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Metal catalysed Brooke rearrangement of 3-Halo-1-(trimethylsilyl) propan-2-one (Halo = Cl or Br)

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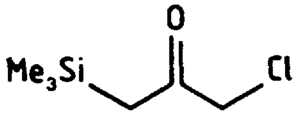
The complexes [IrH(CO)(PPh$_3$)$_3$], *trans*-[IrCl(CO)(PPh$_3$)$_2$], [RhH(PPh$_3$)$_4$], [Pd(PPh$_3$)$_4$], [Pt(*trans*-stilbene)(PPh$_3$)$_2$] and [Pt(η^3-CH$_2$-COCH$_2$)(PPh$_3$)$_2$] catalyse the rearrangement of Me$_3$SiCH$_2$C(O)CH$_2$Cl to CH$_2$=C(OSiMe$_3$)-CH$_2$Cl.

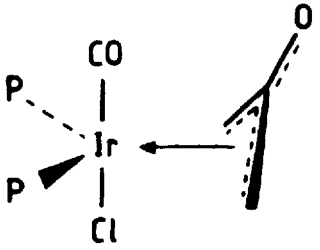
Keywords Catalysis, Brooke rearrangment, iridium, palladium, platinum, complexes

RESULTS AND DISCUSSION

During an investigation[1] of the reaction of 3-chloro-1-(trimethylsilyl)propan-2-one (1) with [IrH(CO)(PPh$_3$)$_3$] in refluxing toluene we observed that formation of the η^3-oxodimethylenemethane complex [Ir(η^3-CH$_2$COCH$_2$)(Cl)(CO)(PPh$_3$)$_2$] (2) was accompanied by complete 'Brooke rearrangement'[2] of the excess ketone (1) to 3-chloro-2-(trimethyl-siloxy)prop-1-ene (3). Further studies reveal that a number of low-valent metal complexes catalyse this rearrangement. Thus treatment of the ketone (1) with catalytic amounts of the complexes [IrH(CO)(PPh$_3$)$_3$], *trans*-[IrCl(CO)(PPh$_3$)$_2$], [RhH(PPh$_3$)$_4$], [Pd(PPh$_3$)$_4$] and [Pt(η^2-*trans*-stilbene)(PPh$_3$)$_2$] afforded the silylenol ether (3). The most effective catalysts for this 'Brooke rearrangement' were either [Pd(PPh$_3$)$_4$] or [Pt(η^2-*trans*-stilbene)(PPh$_3$)$_2$] which both caused an almost instantaneous isomerisation of the ketone (1) to the silylenol ether (3) at room temperature. Interestingly, the platinum complex (4),[1] which is formed in the reaction of the ketone (1) with [Pt(*trans*-stilbene)(PPh$_3$)$_2$], is also an effective catalyst for the isomerisation of the ketone (1) to the silylenol

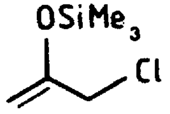


(1)

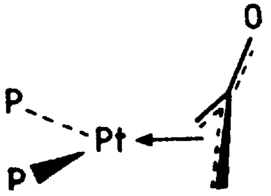


(2)

P=PPh$_3$



(3)



(4)

P=PPh$_3$

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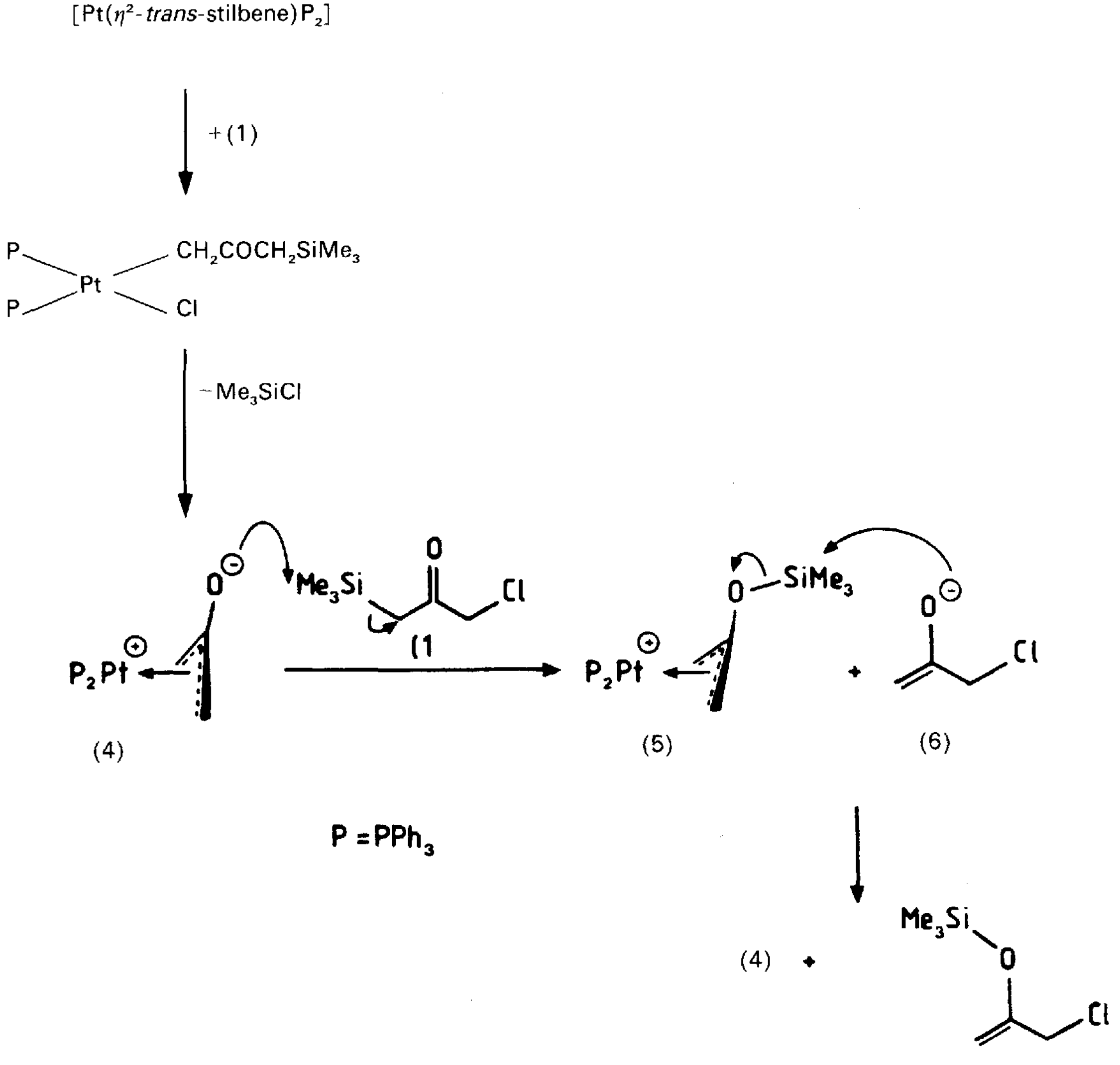
ether (3). Thus the mechanism of the platinum (O) catalysed 'Brooke rearrangement' may proceed via oxidative addition of the carbon-chlorine bond of the ketone (1) to the low valent metal centre followed by elimination of Me_3SiCl to afford the η^3-oxodimethylenemethane complex (4), Scheme 1. A consequence of viewing (4) as a dipolar η^3-oxodimethylenemethane complex, Scheme 1, rather than a metallacyclobutan-3-one[3-6] suggests that the carbonyl oxygen will be quite basic. It has previously been noted that the oxygen of the oxodimethylenemethane ligand does have co-ordinating properties.[7] Thus it is possible that the oxygen is sufficiently nucleophilic to attack the trimethylsilyl-group of excess ketone (1) generating a trimethylsiloxyallyl complex (5) and the enolate (6). Attack of the enolate (6) at the silicon group of the trimethlsiloxyallyl species (5) regenerates the oxodimethlenemethane catalyst and the silylenol ether (3), Scheme 1.

The use of zero-valent palladium or platinum catalysts in the generation of the silylenol ether (3) was used in preference to the published method for this conversion which employs mercury(II) iodide.[8,9] This latter route was unsuccessful and the ketone (1) was recovered unchanged. The most convenient method for generating the silylenol ether (3) involved treating the ketone (1) with approximately 5 mole % of $[Pd(PPh_3)_4]$ in dichloromethane or benzene at



Scheme 1

room temperature. A simple trap-to-trap distillation was the most effective way of removing the desired product from the metal catalyst and the silylenol ether (3) was isolated in almost quantitative yield. The fact that this is a metal-catalysed reaction was demonstrated by a control experiment using the ketone (1) and triphenylphosphine (10 mole%) in refluxing toluene. After 24 h only starting material was isolated.

EXPERIMENTAL

The complexes $[IrH(CO)(PPh_3)_3]$,[10] $[Pt(\textit{trans}\text{-stilbene})(PPh_3)_2]$,[11] $[Pd(PPh_3)_4]$,[12] $[RhH(PPh_3)_4]$,[13] *trans*-$[IrCl(CO)(PPh_3)_2]$,[14] $[RhH(CO)(PPh_3)_3]$[13] and *cis*-$[PtCl_2(PPh_3)_2]$,[15] trimethylsilylmethylmagnesium chloride[16] and 1-(trimethylsilyl)propan-2-one[9] were prepared by the literature procedures.

Preparation of 3-chloro-1-(trimethylsilyl)propan-2-one (1)

A solution of trimethylsilylmethylmagnesium chloride (6 mmol) in diethyl ether (10 cm^3) was added dropwise to a solution of chloroacetic anhydride (1.0 g, 6 mmol) in diethyl ether (10 cm^3) at −78°C. The solution was stirred at −78°C for 8 h and allowed to warm slowly to 0°C. The reaction mixture was recooled to −10°C and 10% aqueous ammonium chloride solution (20 cm^3) was added. The organic layer was separated, washed with aqueous sodium bicarbonate solution, and dried over anhydrous potassium carbonate. The solvent was removed in vacuo (15 mmHg) and the residue purified by vacuum distillation to give a colourless oil (0.69 g, 70%), b.p. 40°C (1 mmHg) which was identified as 3-chloro-1-(trimethylsilyl)propan-2-one (1).[8] I.r. (film) 2960 m, 2900 w, 1710 s, 1405 m, 1300 w, 1250 s, 1190 m, 1100 s, 1065 m, 1040 m, 910 w, 850 vs, 810 w, 760 w, 695 w, 670 w and 660 w cm^{-1}; n.m.r. ($CDCl_3$): ^1H (90 MHz), δ 0.1 (s, 9H, $SiMe_3$), 2.3 (s, 2H, $\underline{CH_2}$-$SiMe_3$), and 3.8 p.p.m. (s, 2H, $\underline{CH_2}$-Cl).

The same procedure as above was carried out for the preparation of 3-bromo-1-(trimethylsilyl)propan-2-one using trimethylsilylmethylmagnesium chloride and bromoacetic anhydride. The same work-up as above gave a colourless oil which was identified as 3-bromo-1-(trimethylsilyl)-propan-2-one (59%).[8] I.r. (film), 2960 m, 2900 w, 1695 s, 1415 m, 1305 w, 1260 s, 1180 w, 1095 m, 1040 m, 855 vs, 760 w, and 700 m cm^{-1}; n.m.r. ($CDCl_3$): ^1H (90 MHz), δ 0.2 (s, 9H, $SiMe_3$), 2.5 (s, 2H, $\underline{CH_2}$-$SiMe_3$), and 3.9 p.p.m. (s, 2H, $\underline{CH_2}$-Br).

Isomerisation reactions of 3-chloro-1-(trimethylsilyl)propan-2-one

(i) HgI_2

To 3-chloro-1-(trimethylsilyl)propan-2-one (1) (0.3 g, 1.8 mmol) was added mercury(II) iodide (0.05 g, 0.1 mmol) and the mixture was stirred for 1 h. The ^1H n.m.r. spectrum of a sample indicated that the starting compound was still present and no sign of any reaction was observed. The reaction was stirred for 12 h and the ^1H n.m.r. spectrum showed no evidence of any reaction. These conditions isomerise 1-(trimethylsilyl)propan-2-one to 2-(trimethylsiloxy)prop-1-ene.[9]

(ii) Thermal reaction

An n.m.r. sample of (1) in $[^2H_8]$-toluene was heated to 120°C for 2 h. The ^1H n.m.r. spectrum indicated that only starting material was present.

(iii) $[IrH(CO)(PPh_3)_3]$

To the n.m.r. sample in (ii) was added $[IrH(CO)(PPh_3)_3]$ (0.01 g, 1×10^{-5} mol). There was no initial change in the ^1H n.m.r. spectrum. The solution was heated to 115°C for 2 h. The ^1H n.m.r. spectrum showed complete isomerisation of (1) to 3-chloro-2-(trimethylsiloxy)prop-1-ene (3) which was identified by comparison of the ^1H n.m.r. spectrum with an authentic sample.[8]

(iv) $[Pt(\eta^2\text{-}\textit{trans}\text{-stilbene})(PPh_3)_2]$

To a solution of (1) (0.3 g, 1.8 mmol) in $[^2H_6]$-benzene (1 cm^3) was added $[Pt(\eta^2\text{-}\textit{trans}\text{-stilbene})(PPh_3)_2]$ (0.1 g, 0.1 mmol). The ^1H n.m.r. spectrum showed complete isomerisation of the ketone (1) to 3-chloro-2-(trimethylsiloxy)prop-1-ene (3) after five minutes at room temperature.

(v) $[Pd(PPh_3)_4]$

The reaction was repeated as in (iv) using (1) (0.1 g, 0.6 mmol) and $[Pd(PPh_3)_4]$ (0.05 g, 0.04 mmol). The ^1H n.m.r. spectrum showed complete isomerisation to 3-chloro-2-(trimethylsiloxy)prop-1-ene (3) by comparison of the ^1H n.m.r. spectrum with an authentic sample.[8] This reaction can be carried out in dichloromethane.

The pure silylenol ether (3) can be isolated by a simple trap-to-trap distillation. The required product is isolated in about 90% yield.

(vi) PPh_3

(1) (0.1 g, 0.6 mmol) and triphenylphosphine (0.016 g, 0.06 mmol) in $[^2H_8]$-toluene (1 cm^3) were heated to reflux for 24 h. The ^1H n.m.r. spectrum showed no sign of any rearranged product.

(vii) Other catalysts

The reaction (iii) was repeated with various other metal catalysts to assess their activity. $[RhH(PPh_3)_4]$ and *trans*-$[IrCl(CO)(PPh_3)_2]$ also catalyse the isomerisation reaction of 3-chloro-1-(trimethylsilyl)-propan-2-one (1) to 3-chloro-2-(trimethylsiloxy)prop-1-ene (3) on refluxing for 12 h in toluene. $[RhH(CO)(PPh_3)_3]$ and *cis*-$[PtCl_2(PPh_3)_2]$ do not catalyse the 'Brooke rearrangement' under analogous conditions.

The platinum complex (4) caused a rapid isomerisation of the ketone (1) to the silylenol ether (3) at room temperature.

Reaction of 1-trimethylsilyl)propan-2-one with [Pt(η^2-*trans*-stilbene)-$(PPh_3)_2$]

A solution of 1-(trimethylsilyl)propan-2-one (0.06 g, 0.46 mmol) and [Pt(η^2-*trans*-stilbene)$(PPh_3)_2$] (0.03 g, 3.3×10^{-5} mol) in $[^2H_2]$-dichloromethane (0.5 cm^3) was stirred for 3 h at room temperature. The ^1H n.m.r. spectrum showed no signs of any reaction. The starting compound remained unchanged.

Reactions of 3-bromo-1-(trimethylsilyl)-propan-2-one

(i) [Pt(η^2-*trans*-stilbene)$(PPh_3)_2$]

A solution of 3-bromo-1-(trimethylsilyl)propan-2-one (0.1 g, 0.5 mmol) and [Pt(η^2-*trans*-stilbene)$(PPh_3)_2$] (0.03 g, 3.3×10^{-5} mol) in $[^2H_8]$-toluene was stirred for 15 min at room temperature. The ^1H n.m.r. spectrum showed complete isomerisation of the starting compound to 3-bromo-2-(trimethylsiloxy)prop-1-ene by comparison of its ^1H n.m.r. spectrum with an authentic sample.[8]

(ii) HgI_2

To 3-bromo-1-(trimethylsilyl)propan-2-one (0.2 g, 0.9 mmol) was added mercury(II) iodide (0.1 g, 0.2 mmol). The mixture was stirred for 1 h. A ^1H n.m.r. spectrum of a sample showed complete isomerisation of the starting compound to 3-bromo-2-(trimethylsiloxy)prop-1-ene by comparison of its ^1H n.m.r. spectrum with an authentic sample. The product was contaminated with 1-bromopropan-2-one.

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