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Synthesis of manganese and ruthenium complexes of phenyltrimethylsilane, diphenyltetramethyldisilane and poly(methylphenylsilane)

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Abstract

The reaction of $[Mn(CO)_5]^+$ with phenyltrimethylsilane (L^1) or diphenyltetramethyldisilane (L^2) affords $[Mn(CO)_3L^1][BF_4]$ and $[Mn(CO)_3L^2][BF_4]$ in which the silane ligand is η^6-coordinated via an aromatic ring. A similar procedure using poly(methylphenylsilane) (PMPS) as the ligand resulted in very low incorporation of $Mn(CO)_3^+$ fragments into the polymer. A loading of 10% was achieved, however, by using $[(naphthalene)Mn(CO)_3][BF_4]$ as a $Mn(CO)_3^+$ transfer reagent to form the copolymer poly(methylphenylsilane-*stat*-methyl(η^6-phenyltricarbonylmanganesetetrafluoroborate)silane). Reaction of $[(p\text{-cymene})Ru(O_3SCF_3)_2]_x$ (*p*-cymene = 4-isopropyltoluene) with L^1 affords air sensitive $[Ru(p\text{-cymene})L^1][O_3SCF_3]_2$. Higher yields of the related complex $[Ru(p\text{-cymene})L^1][BF_4]_2$ were obtained by addition of L^1 to a mixture of $[(p\text{-cymene})RuCl_2]_2$ and $AgBF_4$. Only poorly characterised copolymers containing ruthenium were obtained by analogous reactions with PMPS. © 1997 Elsevier Science S.A.

Keywords: Manganese; Ruthenium; Silanes; Arenes; Polysilanes

1. Introduction

Our interest in transition metal complexes of arylsilanes stems from the potential applications of polysilanes which have interesting and unusual electronic properties arising from the delocalisation of σ-electrons within the catenated silicon backbone [1]. Most investigations have involved the tractable high molecular weight polymer, poly(methylphenylsilane) (PMPS), that can be prepared in good yield by a *Wurtz* type reductive–dechlorination reaction [1]. Attachment of metal ligand fragments to the arene rings in PMPS should result in a perturbation of the σ-delocalised electrons of the polymer backbone and modification of the electronic properties. We have previously demonstrated interplay between the backbone and π-coordinated tricarbonylmolybdenum fragments in the copolymer poly(methylphenylsilane-*stat*-methyl(η^6-phenyltricarbonylmolybdenum)silane) [1]. The full characterisation of the copolymer was supported by the synthesis and characterisation of the model compounds (η^6-phenyltricarbonylmolybdenum)trimethylsilane, 1-phenyl-2-(η^6-phenyltricarbonylmolybdenum)tetramethyldisilane and 1,2-di(η^6-phenyltricarbonylmolybdenum)tetramethyldisilane.

We have prepared model compounds of manganese and ruthenium to establish possible methodologies for copolymer synthesis incorporating other transition metal ligand fragments. The fragile nature of the polysilane backbone limits the use of harsh reaction conditions such as strong acids and high temperatures. A survey of the literature indicated that it might be possible to incorporate mono-cationic tricarbonylmanganese and dicationic *p*-cymeneruthenium fragments into PMPS under mild conditions.

The scope of $[(\eta^6\text{-arene})Mn(CO)_3]^+$ synthesis has recently been discussed [2]. Methods of preparation involve abstraction of bromide from $[Mn(CO)_5Br]$ by $AlCl_3$ or Ag(I) salts or, alternatively, by oxidation of $[Mn_2(CO)_{10}]$ with strong acid. It has been found that arenes bearing any of the following substituents can be coordinated: alkyl, aryl, alkoxy, chloro, hydroxy, fused heterocyclic aromatic rings and non-conjugated carbonyls. The principle factor in determining whether

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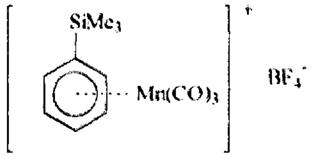
coordination will be successful is the degree of electron donation by the ring to the metal. Arenes bearing mild acceptor groups (e.g. chloro) can be metallated, but highly electron-deficient aromatics containing nitro, cyano or conjugated carbonyl substituents will not coordinate. More recently, it has been reported that tricarbonylmanganese fragments can be transferred from (polyarene)$Mn(CO)_3^+$ complexes [3]. The synthesis and reactivity of (phenylsilatrane)manganesetricarbonyl perchlorate has been reported [4].

A wide range of bis-η^6-arene-ruthenium(II) salts of the general formula $[Ru(arene^1)(arene^2)]X_2$ can be prepared by treatment of $[RuCl_2(\eta^6\text{-arene}^1)]_2$ with Ag(I) salts and arene^2 [5]. The compound $[(p\text{-cymene})Ru(OTf)_2]_x$ has been found to be a reactive precursor to $[Ru(p\text{-cymene})(arene)]^{2+}$ salts [6,7].

2. Results and discussion

Although in many cases the TFA anhydride method has been found to give the highest yields of $[(\eta^6\text{-arene})Mn(CO)_3]^+$ complexes, in view of the known instability of PMPS to harsh reaction conditions, it was decided to use the Ag(I) route as a more mild alternative. Generation of $[Mn(CO)_5]^+$ in situ by bromide abstraction from $[Mn(CO)_5Br]$ with $AgBF_4$ followed by treatment with phenyltrimethylsilane (L^1) or diphenyltetramethyldisilane (L^2) affords **1** and **2** in good yields (see Section 3). The compounds were characterised by elemental analysis, IR spectroscopy and FAB mass spectroscopy (Table 1) as well as ^1H and ^{13}C NMR spectroscopy (Table 2). Compound **1** has been reported previously but no details of its preparation or characterisation were mentioned [4]. The infrared spectrum of **1** recorded as an evaporated film on a KBr plate contains two strong carbonyl stretching absorptions at 2068 and 2004 cm^{-1}. When recorded in CH_2Cl_2 solution, for comparison with literature data of related compounds, the absorptions appear at 2080 and 2018 cm^{-1}. The positive inductive effect of the trimethylsilyl group results in lower energy carbonyl stretching absorptions compared with the analogous benzene derivative (2086 and 2026 cm^{-1}) [8,9]. The spectrum of **2** contains two carbonyl absorptions at 2074 and 2007 cm^{-1} indicating a decrease in electron donation by the aromatic ring in **2** compared with that in **1**. The ^1H and ^{13}C NMR spectra of **1** show an upfield shift for the aromatic resonances compared with the uncomplexed ligand. This is also observed in the spectra of **2** which contains both complexed and uncomplexed rings. No evidence was found for the formation of a complex in which L^2 is coordinated to two tricarbonylmanganese fragments.



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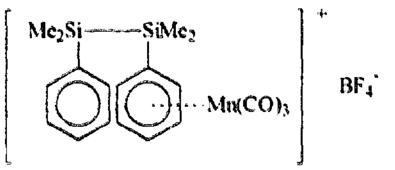

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Reaction of PMPS with $[Mn(CO)_5][BF_4]$ in the ratio of Mn:Si = 1:2 under similar conditions to those used in the synthesis of **1** and **2** resulted in a very low incorporation of $Mn(CO)_3^+$ fragments (ca. 4% as estimated by atomic absorption spectroscopy). This result is consistent with the observation that electron poor rings are coordinated poorly via this method [2]. However, using the labile complex $[(naphthalene)Mn(CO)_3][BF_4]$ as a $Mn(CO)_3^+$ transfer reagent a much higher incorporation of manganese was achieved. Refluxing PMPS with $[(naphthalene)Mn(CO)_3][BF_4]$ in the lower ratio of

Table 1
Analytical [a] and physical data

Compound	Appearance	Yield (%)	$\nu_{max}(CO)/cm^{-1}$ [b]	Analysis (%)		m/z [c]
				C	H	
1	Yellow/tan solid	56	2068s, 2004 br s	38.3 (38.3)	3.7 (3.8)	290 ($M + H-BF_4$)
2	Yellow solid	85	2074s, 2007 br s	45.7 (46.0)	4.3 (4.5)	409 ($M-BF_4$)
3	Pale yellow solid	22	–	37.1 (36.7)	3.7 (3.6)	386 (M + H-2OTf)
4	Yellow solid	68	–	40.7 (40.8)	4.9 (5.0)	473 ($M-BF_4$)

[a] Calculated values are given in parentheses.
[b] Recorded as film evaporated from dichloromethane on a KBr plate.
[c] Fast atom bombardment (FAB) mass spectroscopy.

Table 2
Hydrogen-1 and carbon-13 NMR data [a]

Complex	^{1}H(δ)	^{13}C(δ) [b]
1	6.83 (br s, 1 H, Ph), 6.60 (br s, 2 H, Ph), 6.51 (br s, 2 H, Ph), 0.46 (s, 9 H, Me)	214.6 (CO), 112.0, 107.1, 104.3, 99.2 (Ph), −1.7 (Me)
2	7.32 (br s, 5 H, Ph), 6.71 (br s, 1 H, Ph), 6.39 (br s, 2 H, Ph), 6.14 (br s, 2 H, Ph), 0.50 (s, 6 H, Me), 0.46 (s, 6 H, Me)	214.6 (CO), 136.0, 134.1, 129.9, 128.8 ($Ph_{uncoord}$), 114.0, 105.5, 102.9, 99.7 (Ph_{coord}), −4.6, −4.7 (Me)
3	[c]7.02–6.68 (m, 9 H, Ph and C_6H_4), 2.98–2.86 (m, 1 H, $CHMe_2$), 2.46 (s, 3 H, $C_6H_4CH_3$), 1.30 [d, 6 H, $CH(CH_3)_2$, J(HH) 7], 0.45 (s, 9 H, $SiMe_3$)	[c]123.6, 114.3, 110.4, 98.4, 95.5, 95.0, 94.7, 92.7 (Ph and C_6H_4) 33.0 ($CHMe_2$), 22.9 ($CHMe_2$), 20.3 (Me), −1.6 ($SiMe_3$)
4	[c]6.98–6.69 (m, 9 H, Ph and C_6H_4), 2.91 [spt, 1 H, $CHMe_2$, J(HH) 6.9], 2.45 (s, 3 H, $C_6H_4CH_3$), 1.28 [d, 6 H, $CH(CH_3)_2$, J(HH) 6.9], 0.44 (s, 9 H, $SiMe_3$)	[c]123.4, 114.3, 110.3, 98.3, 95.4, 94.9, 94.7, 92.6 (Ph and C_6H_4) 32.9 ($CHMe_2$), 22.8 ($CHMe_2$), 20.1 (Me), −1.6 ($SiMe_3$)

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. Measured in CD_2Cl_2 unless otherwise stated.
[b] ^{1}H decoupled.
[c] Recorded in CD_3CN.

Mn:Si = 3:17 in CH_2Cl_2 solution for 1 h resulted in 10% incorporation of $Mn(CO)_3^+$ fragments as determined by atomic absorption spectroscopy. The infrared spectrum of the polymer contains carbonyl absorption peaks at 2074 and 2013 cm^{-1}. This further increase in the carbonyl stretching frequencies compared with those of **1** and **2** is consistent with electron delocalisation in the polymer backbone and parallels the results obtained for $Mo(CO)_3$ fragments [1].

Reaction of [(p-cymene)$RuCl_2$]$_2$ and AgO_3SCF_3 affords [(p-cymene)$Ru(O_3SCF_3)_2$]$_x$ which when treated with phenyltrimethylsilane affords air sensitive [Ru(p-cymene)L^1][O_3SCF_3]$_2$ (**3**). Higher yields were obtained when $AgBF_4$ was used in place of AgO_3SCF_3 to obtain [Ru(p-cymene)L^1][BF_4]$_2$ (**4**). The new compounds were characterised by elemental analysis and FAB mass spectrometry as well as ^{1}H and ^{13}C NMR spectroscopy which shows upfield shifts for the aromatic resonances compared with the free ligand.

Treatment of [(p-cymene)$RuCl_2$]$_2$ and $AgBF_4$ followed by L^2 afforded a complicated product mixture containing [Ru(p-cymene)L^2][BF_4]$_2$ that could not be satisfactorily purified. Reaction of [(p-cymene)$Ru(O_3SCF_3)_2$]$_x$ with PMPS afforded a poorly characterised copolymer whose ^{1}H NMR spectrum contains upfield resonances indicative of incorporation of (p-cymene)Ru^{2+} fragments.

3. Experimental

All reactions were carried out under an atmosphere of either nitrogen (for manganese compounds) or argon (for ruthenium compounds) using standard Schlenk tube and vacuum line techniques, and all solvents were freshly distilled under a nitrogen atmosphere and over appropriate drying reagents. Acetonitrile and dichloromethane were distilled over calcium hydride and diethyl ether was distilled over a sodium/potassium alloy. $Mn(CO)_5Br$ [10], [(naphthalene)$Mn(CO)_3$]$^+$ [3] and [(p-cymene)$RuCl_2$]$_2$ [11] were prepared by literature methods. ^{1}H and ^{13}C NMR spectra were recorded with a JEOL GX270 instrument. Infrared spectra were obtained with a Mattson Instruments spectrophotometer. Elemental analyses were performed by Mr. A. Fassam at the University of Kent. Atomic absorption spectroscopy was conducted on a Perkin-Elmer 1100B instrument. Fast atom bombardment spectra were recorded by the EPSRC mass spectrometry service at the University of Swansea with a VG ZAB-E instrument from a NOBA matrix.

3.1. Synthesis of [$Mn(CO)_3L^1$][BF_4] (1)

A solution of [$Mn(CO)_5Br$] (0.50 g, 1.82 mmol) and $AgBF_4$ (0.39 g, 2.00 mmol) in CH_2Cl_2 (25 ml) was refluxed for 90 min in the dark to afford a yellow solution with a yellow/grey precipitate. A solution of phenyltrimethylsilane (0.94 ml, 5.46 mmol) in CH_2Cl_2 (15 ml) was added dropwise over 10 min and then, the mixture was refluxed for 19 h to give a darker yellow solution and a small quantity of dark precipitate The solution was filtered and the volume of solution reduced to ca. 10 ml in vacuo. Addition of diethyl ether (20 ml) precipitated the product which was collected by filtration, washed with diethylether (2 × 20 ml) and dried under vacuum to afford (**1**) (0.382 g, 56%).

3.2. Synthesis of [$Mn(CO)_3L^2$][BF_4] (2)

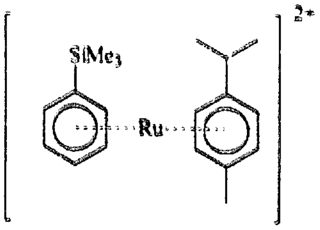
A solution of [$Mn(CO)_5Br$] (0.57 g, 2.07 mmol) and $AgBF_4$ (0.44 g, 2.26 mmol) in CH_2Cl_2 (35 ml) was refluxed for 90 min in the dark to afford a yellow solution with a yellow/grey precipitate. A solution of diphenyltetramethyldisilane (1.00 g, 3.70 mmol) in CH_2Cl_2 (20 ml) was added dropwise over 10 min and the mixture refluxed for 21 h to afford a straw yellow solution with a dark precipitate. The solution was filtered and the volume reduced to ca. 10 ml in vacuo, before it was added dropwise to stirred diethylether (100 ml) to produce a yellow precipitate. The solid was recrystallised (CH_2Cl_2/Et_2O) to afford **2** (0.88 g, 85%).

3.3. Synthesis of poly(methylphenylsilane-stat-methyl-(phenyltricarbonylmanganesetetrafluoroborate)silane)

PMPS (0.205 g, 1.7 mmol) and [(naphthalene)$Mn(CO)_3$][BF_4] (0.089 g, 0.3 mmol) were refluxed in CH_2Cl_2 (20 ml) for 1 h, after which time the solvent was reduced in volume to 5 ml and the product precipitated with diethyl ether (70 ml). The product was washed with diethyl ether (2 × 20 ml), dissolved in CH_2Cl_2 (2 ml) and reprecipitated with diethyl ether (100 ml) before being ground to powder and washed with acetone (50 ml) and dried under vacuum (0.08 g, 10% loading of Mn).

3.4. Synthesis of [Ru(p-cymene)L^1][O_3SCF_3]$_2$ (3)

A mixture of [(*p*-cymene)$RuCl_2$]$_2$ (0.70 g, 1.14 mmol) and AgO_3SCF_3 (1.20 g, 4.67 mmol) was stirred in Et_2O (50 ml) for 15 min. The red/orange solution was filtered and added to phenyltrimethylsilane (0.50 ml, 3.81 mmol). The mixture was stirred for 17 h after which time a pale yellow precipitate had formed which was isolated by filtration and washed with Et_2O (20 ml) before drying under vacuum to afford **3** (0.19 g, 22%).



3 $X = O_3SCF_3^-$
4 $X = BF_4^-$

3.5. Synthesis of [Ru(p-cymene)L^1][BF_4]$_2$ (4)

A mixture of [(*p*-cymene)$RuCl_2$]$_2$ (1.02 g, 1.66 mmol), $AgBF_4$ (1.33 g, 6.68 mmol) and CH_2Cl_2 (50 ml) was stirred for 3 h. The resultant red solution was filtered and added to phenyltrimethylsilane (0.58 ml, 4.42 mmol) to produce a yellow precipitate. The mixture was stirred for 30 min and then, the solid isolated by filtration, dissolved in CH_3CN (20 ml), filtered into Et_2O (80 ml) to reprecipitate and washed with Et_2O (4 × 10 ml) before drying under vacuum to afford **4** (1.30 g, 68%).

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