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AN ISOMER-FREE HEXACOORDINATE BIS(ACETYLACETONE)-SILICON(IV) COMPLEX

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Summary

The reaction of diphenyldichlorosilane with acetylacetone in the presence of imidazole yields the known dienolate (**1**) and the new stable, isomer-free hexacoordinate silicon complex (**2**).

Introduction

Only a few neutral hexacoordinate complexes of silicon with 1,3-diketo ligands have been reported [1–5]. The first complexes of the type $(acac)_2SiRR'$ ($R = Cl$, $R' = Me$, Ph) were found to be highly unstable [1,2]. Attempts to prepare more stable compounds by replacement of the chloride by fluoride ligands proved unsuccessful [6]. The isomeric mixtures of bis(acetylacetonato)diacylsilicon complexes [2–4] are more stable, as would be expected because of the greater electronegativities of the ligands donor set. As far as we are aware, no isomer-free neutral hexacoordinate silicon complex has been reported to date [1–4].

Recently the reactions of various dialkyl- (or aryl-)dichlorosilanes with acetylacetone and other 1,3-diketones were investigated in the hope of obtaining additional hexacoordinate silicon compounds [7]; dienolates were obtained in all cases, and no hexacoordination was observed. We describe below the synthesis and characterisation of a stable isomer-free hexacoordinate silicon compound containing O_4C_2 ligands. This new silicon complex was found in the course of our investigations of various acetylacetone-based reagents [8].

Results and discussion

The reaction of acetylacetone (2 equiv.) with dichlorodiphenylsilane (1 equiv.) in THF in the presence of imidazole (2 equiv.) at room temperature gave two products in the ratio 2/1, namely the known dienolate **1** [7], which was isolated in 59% yield, and a pentane-insoluble solid **2** (27%). The product was **2** recrystallised from THF to

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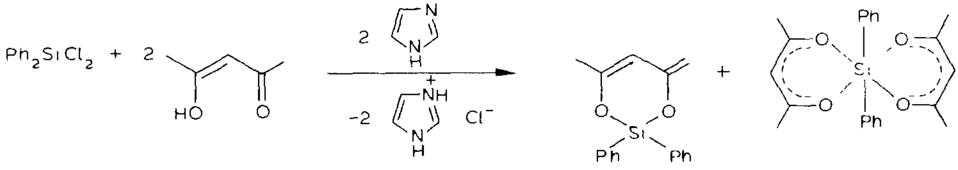
give small colourless crystals with m.p. 105–108°C (decomp.).



(1) (2)

Elemental analyses and ^{1}H NMR of **2** indicated that it contained two acetylacetonate ligands and two phenyl groups. As no free carbonyl groups could be detected by IR spectroscopy, it is evident that this product is the hexacoordinate silicon complex **2**. Although no M^+ is found in the mass spectrum of **2**, the base-peak at m/e 303 corresponds with the ion $[M - \text{Ph}]^+$.

The ^{1}H NMR and ^{13}C NMR spectra of **2** are fully consistent with a symmetrical structure having the two chelating acetylacetonate moieties in one plane, with the two phenyl groups *trans* to one another. Only seven signals are observed in the ^{13}C NMR spectrum, as expected (see Fig. 1). The ^{29}Si NMR resonance at δ −161.7 ppm is in the expected region [5].

Compound **2** is remarkably stable towards hydrolysis, in contrast to both the previously reported hexacoordinate complexes and the highly reactive dienolate **1**. Thus, it only reacts with diols in the presence of acid catalysts whereas **1** reacts smoothly to give *O*-silylene derivatives in the absence of any catalyst. The apparent discrepancy between our findings and those of Cella and Mitchell [7], who obtained only the dienolates on reaction of dichlorodiphenylsilane with 1,3-diketones, can possibly be attributed to the fact that different bases were used. Triethylamine can only act as an acid acceptor, whereas imidazole can have a double function as acid-acceptor and as a silylating reagent after reacting with diphenyl-dichlorosilane. It is possible that in our preparative route competing reactions take place in which imidazole acts either as a base (to give **1**) or as a reagent (to give **2**). A preliminary investigation of the reactions of dichlorodiphenylsilane with imidazole showed them to be very complex.

We have also found that hexacoordinate silicon(IV) complexes are formed on reaction of dibenzoylmethane with diphenyldichlorosilane. The results obtained with this diketone, which gives rise to isomeric complexes, will be reported later [10].

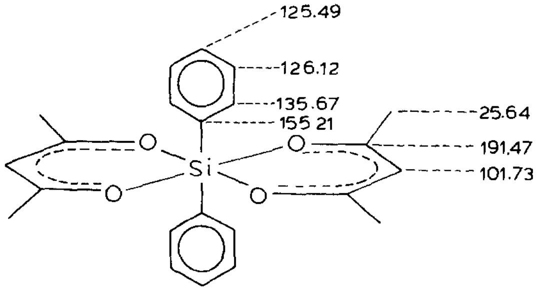


Fig. 1. ^{13}C NMR assignments for **2** [9] [δ(ppm) in THF-d_8].

Experimental

All experiments were carried out under dry argon. Mass spectra were determined with a Finnigan MAT CH-5 spectrometer at an ionising voltage of 70 eV [11a]. The ^1H NMR spectra at 60 MHz were measured with a Varian EM 360A. ^{13}C NMR and ^{29}Si NMR spectra were obtained with a Bruker WM 300 spectrometer [9]. UV spectra were recorded with a Carry 14 and IR spectra were measured with a Nicolet 7000 [11b]. Elemental analyses were carried out by Dornis and Kolbe, Mülheim an der Ruhr.

Preparation of 1,1-diphenyl-2,6-dioxa-3-methyl-5-methylene cyclohexylsilyl-3-ene (1) and diphenylsilyl-bis(-2-oxy-pent-2-ene-4-one) (2)

To a solution of imidazole (5.95 g, 87.4 mmol) in tetrahydrofuran (THF, 80 ml) was added diphenyldichlorosilane (11.16 g, 44.1 mmol) followed by acetylacetone (8.82 g, 88.1 mmol). The mixture was stirred at room temperature for ca. 15 h. The precipitate was then filtered off and the filtrate concentrated to give a pasty residue, which was triturated with pentane (4 × 30 ml). The pentane solutions were concentrated to give **1** (7.27 g, 59%). Elemental analysis: Found: C, 72.46; H, 6.31; Si, 9.89. $C_{17}H_{16}O_2Si$ calcd.: (280.39). C, 72.82; H, 5.75; Si, 10.01%. ^1H NMR (60 MHz, $CDCl_3$): δ (ppm): 2.35 (s, 3H), 4.45, 4.85 (d, 2H), 5.65 (s, 1H), 7.7–8.4 (m, 10H). ^{13}C NMR ($CDCl_3$), δ (ppm): 89.9, 152.3, 102.1, 151.4, 22.01, 134.6, 131.8, 130.6, 128. ^{29}Si NMR ($CDCl_3$), δ (ppm): -27.8. MS (70 eV): m/e 280 (relative intensity 100%), 237 (59%), 139 (16%). IR (cm^{-1}, film): ν 1660, 1600 (C=C) phenyl, 1000–1150 (Si–OC). UV (nm, λ_{max} ($\log\epsilon$)); 380 (107), 250 (470), 215 (770).

The solid material obtained on trituration was recrystallised from hot THF (80 ml) to give **2** (4.54 g, 27%), m.p. 105–108°C (decomp.). Elemental analyses: Found: C, 69.35; H, 6.45; Si, 7.42. $C_{22}H_{24}O_4Si$ calcd.: (380.5). C, 69.47; H, 6.35; Si, 7.38%. ^1H NMR (60 MHz, THF-d_8): δ (ppm) 1.40 (s, 6H, CH_3), 4.90 (s, 2H. CH), 6.25–7.25 (m, 10H, Ar). ^{13}C NMR (THF-d_8): δ (ppm) 191.47 (s), 155.21 (s), 135.67 (d), 126.12 (d), 125.49 (d), 101.73 (d), 25.64 in the ratio 4/2/4/4/2/2/4. ^{29}Si NMR (THF-d_8): δ (ppm) -161.7. MS (70 eV): $m/e = 303$ (relative intensity 100%), 281 (57%), 221 (28%), 139 (22%), 43 (56%). IR (cm^{-1}, KBr): ν 1540 (ĊO), 1010, 700 (Si–Ph).

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