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SILYLMETHYL AND RELATED COMPLEXES

III* REACTION OF (TRIMETHYLSILYL)METHYL, (DIMETHYLSILYL)METHYL OR NEOPENTYL ALKYLATING REAGENTS WITH CHLOROTRIS(TRIPHENYLPHOSPHINE)RHODIUM(I): STERIC ACCELERATION TO DECOMPOSITION OF THE PRESUMED TRANSITION METAL ALKYL INTERMEDIATE

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SUMMARY

Reaction of $(Ph_3P)_3RhCl$ with Me_3CCH_2Li, Me_3SiCH_2MgCl, $(Me_3CCH_2)_4Zr$, $(Me_3SiCH_2)_4Ti$, or $(Me_3SiCH_2)_4Zr$ gives the appropriate alkane (Me_4C or Me_4Si) and $(Ph_3P)_2Rh(o\text{-}C_6H_4PPh_2)$ in equimolar amounts. The intermediate rhodium(I) alkyl $(Ph_3P)_3RhR$ ($R = Me_3SiCH_2$, Me_3CCH_2) was not isolated under conditions where the known methyl analogue ($R = Me$) is stable: it is inferred that the bulky alkyl groups containing no β-hydrogen atoms facilitate the internal metallation of the phenylphosphine ligands leading to the observed products. When $R = HMe_2SiCH_2$, decomposition is predominantly via β-elimination but $(Ph_3P)_4RhH$ is the isolated hydridic product.

INTRODUCTION

(Trimethylsilyl)methyl and neopentyl transition metal alkyls, LMR, are thermally more stable than analogous compounds containing methyl or ethyl ligands[1,2]. In some cases, the difference in stability is very marked [*e.g.*[3], $(Me_3SiCH_2)_4Ti \gg Me_4Ti$]. This is attributed[1-3] essentially to kinetic stabilisation due, *inter alia*, to (1) the absence of β-hydrogen atoms in R, precluding the olefin-elimination decomposition pathway; and (2) the large steric requirements of the bulky groups R hindering access to vacant coordination sites, making inter- or intra-molecular reactions high activation energy processes. It is not axiomatic, however, that such a stability pattern will invariably be followed. It is the purpose of this paper to draw attention to what we believe to be examples of the converse phenomenon, namely steric acceleration in transition metal alkyl decomposition. These conclusions serve to emphasise the significance of kinetic rather than thermodynamic factors in determining stability of transition metal alkyls.

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* Part II see ref. 2.

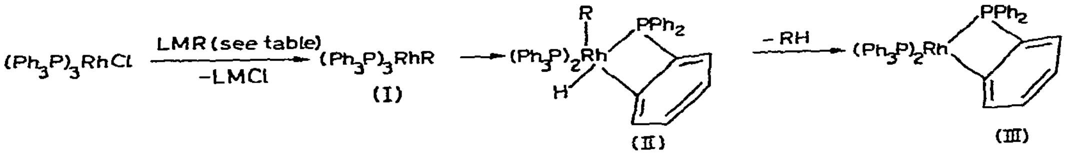
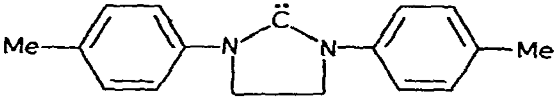


Fig. 1. Schematic representation of chlorotris(triphenylphosphine)rhodium(I) alkylation (R has no β-hydrogen atom).

Methyltris(triphenylphosphine)rhodium(I) [(I), R=Me] (Fig. 1) can be prepared by methylation of chlorotris(triphenylphosphine)rhodium(I) using methylmagnesium bromide in diethyl ether at 0–10°[4]. However, this compound decomposes, both in the solid state and in solution, by elimination of methane to give [*o*-(diphenylphosphido)phenyl]bis(triphenylphosphine)rhodium(I), (III) (Fig. 1). The reaction is thought[4,5] to proceed via internal metallation of a phosphorus-ligand phenyl substituent giving the intermediate (II) (R=Me), and subsequent reductive elimination of methane to yield (III) (see Fig. 1). We have attempted the preparation of the (trimethylsilyl)methyl and neopentyl analogues of (I) (R=Me_3SiCH_2, Me_3CCH_2) by a similar method at or below 0° but were unable to isolate such compounds under these conditions; only (III) and the corresponding alkane (tetramethylsilane or neopentane) were identified. Also presented are related results involving the (dimethylsilyl)methyl group. Alkyls of Ti or Zr[2,3] have not previously been employed as alkylating agents.

RESULTS AND DISCUSSION

Reactions between chlorotris(triphenylphosphine)rhodium(I) and the alkylating agents [(trimethylsilyl)methyl]magnesium chloride (or iodide), neopentyllithium, tetrakis[(trimethylsilyl)methyl]titanium or -zirconium, or tetraneopentylzirconium proceeded readily at or below 5°, but in each case (III) and the appropriate alkane (Me_4Si or Me_4C) were obtained instead of a rhodium(I) alkyl [(I), R=Me_3SiCH_2 or Me_3CCH_2]. Details are in the Table. The similarity in products and yields suggests that halogen/alkyl exchange does indeed take place but that the products are unstable under conditions of reaction, and decompose by a mechanism akin to that for the methyl complex. [(Trimethylsilyl)methyl]rhodium(I) complexes are not inherently unstable: a carbene complex (1,5-C_8H_{12})QRh(CH_2SiMe_3) where Q=



[yellow crystals, m.p. 132° (dec.), $J(^{103}Rh\text{–}C\text{–}^{1}H)$ 3 Hz] has been prepared from the corresponding chlororhodium(I) compound and Me_3SiCH_2Li in benzene/hexane at room temperature[6].

Only reactions involving ether solutions of (trimethylsilyl)methyl-Grignard reagent or of neopentyllithium are strictly comparable with those of their methyl analogues. Nevertheless, it is clear that for complex (I) stability decreases in the order

TABLE 1

ALKYLATION OF $(Ph_3P)_3RhCl$

Alkylating agent LMR[a]	*Yields (%)*[a]		*Conditions*
	(III)	*RH*[b]	
Me_3SiCH_2MgCl	93	105	$Et_2O/0°/24$ h
Me_3CCH_2Li	[c]	[d]	$Et_2O/-30°/20$ h
Me_3CCH_2Li	91	95	C_6H_6/ca. 5°/2 h
$(Me_3CCH_2)_4Zr$	82	87	C_6H_6/ca. 5°/2 h
$(Me_3SiCH_2)_4Ti$	71	115	C_6H_6/ca. 5°/2 h
$(Me_3SiCH_2)_4Zr$	85	104	C_6H_6/ca. 5°/2 h

[a] See Fig. 1. [b] Autocatalytic decomposition or adventitious hydrolysis may give high values. [c] Incomplete reaction [d] Not measured.

$Me > Me_3SiCH_2 \approx Me_3CCH_2$. The following factors will be considered: (*i*) the electronic properties of the alkyl ligands, (*ii*) the greater solubility conferred by the (trimethylsilyl)methyl or neopentyl groups, and (*iii*) the larger size of the (trimethylsilyl)methyl and neopentyl ligands.

The electron-releasing properties of the three groups R, as judged by their *trans*-influence in appropriate Pt^{II} complexes, are rather similar, $Me_3CCH_2 > Me \approx Me_3SiCH_2$[1,7]. Hence, the most obvious electronic argument, namely that high electron release from the alkyl ligand destabilises (I) with respect to (II) by increasing the tendency of (I) to undergo oxidative addition, may be discounted.

(Trimethylsilyl)methyl and neopentyl complexes are in general more soluble than their methyl counterparts[1-3]. It may be argued that the isolation of $(Ph_3P)_3RhMe$ is due in part to its low solubility in the reaction medium (ether at ca. 0°); *i.e.*, sparingly soluble $(Ph_3P)_3RhCl$ is converted into sparingly soluble $(Ph_3P)_3RhMe$ which is then to some extent protected from undergoing the methane elimination reaction in solution. However, it has recently been stated that a compound thought to be $(Ph_3P)_3IrMe$ is *stabilised* by ether (the effect being attributed to blocking of otherwise vacant coordination sites) and decomposes at 0° to the proposed iridium analogue of (III) in its absence[8]. Thus, solubility differences may not play a dominant role. It should be noted in this context that reports[4,5,9] on the thermal decomposition of (I) (R = Me) into (III) in solid- and liquid-phase reactions may lead to misleading conclusions[8]. Thus, while the experimental data for the conversion are not in question, it has not been stated that these are the *minimum* conditions necessary for complete reaction. Indeed, since the thermolyses were presumably carried out largely with the object of optimising the yield of methane, it is reasonable to assume that exhaustive conditions were chosen. We find that (I) decomposes rather rapidly in benzene (in which it is fairly soluble) even at, or just above, room temperature. By PMR study of the RhMe resonance (τ 9.46; C_6H_6, τ 2.73), (I) (12.7 mg) in benzene (0.50 ml; solution made up rapidly at ca. 6°) was found to have a half-life of about 15 min at 34° [10].

The most compelling explanation for the observed stability order of the rhodium alkyls (I) (R = Me, Me_3SiCH_2, or Me_3CCH_2) lies in the differing steric requirements of the ligands R. In the metallation step (Fig. 1), producing the postulated intermediate (II), increasing size of the alkyl group should lead to an increase in the rate of the *o*-metallation reaction; implicitly, this step is rate-determining for the conversion (I)→(III). Steric acceleration of *o*-metallation has recently been elegantly demonstrated for a series of tertiary phosphine/Pt^{II} or Pd^{II} halide complexes, in which the bulk of the organic substituents at phosphorus was varied[11].

Reaction of chlorotris(triphenylphosphine)rhodium(I) with the Grignard reagent prepared from (dimethylsilyl)methyl chloride and magnesium in ether took a different course, giving (−20°) hydridotetrakis(triphenylphosphine)rhodium(I) and rhodium metal; trimethylsilane and [(trimethylsilyl)methyl]dimethylsilane were also found in the reaction mixture. The hydride is thought to arise via β-elimination from the unstable alkylrhodium intermediate [(IV) = (I), R = HMe_2SiCH_2], but the apparent disproportionation (Fig. 2) to give $(Ph_3P)_4RhH$ is not understood. A small amount of (III), formed together with Me_3SiH in the alkane-elimination (Fig. 1), would have escaped detection. The fate of the presumed silaolefinic fragment (V) (Fig. 2), is not known with certainty; insertion into the Mg–C bond of the Grignard reagent (present in large excess) is most likely. The dimer, *i.e.*, $Me_2Si\diamond SiMe_2$, was not produced in the reaction. Pertinent to the mechanism of the reaction are observations on the reduction of Ph_3SiCl to Ph_3SiH by HMe_2SiCH_2MgCl[12]. Speculation on the origin of Me_3SiH and $Me_3SiCH_2SiMe_2H$ found in our system is not appropriate, since these products were found also to be present in the ethereal Grignard reagent itself. An account of these anomalies is in the experimental section.

It has previously been found that $CpFe(CO)(Ph_3P)SiMe_3$ is the product from the reaction: $[CpFe(CO)_2]^-/HMe_2SiCH_2Cl/Ph_3P$[13]. We were unable to isolate $(HMe_2SiCH_2)_4Ti$ from the reaction of $TiCl_4$ with the HMe_2SiCH_2Cl/Mg reagent, nor found evidence for the unknown $(Me_3Si)_4Ti$. Perhaps β-elimination occurs despite the anticipated high activation energy of formation of the unstable sila-olefin (V)[14].

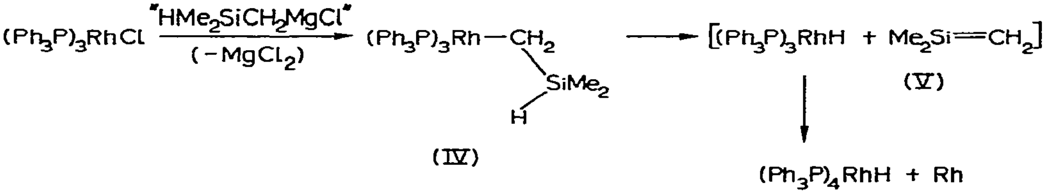


Fig. 2. Schematic representation of chlorotris(triphenylphosphine)rhodium(I) alkylation using "HMe_2SiCH_2MgCl".

EXPERIMENTAL

$(Ph_3P)_3RhCl$[15] and $(Ph_3P)_3RhMe$[4] were prepared by published procedures. The yields of Me_4Si and Me_4C were determined from PMR signal intensities using ether solvent or an added known quantity of toluene or anisole as integration standard (Varian Associates T60 spectrometer). IR spectra (4000–250 cm^{-1}) were run as nujol mulls in CsI discs on a Perkin–Elmer 457 spectrometer. All reactions were carried out under dry nitrogen or argon in dried solvents.

Reaction of $(Ph_3P)_3RhCl$ with:

(*a*). *Me_3SiCH_2MgCl*

A solution of [(trimethylsilyl)methyl]magnesium chloride (10.5 mmol) in ether

(10 ml) was added dropwise over 10 min to a stirred suspension of chlorotris(triphenylphosphine)rhodium(I) (985 mg, 1.065 mmol) in ether (20 ml) at 0° and the resulting mixture was stirred for 24 h (0°). Filtration gave a yellow-orange solid which was washed with ether, and hexane, and dried *in vacuo* (0°). The resulting air-sensitive powder (880 mg) showed no ν(Rh–Cl) or ν(Rh–H) in its IR spectrum and no Me_3Si-CH_2 signals in its PMR spectrum (C_6H_6) but corresponded to the complex $(Ph_3P)_2$-$Rh(o\text{-}C_6H_4PPh_2)$, (III), described by Keim[4], (yield 93%). Recrystallisation of a portion from toluene gave yellow-orange microcrystals, m.p. 105–120° (dec.), lit.[4] 110–130° (dec.), of identical IR spectrum (Found: C, 72.7; H, 5.4. $C_{54}H_{44}P_3Rh$ calcd.: C, 72.9; H, 5.1%.) The PMR spectrum of the ethereal filtrate (distilled *in vacuo*) showed the presence of tetramethylsilane (1.13 mmol).

A similar experiment using Me_3SiCH_2MgI also gave (III) (91%).

(*b*). Me_3CCH_2Li

(*i*). A solution of neopentyllithium (0.48 mmol) in ether (5 ml) was added over 2 min to a suspension of $(Ph_3P)_3RhCl$ (358 mg, 0.387 mmol) in ether (5 ml) at −30° and the resulting mixture was stirred at −30° for 20 h. Filtration (−30°) gave a light red-brown solid which was washed with ether (2 ml) and dried. The IR spectrum of this solid (319 mg) indicated that it was a mixture of $(Ph_3P)_3RhCl$ and (III). Extraction with benzene (3 ml) gave a deep red solution (showing no Me_3CCH_2 PMR signals) and a small quantity of a red-brown solid.

(*ii*). A solution of neopentyllithium (0.48 mmol) in n-hexane was added to $(Ph_3P)_3RhCl$ (358 mg, 0.387 mmol) and solvent removed. Benzene (7 ml) was condensed in and the mixture was stirred at ca. 5° for 2 h to give a homogeneous deep orange-red supernatant solution above a fine white deposit. Toluene (90 μl) was added and the yield of neopentane determined by PMR (0.368 mmol, 95%). Volatile material was removed and the residual solid washed with n-pentane and dried to give (III) as a yellow-brown powder (340 mg, 91%).

(*c*). $(Me_3CCH_2)_4Zr$

A mixture of tetraneopentylzirconium (82 mg, 0.218 mmol) and $(Ph_3P)_3RhCl$ (186 mg, 0.201 mmol) in benzene (3 ml) was stirred at ca. 5° for 2 h to give a homogeneous deep orange-red solution. Treatment as in (*b*), (*ii*) allowed estimation of Me_4C and isolation of (III) (see Table).

(*d*). $(Me_3SiCH_2)_4Ti$ *and* $(Me_3SiCH_2)_4Zr$

Method as (*c*); for yields see Table.

(*e*). "HMe_2SiCH_2MgCl"

(*i*). *Preparation of "Grignard Reagent"*. A solution of HMe_2SiCH_2Cl (572 mg, 5.25 mmol) in ether (5 ml) was added to Mg turnings (140 mg, 5.75 mmol). Reaction was started by vigorous stirring and allowed to proceed unchecked, after which the mixture was stirred at 20° for 1h and then filtered. The resulting clear, colourless solution slowly deposited a white solid.

(*ii*). *Reaction of the "Grignard Reagent" with* $(Ph_3P)_3RhCl$. The reagent from (*i*) was added dropwise over 10 min to $(Ph_3P)_3RhCl$ (493 mg, 0.533 mmol) in ether (10 ml) at −20°. After vigorous stirring (−20°) for 3 h, treatment (−20°) of the mixture as in (*a*) yielded a dull yellow powder and a vacuum-distilled ether filtrate. The powder showed no HMe_2SiCH_2 signals in its PMR spectrum (filtered C_6H_6 extract) but in its IR spectrum showed ν(Rh–H) at 2050 cm^{-1}. Washing with benzene (20°) caused 410 mg of the powder to dissolve, leaving a small black residue. Concentration of the filtered deep-orange benzene solution followed by addition of ether gave yellow microcrystals (269 mg) of identical IR spectrum to the dull yellow material and to an authentic sample of $(Ph_3P)_4RhH$[16]. (Found: C, 74.8; H, 5.5. $C_{72}H_{61}P_4Rh$ calcd.: C, 75.0; H, 5.35%.) GLC and GLC/mass-spectrometric analysis of the ether solution showed the presence of Me_3SiH (0.11 mmol) and $Me_3SiCH_2SiMe_2H$ (0.27 mmol). Since this corresponds to a total yield of 120% based on a $(Ph_3P)_3RhCH_2SiMe_2H$ intermediate, experiments (*iii*) (*A*)–(*iii*) (*E*) were carried out. [Yields of Me_3SiH are probably underestimated throughout, especially in (*E*), owing to the volatility of this material.]

(*iii*). *Other studies on the Grignard reagent.* (*A*), Preparation (*e*), (*i*) was repeated on a tripled scale; one-third portions of the product solution were used for (*B*)–(*D*); (*B*), Volatile material was removed from the "Grignard solution" and found to contain Me_3SiH (0.06 mmol) and $Me_3SiCH_2SiMe_2H$ (0.34 mmol); (*C*), Experiment (*B*) was repeated with "Grignard solution" which had been set aside at 20° for 24 h, to give Me_3SiH (0.09 mmol) and $Me_3SiCH_2SiMe_2H$ (0.35 mmol); (*D*), Experiment (*e*), (*ii*) was repeated using only 5 mg (0.005 mmol) $(Ph_3P)_3RhCl$, to give Me_3SiH (0.14 mmol) and $Me_3SiCH_2SiMe_2H$ (0.24 mmol); (*E*), The involatile residue from (*C*) was hydrolysed with aqueous ether at 0°. After work-up, the ether was found to contain Me_3SiH (1.19 mmol) and $Me_3SiCH_2SiMe_2H$ (0.14 mmol).

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