, and the yellow oil which separated was washed with light petroleum to remove unchanged germane, and then dissolved in benzene (5 ml). Addition of pentane precipitated unchanged *trans*-[PtHCl(PMe<sub>2</sub>Ph)<sub>2</sub>] which was filtered off, and the mother liquor was concentrated to give the crude product as an oil (0.72 g, 75%) which was recrystallized from benzene–petroleum to give pure (+)-*trans*-{PtCl[GeEt(1-C<sub>10</sub>H<sub>7</sub>)Ph](PMe<sub>2</sub>Ph)<sub>2</sub>} (nc), m.p. 145–146°,  $[\alpha]_D^{25} + 12.9^\circ$  (c, 2.29 in benzene) (Found: C, 50.25; H, 4.95. C<sub>34</sub>H<sub>39</sub>ClGeP<sub>2</sub>Pt calcd.: C, 50.25; H, 4.8%).

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