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Rhodium(I) complexes of β-diketonates and related ligands as hydrosilylation catalysts

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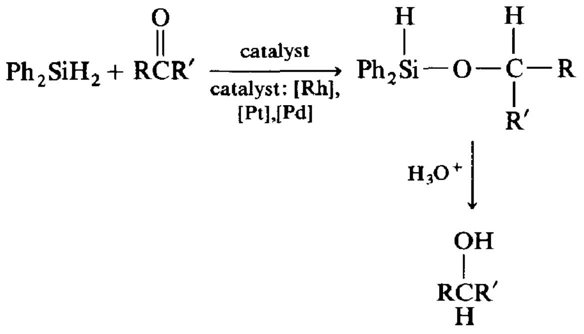
Abstract

The complexes $(O{-}O)Rh(CH_2CH_2)_2$ ($(O{-}OH) = FcC(O)CH_2C(O)CH_3$, $PhC(O)CH_2C(O)CH_3$, 1,2-$(CH_3CO)(OH)C_6H_4$, 3-benzoyl-(+)-camphor) are catalysts for the hydrosilylation of PhMeCO with Ph_2SiH_2. The optical yield from the reaction catalyzed by the camphor derivative is too low to measure. Only low optical yields (max 8.7% e.e.) are obtained from the same reaction by using similar in situ catalysts with ligands prepared from (+)-PhCH(Me)NH_2. Bases such as H^- and PhCH(Me)NH^- catalyze the hydrosilylation reaction in the absence of rhodium salts, but only low optical yields are obtained. Ph_2SiH_2 reacts with 2-cyclohexen-1-one under these conditions and the mode of reaction depends on the reaction conditions.

Introduction

The hydrosilylation of ketones is a useful reaction because the products, silyl ethers, are important reagents in their own right [1–4] and because hydrolysis of the silyl ethers affords alcohols, thus providing a pathway for the reduction, possibly asymmetrically, of ketones (eq. 1) [5].



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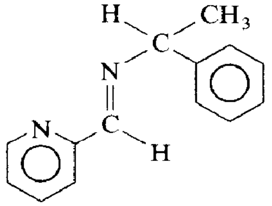
The use of complexes of the platinum metals to catalyze the hydrosilylation of ketones has been studied for a variety of ketones, silanes, ligands, and metals [6–15]. The first reported asymmetric hydrosilylation of ketones employed the [P(Me)(Ph)(CH_2Ph)] (BMPP) and [P(Me)(Ph)(Pr^i)] (MPPP) complexes of platinum as catalysts for the hydrosilylation of aromatic ketones by methyldichlorosilane, optical yields of 2.4–18.6% e.e. were obtained [16].

The hydrosilylation of ketones by rhodium complexes of chiral phosphorus-based ligands affords moderate optical yields of the silyl ether product and the highest optical yield obtained for the 'model' asymmetric hydrosilylation system, the addition of diphenylsilane to acetophenone [6], is 74% e.e. The ligand in this case is DIOP [17]. Other results obtained for the model system when using rhodium(I) complexes of chiral phosphorus-based ligands are lower (< 55% e.e.) 18–22.

Brunner and coworkers have reported asymmetric hydrosilylation catalyst systems that can give high optical yields and that use nitrogen-based ligands such as **1–4** [23–26]. The ligands are prepared from readily available optically active starting materials and the catalysts are prepared in situ by the addition of the (cyclooctadiene)rhodium(I) chloride dimer to a solution of ketone, silane, and ligand. Generally, an excess of ligand is employed (rhodium/ligand is approximately 1/6). Some of the results obtained by using this system are as follows: ligand, reaction time (chemical yield, optical yield); **1**, 23 h (87, 51); **2**, 65 h (94, 78); **3**, 57 h (93, 80); **4**, 94 h (88, 0.1). The (cyclooctadiene)rhodium(I) complex of **1** has been isolated as the PF_6^- salt and the structure shows a square planar cationic rhodium that is bound to the COD olefins and to the iminopyridine ligand that chelates using both nitrogen donor atoms [26].



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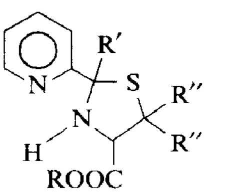
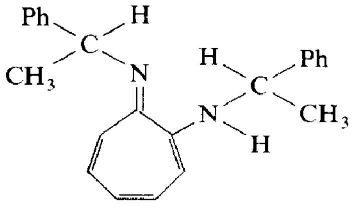


R	R′	R″
2 CH_3	H	H
3 CH_3	CH_3	H



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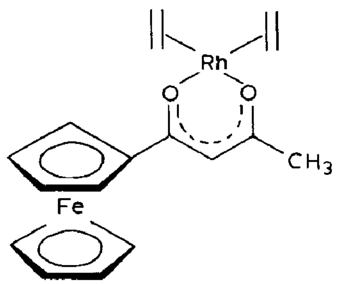
We have recently found that the oxygen-based complexes **5–8** are catalysts for the homogenous hydrogenation of olefins (20 °C, $P(H_2)$ 1 atm) [27]. The present paper describes their use as hydrosilylation catalysts. A base-catalyzed hydrosilylation reaction is also described.

Experimental

The preparation, storage, and handling of the compounds used in this study, unless otherwise stated, were performed under inert atmospheres of either nitrogen or argon, and standard Schlenk and vacuum-line techniques were employed. Solvents were refluxed over appropriate drying agents and distilled prior to use. Diethyl ether and hexane were distilled from calcium hydride; tetrahydrofuran and benzene, were distilled from sodium/benzophenone.

^{1}H NMR spectra were obtained by using a Varian XL-300 spectrometer operat-



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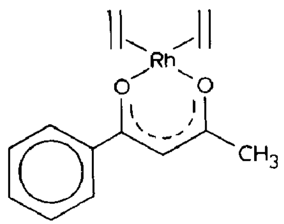

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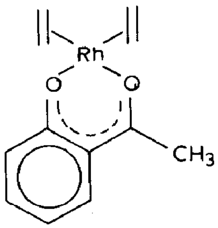

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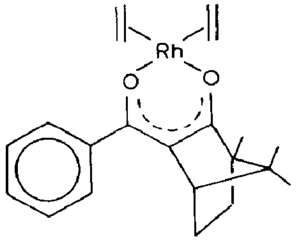

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ing at 300 MHz. Hewlett Packard model 5830A and 5890A gas chromatographs were used for product identification and quantitation. Mass spectrometry data were collected from a Kratos AEI MS50 spectrometer. Optical rotation measurements were obtained by using a Perkin–Elmer 141 polarimeter set at the sodium-D line (589 nm). Elemental analyses were performed by Mr. Peter Borda of the University of British Columbia.

Hydrosilylation reactions

(a) Rhodium-complex-catalyzed hydrosilylation. The hydrosilylation reactions using the rhodium(I) complexes were carried out using the following protocol. The ketone was mixed with diphenylsilane and the mixture was degassed using three freeze-pump-thaw cycles. The appropriate rhodium complex was then added in a flow of argon to maintain the inert atmosphere. The mixture was stirred for the reported amount of time and samples were taken from the reaction mixture and hydrolyzed by stirring with 15% aqueous hydrochloric acid. The hydrolysis mixture was stirred for 4 h before further work-up. The organic compounds were then extracted with ether, the extracts were combined, dried over magnesium sulfate, filtered, and vacuum distilled. Yields were calculated from gas chromatographic data (GLC) and compounds were identified by comparison with authentic samples of the expected products. Optical yields were calculated after measurement of the optical rotation.

Hydrosilylation experiments that involved the in situ generation of the catalyst precursor complex were performed by adding the bis(ethene)rhodium(I) chloride dimer to a degassed solution of ligand (rhodium/ligand ≈ 1/5), ketone, and diphenylsilane. The progress of the reaction was again monitored by GLC of a hydrolyzed sample of the reaction mixture.

(b) Base-catalyzed hydrosilylation. The base-catalyzed hydrosilylations were carried out by adding the given base to a degassed solution of ketone and silane, neat or in the reported solvent. These reactions were performed at 0 ° C unless otherwise stated. A typical experiment of this type is the hydrosilylation of acetophenone. Acetophenone (2.0 ml, 17 mmol) and diphenylsilane (3.4 ml, 18 mmol) were combined, degassed by three freeze-pump-thaw cycles, and placed under an argon atmosphere at 0 ° C. Sodium hydride (5 mg of an 80% dispersion in oil, 0.2 mmol) was added and the mixture was stirred (1 h) and allowed to warm to 20 ° C and stirred for 20 h. After hydrolysis with 10 ml of 10% aqueous potassium carbonate, the product was isolated from the mixture by extraction with diethyl ether and was purified by vacuum distillation.

Preparation of 1,3-dioxobutylferrocene. A lithium diisopropylamide solution was prepared by the addition of butyllithium (14.4 ml of 1.6 *M* solution in hexanes, 23 mmol) to a solution of diisopropylamine (2.5 g, 24.7 mmol) in 50 ml of hexane at 0 ° C. The mixture was stirred for 1 h at 0 ° C, acetylferrocene (5.00 g, 21.9 mmol) was then added in small portions and the mixture was stirred for an additional hour. The reaction mixture was allowed to warm to room temperature and was stirred overnight. The product lithium salt was isolated by filtration, washed with several portions of hexane, dried under vacuum, and used without further purification. The crude yield was 4.1 g (80%) of the light-yellow solid.

The lithioacetylferrocene (1.5 g, 6.4 mmol) was suspended in 20 ml of ether and cooled to 0 ° C. Ethyl acetate (0.68 g, 7.7 mmol) was then added dropwise and the mixture was stirred for 4 h at 0 ° C. The mixture was warmed to room temperature and stirred overnight. The lithium salt of the diketone was isolated by filtration and washed with several portions of ether. The diketonate salt was converted to the diketone by shaking it with 10% aqueous HCl solution and the diketone was extracted from the mixture with ether. The combined ether extracts were dried over magnesium sulfate, filtered, and the solvent removed at reduced pressure, affording a red-orange solid (0.76 g, 44% yield) [28]. Anal. Found: C, 62.35; H, 5.36; O, 11.90. $C_{14}H_{14}FeO_2$ calcd.: C, 62.26; H, 5.19; O, 11.86%.

Preparation of 3-benzoyl-(+)-camphor A solution of lithium diisopropylamide was prepared by adding butyllithium (22.6 ml of 1.6 *M* solution in hexane, 36 mmol) to a solution of diisopropylamine (5.1 ml, 36 mmol) in 80 ml of diethyl ether. After 2 h, (+)-camphor (5.0 g, 33 mmol) was added and the mixture was stirred overnight. The solution was cooled to 0 ° C and ethyl benzoate (6.2 ml, 43 mmol) was added dropwise. After 4 h the ether was removed at reduced pressure and the pinkish solid was washed with hexane. The solid was hydrolyzed with 25 ml of 20% HCl and the product extracted with diethyl ether. The ether extracts were dried over magnesium sulfate. The mixture was then filtered and the ether removed at reduced pressure, yielding 3.4 g (40%) of 3-benzoylcamphor [29]. Anal. Found: C, 79.90; H, 7.88. $C_{17}H_{20}O_2$ calcd.: C, 79.65; H, 7.86%.

Preparation of (N-Methylbenzyl)salicylamide (9). (*R*)-α-Methylbenzylamine (2.00 ml, 15.5 mmol) was dissolved in a mixture of triethylamine (20 ml) and ether (20 ml) and cooled to − 78 ° C. Salicyl chloride (2.24 ml, 18.6 mmol) [30] was added dropwise, stirred for 45 min, and the reaction mixture was allowed to warm to room temperature, and stirred for 2 h. The mixture was hydrolyzed with H_2O and extracted with ether. The ether extracts were combined, dried over magnesium sulfate, filtered, and vacuum distilled (b.p. 160 °C, 1 mmHg), giving 2.18 g of product (58% yield). ^{1}H NMR ($CDCl_3$) δ 1.63 (d, J 8.0 Hz, CH_3), 5.31 (d,qt J 8.0 Hz, CH), 6.49 (d, J 8.0 Hz, NH), 6.8–7.5 (m, C_6H_4). Mass spectrum m/e (relative intensity): 241, P^+, (9.4), 137 (57), 120 (41), 105 (100). Anal. Found: C, 74.88; H, 6.44; N, 5.65. $C_{15}H_{15}NO_2$ calcd.: C, 74.67; H, 6.26; N, 5.80%.

*Preparation of 1-(1-phenyl)(1-(R)-α-methylbenzylamino)buten-3-one (**10**).* Benzoylacetone (2.50 g, 15.4 mmol), (R)-α-methylbenzylamine (2.05 g, 17.0 mmol), and 10 g molecular sieves (3Å) were combined in 50 ml benzene and refluxed. After 6 h analysis by gas chromatography indicated that the reaction was not progressing any further. The solvent was removed at reduced pressure and the product was vacuum distilled (b.p. 185 °C, 1 mmHg), giving 1.95 g (48% yield) of the light-yellow oil. ^{1}H NMR ($CDCl_3$): δ 1.64 (d, J 6.7 Hz, $CHCH_3$), 2.35 (s, CCH_3), 4.94 (q, J 6.7 Hz, $CHCH_3$), 6.8–7.5 (m, C_6H_4). Mass spectrum m/e (relative intensity): 239, P^+, (40), 222 (9), 148 (11), 135 (40), 120 (22), 105 (100). Anal. Found: C, 80.22; H, 7.06; N, 5.68. $C_{16}H_{17}NO$ calcd.: C, 80.30; H, 7.16; N, 5.85%.

*Preparation of (2′-hydroxy)(1-(R)-α-methylbenzylimino)ethylbenzene (**11**).* (R)-α-Methylbenzylamine (3 ml, 23.3 mmol), 2′-hydroxyacetophenone (3.8 g, 27.9 mmol) and 10 g molecular sieves were combined in 30 ml benzene and refluxed. The reaction was monitored by gas chromatography, which indicated that the starting amine was spent after 4 h of reaction. The solvent was removed at reduced pressure and the product was distilled (b.p. 170 °C, 1 mmHg) to give 4.36 g (79% yield) of product. ^{1}H NMR ($CDCl_3$): δ 1.61 (d, J 7.0 Hz, $CHCH_3$), 1.95 (s, $C(O)CH_3$), 4.77 (d, qt, J 7.0 Hz, $CHCH_3$), 5.70 (s, CH), 7.1–8.0 (m, aromatic), 11.85(d, J 7.0 Hz, NH). Mass spectrum m/e (relative intensity: 265, P^+, (24), 250 (4), 222 (12), 208 (4), 167 (4), 160 (39), 145 (6), 120 (11), 105 (100). Anal. Found: C, 81.79; H, 7.34; N, 5.16. $C_{18}H_{19}NO$ calcd.: C, 81.48; H, 7.22; N, 5.28%.

Preparation of the sodium salts of the ligands. The sodium salts of the ligands employed in the hydrosilylation reactions and complex syntheses were prepared by treating sodium hydride with the appropriate ligand in diethyl ether. An excess of the ligand was used to ensure complete reaction of the sodium hydride added (ligand/sodium hydride ≈ 1.5/1). An example is the preparation of the sodium salt of 2′-hydroxyacetophenone. The 2′-hydroxyacetophenone (1.00 g, 7.34 mmol) was dissolved in 25 ml of diethyl ether. Sodium hydride (140 mg of an 80% dispersion in oil, 4.9 mmol) was then added in small portions. After the addition was complete the mixture was stirred overnight. The reaction mixture was then filtered and the white precipitate was washed with several portions of ether. The ligand salt was dried at reduced pressure and stored under an inert atmosphere.

Preparation of the rhodium(I) complexes

Bis(η²-ethene)(1,3-(1-ferrocenyl)butanedionato-O,O′)rhodium(I) (5). A suspension of bis(ethene)rhodium(I) chloride dimer [31] (250 mg, 643 μmol) in 15 ml ether was cooled to −78 °C; 1,3-dioxobutylferrocene (382 mg, 141 μmol), was then added, followed by a solution of potassium hydroxide (180 mg, 3.2 mmol) in 1 ml water. The mixture was then stirred for 4 h, allowed to warm to room temperature, and stirred an additional 4 h. The complex was extracted from the aqueous layer with several portions of ether, which were then combined and concentrated at reduced pressure. Hexane was layered on top of the ether solution to afford 417 mg (87%

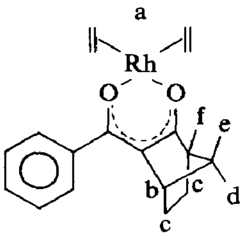
yield) of the red-orange complex. ^{1}H NMR ($CDCl_3$) δ 2.00 (s, CCH_3), 2.90 (bs, C_2H_4), 4.10 (s, C_5H_5), 4.32 and 4.64 (m, C_5H_4), 5.57 (s, CH). Mass spectrum m/e (relative intensity): 428, P^+, (31), 400 (11), 372 (19), 341 (17), 314 (41), 270 (100), 228 (12), 205 (54), 286 (34), 185 (11). Anal. Found: C, 50.82; H, 5.03; O, 7.70. $C_{18}H_{21}O_2Rh$ calcd.: C, 50.50; H, 4.94; O, 7.47%.

Bis(η^2-ethene)(1,3-(1-phenyl)butanedionato-O,O′)rhodium(I) (6). A solution of benzoylacetone (180 mg, 1.11 mmol) and the bis(ethene)rhodium(I) chloride dimer (200 mg, 514 μmol) was cooled to $-78\,^\circ$C. A solution of potassium hydroxide (140 mg, 2.5 mmol) in 1 ml water was added dropwise and the mixture was stirred for 1 h. The solution was allowed to warm to room temperature and was stirred an additional 1 h. The complex was extracted with several portions of ether, the solvent removed at reduced pressure, and the resultant yellow powder recrystallized from hexane to give 293 mg (89% yield) of yellow crystals. ^{1}H NMR ($CDCl_3$): δ 2.14 (s, CH_3), 3.03 (bs, C_2H_2), 6.02 (s, CH), 7.3–7.8 (m, aromatic). Mass spectrum m/e (relative intensity): 320, P^+, (49), 292 (72), 264 (100), 234 (43), 206 (66), 193 (17), 180 (20), 162 (13). Anal. Found: C, 52.57; H, 5.48; O, 10.11. $C_{14}H_{17}O_2Rh$ calcd.: C, 52.52; H, 5.35; O, 9.99%.

Bis(η^2-ethene)(2-acetylphenoxy-O,O′)rhodium(I) (7). (a) Preparation from the ligand. A solution of bis(ethene)rhodium(I) chloride dimer (200 mg, 514 μmol) in 20 ml of hexane was cooled to $-78\,^\circ$C and 2′-hydroxyacetophenone (154 mg, 1.13 mmol) was added via a syringe. A solution of potassium hydroxide (140 mg, 2.50 mmol) in 1 ml water was then added and the solution was stirred for 1 h. The solution was allowed to warm to room temperature and was stirred for an additional 1 h. The complex was extracted from the aqueous layer, the ether removed, and the yellow product recrystallized from hexane to give 263 mg (87% yield) of yellow crystals.

(b) Preparation from the ligand salt. A solution of bis(ethene)rhodium chloride dimer (100 mg, 257 μmol) in 20 ml of hexane was cooled to $-78\,^\circ$C. The sodium salt of 2′-hydroxyacetophenone (90.0 mg, 569 μmol) was then added and the mixture was stirred for 1 h. The solution was allowed to warm to room temperature and was stirred an additional 30 min. The reaction mixture was filtered and the solvent removed to give 147 mg (97% yield) of the product as a yellow crystalline powder. ^{1}H NMR ($CDCl_3$) δ 1.88 (s, CH_3), 2.84 and 3.90 (bs, C_2H_4), 6.31 (m, CH *ortho* to original OH), 6.95–7.15 (m, all other CH). Mass spectrum m/e (relative intensity): 294, P^+, (11), 266 (19), 238 (23), 210 (19), 180 (17), 136 (58), 121 (100). Anal. Found: C, 48.80; H, 5.15; O, 10.79. $C_{12}H_{15}O_2Rh$ calcd.: C, 49.00; H, 5.14; O, 10.88%.

Bis(η^2-ethene)(3-benzoyl-(+)-camphorato-O,O′)rhodium(I) (8). A solution of benzoylcamphor (215 mg, 839 μmol) and bis(ethene)rhodium(I) chloride dimer (150 mg, 386 μmol) was prepared and cooled to $-78\,^\circ$C. A solution of potassium hydroxide (140 mg, 2.00 mmol) in 1 ml water was then added dropwise and the mixture was stirred for 2 h. The solution was allowed to warm to room temperature and was stirred an additional 1 h. The rhodium complex was extracted from the aqueous layer with ether, the solvent removed, and the product recrystallized from hexane, giving 262 mg (82% yield) of the orange complex. ^{1}H NMR ($CDCl_3$): δ 0.72 (s, f), 0.80 (s, e), 0.90 (s, d), 1.0–2.0 (m, c), 2.01 (m, c), 2.61 (m, b), 2.93 (bm, a), 7.3–7.5 (m, aromatic). Mass spectrum m/e (relative intensity): 414, P^+, (15), 386 (30), 358 (24), 328 (31). Anal. Found: C, 61.10; H, 6.38; O, 7.60. $C_{21}H_{27}O_2Rh$ calcd.: C, 60.87; H, 6.57; O, 7.72%.

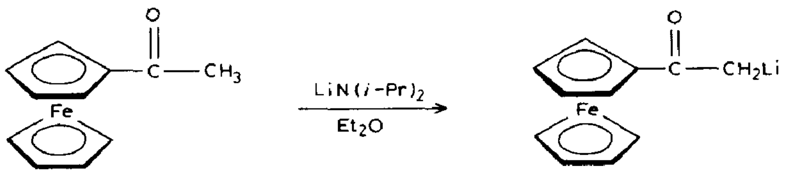


Results and discussion

Preparation of the ligands

The previously known [28, 29] 1,3-dioxobutylferrocene and benzoylcamphor derivatives used in the syntheses of **5** and **8** were prepared by an improved method described below. The ligands used in the syntheses of **6** and **7** are commercially available. All the derivatives **5–8** are well characterized by microanalysis, ^{1}H NMR spectra, and mass spectra.

The ferrocene compound was prepared by treating ethyl acetate with the lithio derivative of acetylferrocene. The lithio derivative, previously unreported, was prepared by the action of lithium diisopropylamide on acetylferrocene (eq. 2) and can be isolated in high yield (88%) by filtration. The yellow solid is readily soluble in THF and sparingly soluble in diethyl ether. Although satisfactory elemental analysis data were not obtained, its reactivity and the products obtained from its use are consistent with the expected formulation.



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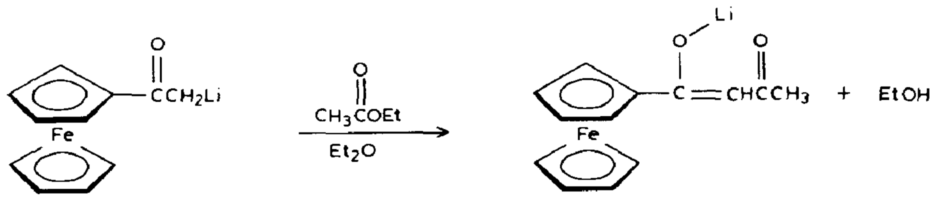

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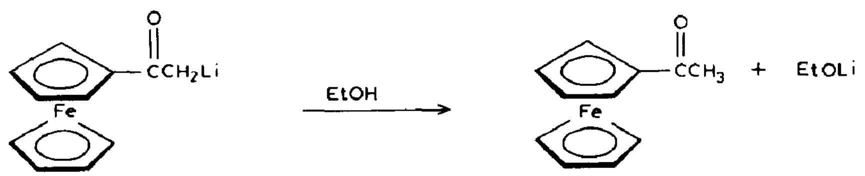

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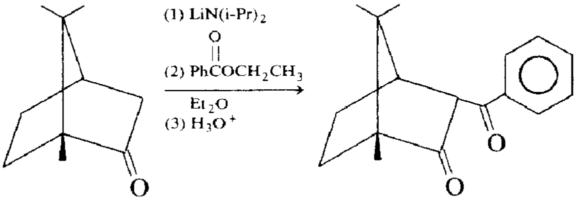
The reaction of lithioacetylferrocene with ethyl acetate affords the lithium salt of the diketone (eq. 3). This lithium salt is easily converted to the diketone by reaction with aqueous HCl, in up to 46.4% yield. The maximum yield expected from the proposed reaction sequence (eq. 2–4) is 50% because the product alcohol is a stronger acid than acetylferrocene and it reacts with the lithioacetylferrocene to afford the lithium salt of the alcohol and acetylferrocene (eq. 4). The acetylferrocene does not react further under these conditions. Thus for every molecule of β-diketonate produced, a molecule of lithioacetylferrocene is deactivated by protonation, resulting in a maximum yield of 50%. This proposed reaction sequence is supported by the yield, by the isolation of the β-diketone as its lithium salt, and by the presence of acetylferrocene in the reaction mixture prior to hydrolysis. A yield of 25% is reported from the same reaction sequence in liquid ammonia when potassium amide is used as the base [28].

The previously known benzoylcamphor ligand was prepared in a manner similar to that of 1,3-dioxobutylferrocene. Camphor was deprotonated by lithium diisopropylamide and then treated with ethyl benzoate (eq. 5). The reaction sequence is expected to be similar to that proposed for the preparation of 1,3-dioxobutylferrocene, and again the isolated yields do not exceed the predicted 50% maximum.



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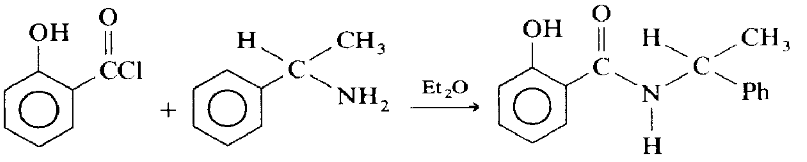
Three new chiral ligands were synthesized from the readily available (R)-α-methylbenzylamine: (R)-N-methylbenzylsalicoylamide (**9**); 1-(1-phenyl)(1-(R)-α-methylbenzylamino)butene-3-one (**10**); and (2′-hydroxy)(1-(R)-α-methylbenzylimine)ethylbenzene (**11**) (eq. 6–8). These were used in in situ catalytic systems.



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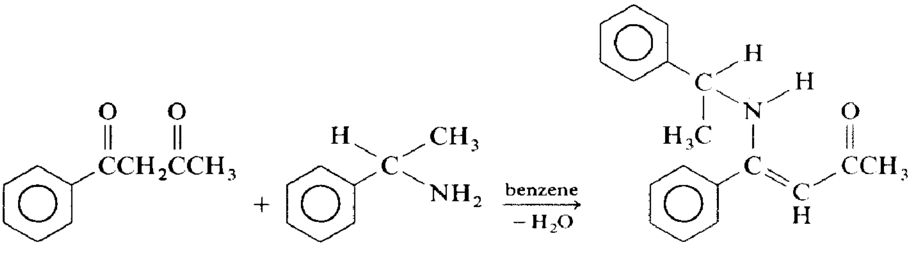
(**9**)



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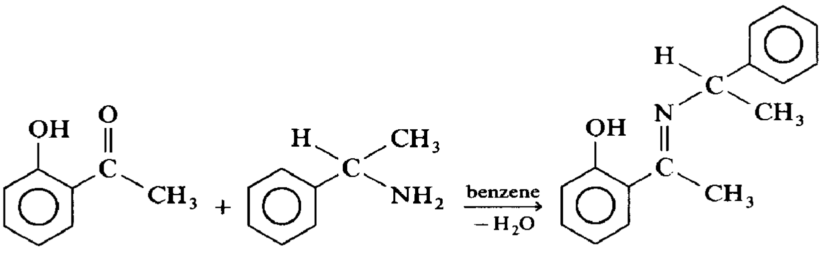

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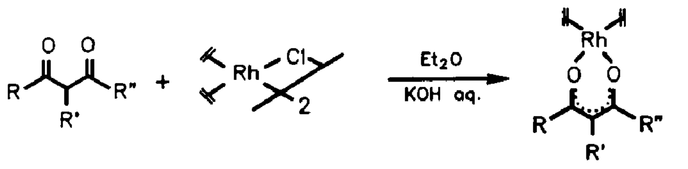
(11)

The addition of molecular sieves directly to the reaction mixture facilitates the production of **10** and **11**. The analytical and spectroscopic data recorded for **9**–**11** are consistent with the structures shown. The solid-state structure of **9** shows the presence of a hydrogen bond between the N*H* and OH groups, i.e., not between the O*H* and C=O groups [27].

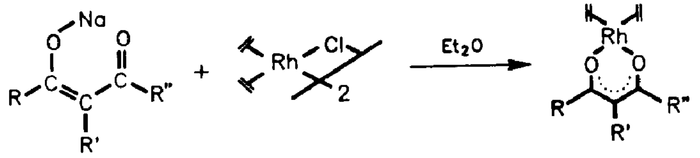
Preparation of complexes 5–8

The complexes can be prepared by using the procedure described by Cramer [32] for the synthesis of $Rh(acac)(C_2H_4)_2$ (eq. 9). However, the rhodium(I) complexes of



(9)

these β-diketonate ligands are best isolated in near quantitative yields ($\approx$ 97%), and in anhydrous conditions, by the addition of the sodium salt of the ligand to the bis(ethene)rhodium(I) choride dimer or the (1,5-cyclooctadiene)rhodium(I) chloride dimer (eq. 10).



(10)

This method of preparation is useful not only because of the high yields and exclusion of water, but also because it allows the possibility of preparing the complexes in situ in the reaction vessel. Further purification of the product complex is unnecessary, as filtration of the reaction mixture and removal of the solvent leaves the analytically pure complex.

The elemental analysis and spectroscopic data for complex **5** are consistent with its proposed structure. The broad resonance at 4.10 ppm has an integral indicative of eight protons and is assigned to the ethylene protons; this resonance broadens at low temperature and at $-43.5\,^\circ C$ it is split into two multiplets, each with an integral indicative of four protons. Using the rationale of Cramer [32], the multiplet at 3.38 ppm is assigned to the "outer" protons and the multiplet at 2.36 ppm is assigned to the "inner" protons. This topic will be treated in more detail elsewhere [27]. The data for **6–8** are equally supportive of the proposed structures. The ethylene resonance in **6** at 3.03 ppm resolves into two multiplets at $-43.5\,^{\circ}C$ (3.59 ppm outer; 2.54 ppm inner). The ethylene resonances in **7** are separate in the ambient-temperature spectrum, while those in **8** are not.

Hydrosilylation reactions

The bis(ethene)rhodium(I) complexes are catalysts for the hydrosilylation of acetophenone; Table 1 shows some results. The reaction rates are comparable to those reported by Brunner and coworkers for the same reaction when rhodium(I) complexes of the hard ligands **1–4** are used as the in situ catalysts. The only chiral catalyst listed in Table 1 is the camphor derivative **8**; unfortunately, the optical yield of the product alcohol is too low to be measured.

In order to explore this reaction further, the optically active ligands **9–11** were prepared, bearing in mind the desirability of placing the center of chirality close to the metal atom [7].

Two methods were devised for using these ligands. The first involved adding the bis(ethene)rhodium(I) chloride dimer to a solution of diphenylsilane, acetophenone, and the free ligand. The second was to add the bis(ethene)rhodium(I) chloride dimer to a solution of diphenylsilane acetophenone and the sodium salt of the ligand. The first method is similar to that used by Brunner for the asymmetric hydrosilylation of ketones by diphenylsilane using ligands **1–4** and the (cyclooctadiene)rhodium(I) chloride dimer as the rhodium source [23–25]. The second method was devised because of the success in preparing the rhodium(I) complexes described above by the sodium salts of the ligands.

The results obtained for the hydrosilylation of acetophenone using the first method are shown in Table 2. Although the use of these catalysts resulted in reasonable chemical yields, the optical yields are disappointing. It was hoped that the reaction employing the catalyst generated from ligand **11** and the rhodium dimer would give high optical yields because of its structural similarity to **1**. However, the differences must be crucial (probably a neutral chelate complex with a six-membered ring for **11**; a cationic chelate complex with a four-membered ring for **1** [26]). The catalyst from ligand **10** affords the highest optical yield, surpassing some of the yields described in the Introduction for complexes with hard donor atoms; however, the yield is low when compared with the results from phosphorus- or other nitrogen-based ligands. The reasons for these successes and failures are not obvious.

Table 1

Hydrosilylation of acetophenone catalyzed by bis(ethene)rhodium(I) compexes [a,b]

Complex	Time (h)	Chemical yield (%)
5	150	27.4
6	61	83.7
7	150	62.0
8	64	44.7

[a] Conversion was monitored by hydrolyzing the silyl ether to the corresponding alcohol, which was then analyzed by GLC. [b] All reactions were performed at room temperature with a silane-to-ketone ratio of 105/100, catalyst = 1.0 mol percent. Lower catalyst concentrations, down to 0.01 mol percent, afford similar results.

Table 2

Hydrosilylation of acetophenone catalyzed by rhodium(I) complexes of chiral oxygen/nitrogen donor ligands [a,b,c]

Ligand	Time (h)	Chemical yield (%)	Optical yield (%)
9	142	83.4	2.39
10	52	96.2	8.65
11	67	88.0	0.04

[a] Conversion was monitored by GLC. Conversions were calculated by the relative amounts of ketone and alcohol present after hydrolysis of the silyl ether. [b] Enantiomeric excess was calculated from optical rotation measurements. [c] All reactions were performed at room temperature with a silane-to-acetophenone ratio of 105/100, rhodium-to-ligand ratio of 1/5, rhodium 0.8 mol%. Lower catalyst concentrations, down to 0.08 mol percent, afford similar results.

As mentioned above, the second method that could be used for in situ catalyst preparation from **9**–**11** would involve the use of the performed salts of the ligands. When this method was attempted with **10**, the planned protocol had to be abandoned because a vigorous reaction was initiated by the addition of the sodium salt in the absence of any rhodium compound. Further investigation revealed that the product of the reaction was the silyl ether expected from the rhodium-catalyzed reaction. This novel and unexpected reaction was studied to determine its utility for a variety of ketones, and its selectivity was tested using 2-cyclohexene-1-one; some of the results from these studies are presented in Tables 3 and 4.

Bases such as sodium hydride, sodium methoxide, or lithium diisopropylamide catalyze the hydrosilylation of ketones by diphenylsilane. The ketone hydrosilylation reaction affords high yields of the corresponding silyl ether. The reaction also shows some selectivity in the hydrosilylation of 2-cyclohexen-1-one.

The hydrosilylation reaction is performed by adding the base to a mixture of diphenylsilane and ketone with or without solvent. The use of dilute conditions slows the rate, but does not affect the overall yield. The reaction does not seem to be affected by aromatic substituents, but is affected by steric hindrance in the substrate, Table 3.

The base-catalyzed hydrosilylation of 2-cyclohexen-1-one by diphenylsilane shows preference for either mode of reaction (1,2-addition or 1,4-addition), depending on the initial molar ratio of silane to enone, Table 4. High enone-to-silane ratios favor

Table 3

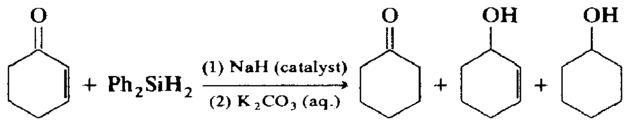
Base catalyzed hydrosilylation results

Ketone	Conditions [a]	Alcohol	Conversion (%) [b]
$C_6H_5C(=O)CH_3$	20 °C, 20 h	$C_6H_5C(OH)HCH_3$	99
$C_6H_5C(=O)CH_2CH_2CH_3$	20 °C, 24 h	$C_6H_5C(OH)CH_2CH_2CH_3$	95
$C_6H_5C(=O)CH(CH_3)_2$	20 °C, 24 h	$C_6H_5C(OH)CHCH(CH_3)_2$	79
$CH_3C(=O)CH_2CH(CH_3)_2$	20 °C, 24 h	$CH_3C(OH)CHCH_2CH(CH_3)_2$	97

[a] The reactions are carried out in the absence of solvent starting with a 1.0/1.1 ratio of ketone to silane, to which the base is added (1 mol percent). The base employed here is sodium hydride; the other bases afford comparable results. The reactions are highly exothermic. [b] Determined on the basis of gas chromatographic data.

Table 4

Base-catalyzed hydrosilylation of 2-cyclohexen-1-one



(A) (B) (C)

Enone/silane	Conversion (%) [a]	A	B	C	Conditions [b]
2/1	36.6	47.4	38.4	14.2	100 h, neat
1/1	81.6	11.4	52.5	36.1	72 h, neat
1/2	100	–	65.4	34.6	100 h, neat
2/3	90.0	9.4	74.6	16.0	75 h, THF
1/2	94.8	7.9	78.1	14.0	100 h, THF

[a] Determined on the basis of gas chromatographic data. [b] Reactions cooled to 0 °C during the addition of sodium hydride (base/ketone 1/100), all reactions are highly exothermic.

1,4-addition, to give product **A**, whereas low ratios favor 1,2-addition, to give product **B** after hydrolysis. Compound **C**, which is the product of the addition of diphenylsilane across the carbonyl group and "dihydrogen" across the C=C group, is present in greater amounts when high ratios of silane/enone are used, and is less abundant when dilute reaction conditions are employed.

Attempts were made to effect the asymmetric hydrosilylation of acetophenone by using chiral bases, but without success. For example, when (R)-(+)-α-methylbenzylamine was chosen as the source of chirality, lithium methylbenzylamide was prepared from it by treating the amine with butyllithium in THF. The catalytic reaction was carried out by adding a mixture of ketone and silane to a solution of the chiral amide. Use of the optically active base does give rise to asymmetry in the hydrosilylation product; however, optical yields are low. For a ratio of amide/ketone/silane of 1/100/105, a chemical yield of 91.3% and an optical yield of 0.1% e.e. resulted after 15 h. Doubling the amount of amide present gave a chemical yield of 96.4% and an optical yield of 0.50% e.e. after 40 h.

Alkali metal trialkylsilanes have been reported to add across carbon–oxygen double bonds to give the corresponding silyl ether [33]. The addition of lithium trimethylsilane to enones also has been reported to proceed selectively in a 1,4-mode of addition [34]. These stoichiometric addition reactions do not account for the present results; a possible explanation for the catalytic results may be as follows.

Organosilicon compounds are known to form anionic species with enhanced reactivity towards nucleophiles in the presence of a fluoride ion [35]. When the organosilicon compound is a silane, fluoride activation results in an activated hydrogen on the silicon atom; this effect is explained by a weakening of the silicon–hydrogen bond due to coordination of the fluoride ion to the silicon atom [36]. Thus a five-coordinate anionic silane species formed by the addition of cesium fluoride to diphenylsilane adds stoichiometrically across carbon–oxygen double bonds [37]. It is possible that a five-coordinate silane anion may be responsible for the catalytic reaction and that the base, a H^- ion, is activating the silicon species. A possible mechanism for this reaction is outlined in Fig. 1. The initial step of the mechanism involves the production of a five-coordinate silyl anion intermediate (**D**)

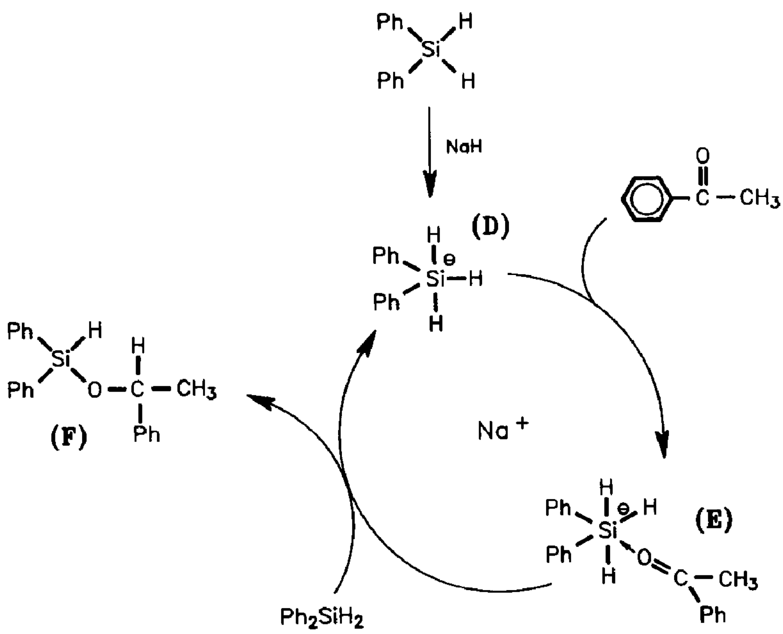


Fig. 1. Possible mechanism for base-catalyzed hydrosilylation.

by the reaction between sodium hydride and diphenylsilane. The reaction then proceeds by oxygen coordination to the silane (**E**). In order for the reaction to proceed, **E** must react to regenerate the catalyst. This may occur from **E** or from the silyl ether anion derivative of **E** formed by insertion of a hydride into the ketone bond. The most likely route for catalyst regeneration is the exchange of a hydride from **E**, or its silyl ether, with a molecule of diphenylsilane to give **D**, and the silyl ether product, **F**.

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