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PREPARATION OF SILOXYCARBENEMANGANESE COMPLEXES INCLUDING A CHELATED SILOXYCARBENE-ALKENE COMPLEX

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Summary

Reaction of Li{(η^5-C_5H_4Me)Mn$(CO)_2$[C(O)Ph]} with one equivalent of $RSiMe_2Cl$ yields (η^5-C_5H_4Me)Mn$(CO)_2$[C(Ph)($OSiMe_2R$)] for R = CH_3, CH=CH_2, and CH_2CH=CH_2 (**1a–c**, respectively). Low temperature photolysis of the vinyl derivative, **1b**, results in formation of a chelated manganese siloxycarbene-alkene complex, (η^5-C_5H_4Me)Mn(CO)[C(Ph)(η^2-$OSiMe_2CH$=CH_2)] (**2**). Photolysis of the allyl derivative, **1c**, under similar conditions leads to uncharacterized decomposition products. Infrared, ^1H, ^{13}C, and ^{29}Si NMR data are reported for these new siloxycarbenemanganese derivatives.

Introduction

Metal carbene-alkene complexes have been postulated as intermediates in both olefin metathesis [1] and in metal mediated cyclopropanation reactions [2]. The carbene-alkene species is postulated to collapse to a metallacyclobutane intermediate or pass through a metallacyclobutane-like transition state in each of these reactions. Casey has reported a series of [(π-alkenyl)oxy](aryl)carbene and [(π-alkenyl)amino](aryl)carbene complexes of tungsten [3], some of which decompose to cyclopropanes. Rudler and co-workers have also observed cyclopropane products from (π-alkenyl)(alkoxy)carbene complexes of tungsten [4]. These results illustrate stoichiometric conversion of carbene-alkene complexes to cyclopropane products and are compatible with metallacycle formation somewhere on the reaction coordinate.

Theoretical work by Eisenstein, Hoffmann, and Rossi [5] has suggested that first row transition metal carbene-alkene complexes may differ in geometry and reactivity from second and third row analogues. Few first row carbene-alkene complexes have been reported [6], and little is known about their synthesis, reactivity, and structural properties. The preparation and structure of a chelated allylaminocarbene derivative of manganese, (η^5-C_5H_4Me)Mn(CO)[C(Ph)(η^2-N(H)CH_2CH=CH_2)], was

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reported last year [6a]. We report here the synthesis of $(\eta^5\text{-}C_5H_4Me)Mn(CO)[C(Ph)(\eta^2\text{-}OSi(Me)_2CH{=}CH_2)]$ and related compounds.

Experimental

General

All manipulations were performed using standard Schlenk or dry box techniques. Solvents were dried over appropriate desiccants and distilled under nitrogen immediately prior to use. Infrared spectra were obtained on a Beckmann 4250 spectrophotometer and referenced to the 1601 cm^{-1} band of polystyrene. ^1H NMR spectra were obtained on a Varian XL 100, ^{13}C NMR spectra on a Bruker WM 250, and ^{29}Si NMR spectra on a Bruker AC 200. Mass spectrometry experiments were performed by Triangle Laboratories Inc. using direct ionization methods. Microanalysis was performed by Galbraith Laboratories Inc.

$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2[C(Ph)(OSi(Me)_3)]$ *(1a)*

$Li\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2[C(O)Ph]\}$ (3) (0.66 g, 2.2 mmol) was suspended in 20 ml of methylene chloride. The suspension was cooled to 0 ° C. Chlorotrimethylsilane (0.30 ml, 2.2 mmol) was added via syringe. Ater 10 min the reaction mixture was permitted to warm to room temperature. The reaction mixture gradually turned dark red. After about 1.5 h the solvent was evaporated to afford a red oil. The oil was extracted into hexane and filtered away from solid byproducts. The product was isolated by evaporation of the hexane solvent. Yield: 0.63 g (77%). IR (hexane): ν(CO) 1960s, 1880s cm^{-1}; ^1H NMR (C_6D_6): δ 0.17 (s, 9H, $Si(CH_3)_3$), 1.83 (s, 3H, Cp-CH_3), 4.55 (br s, 4H, C_5H_4-), 6.80–7.50 (br m, 5H, C_6H_5-); ^{13}C NMR (C_6D_6): δ 1.2 (q, *J* 119 Hz, $Si(CH_3)_3$), 13.7 (q, *J* 126 Hz, Cp-CH_3), 88.0 (d, *J* 176 Hz, C_5H_4-), 88.2 (d, *J* 176 Hz, C_5H_4-), 104.3 (s, C_5H_4-*ipso*), 123.1–128.4 (phenyl region, *o*, *m*, *p* carbons), 157.8 (s, *ipso* phenyl), 232.7 (s, CO), 337.2 (s, carbene); ^{29}Si (C_6D_6/hexane, (1/3) (v/v)) (external $SiMe_4$ reference): δ 16.2.

$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2[C(Ph)(OSi(Me)_2CH{=}CH_2)]$ *(1b)*

1b was prepared in the same way as **1a** using 0.66 g (0.22 mmol) $Li\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2[C(O)Ph]\}$ and 0.30 ml (2.2 mmol) chlorodimethylvinylsilane. **1b** was isolated as a red oil. Yield: 0.66 g (78%). IR (hexane): ν(CO) 1960s, 1890s cm^{-1}; ^1H NMR (C_6D_6): δ 0.20 (s, 6H, $Si(CH_3)_2$), 1.66 (s, 3H, Cp-CH_3), 4.54 (m, 2H, C_5H_4-), 4.58 (m, 2H, C_5H_4-), 5.6–6.4 (complex m, 3H, $CH{=}CH_2$), 7.16 (br s, 5H, C_6H_5); ^{13}C NMR (C_6D_6): δ 0.04 (q, *J* 119 Hz, $Si(CH_3)_2$), 14.2 (q, *J* 128 Hz, Cp-CH_3), 88.5 (d, *J* 176 Hz, C_5H_4-), 88.7 (d, *J* 176 Hz, C_5H_4-), 104.8 (s, C_5H_4-*ipso*), 123–130 (phenyl region, *o*, *m*, *p* carbons), 133.9 (t, *J* 160 Hz, Si-CH=*C*H_2), 137.1 (d, *J* 146 Hz, Si-*C*H=CH_2), 158.1 (s, *ipso* phenyl), 233.0 (s, CO), 336.9 (s, carbene); ^{29}Si NMR (C_6D_6/hexane (1/3)(v/v)) (external $SiMe_4$ reference): δ 3.2.

$(\eta^5\text{-}C_5H_4Me)Mn(CO)_2[C(Ph)(OSi(Me)_2CH_2CH{=}CH_2)]$ *(1c)*

1c was prepared in the same way as **1a** using 2.66 g (8.8 mmol) $Li\{(\eta^5\text{-}C_5H_4Me)Mn(CO)_2[C(O)Ph]\}$ and 1.30 ml (8.8 mmol) allylchlorodimethylsilane. **1c** was isolated as a viscous red oil. Yield: 3.20 g (92%). IR (hexane): ν(CO) 1960s, 1890s, ν(C=C) 1630w cm^{-1}; ^1H NMR (C_6D_6): δ 0.12 (s, 6H, $Si(CH_3)_2$), 1.68 (d, 2H, *J* 8.0 Hz, $SiCH_2$), 1.80 (s, 3H, Cp-CH_3), 4.46 (~ q, *J* 2 Hz, 2H, C_5H_4-), 4.52 (~ q, *J* 2 Hz, 2H, C_5H_4-) 5.02 (m, *J* 16 Hz, 1H, *trans*-HC=C*H*), 5.07 (m, *J* 11 Hz, 1H, *cis*-CH=C*H*), 5.7–6.2 (complex m, 1H, C*H*=CH_2), 7.1 (br s, 5H, C_6H_5-); ^{13}C NMR (C_6D_6): δ −0.8 ($Si(CH_3)_2$), 13.7 ($CpCH_3$), 25.5(($SiCH_2$), 88.1 (C_5H_4-), 88.3 (C_5H_4-), 104.3 (C_5H_4-*ipso*), 114.9 (C=CH_2), 123.0-128.7 (phenyl region, *o*, *m*, *p* carbons), 133.1 (*C*H=CH_2), 157.9 (C_6H_5-*ipso*), 232.6 (CO), 336.6 (carbene); ^{29}Si NMR (C_6D_6/hexanes, (1/3) (v/v) (external $SiMe_4$ reference)): δ 13.0.

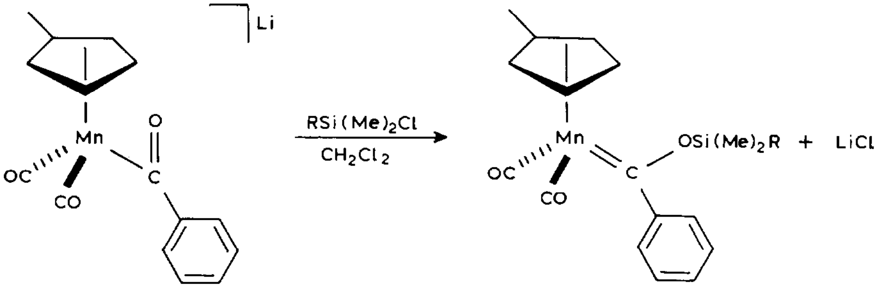
(η^5-C_5H_4Me)Mn(CO)[C(Ph)(η^2-OSi(Me)$_2$CH=CH_2) (2)

A red solution of **1b** (0.66 g, 1.7 mmol) in hexane (150 ml) was transferred to a photolysis chamber and cooled to 0 ° C. The solution was irradiated with a mercury vapor lamp (Hanovia, 679A36) through a pyrex filter for ca. 5 min. A color change from red to orange occurred. The progress of the reaction was monitored by IR. The reaction mixture was filtered and reduced to an oil. The oil was extracted into 100 ml of hexanes and filtered again. Evaporation of the solvent permitted isolation of **2** as an orange oil. Yield: 0.50 g (83%). IR (hexane): ν(CO) 1900s cm^{-1}; ^1H NMR (C_6D_6): δ −0.30 (s, 3H, $Si(CH_3)_2$), 0.14 (s, 3H, $Si(CH_3)_2$), 1.08 (s, 3H, Cp-CH_3), 1.28 (m, 1H, C*H*=CH_2), 1.82–2.20 (complex m, 2H, C=CH_2), 3.42, 3.54, 3.64, 3.90 (br s, 1H each, C_5H_4-), 6.74 (br s, 5H, C_6H_5-); ^{13}C NMR (C_6D_6): δ −3.7 (q, *J* 119 Hz, $Si(CH_3)_2$), 1.4 (q, *J* 119 Hz, $Si(CH_3)_2$), 12.7 (q, *J* 127 Hz, Cp-CH_3), 39.8 (d, *J* 140 Hz, *C*H=C), 45.3 (t, *J* 156 Hz, C=*C*H_2), 84.7, 86.6, 87.0, 88.5 (C_5H_4-), 101.4 (s, C_5H_4-*ipso*), 125.1–129.4 (phenyl region, *o*, *m*, and *p* carbons), 154.5 (s, C_6H_5-*ipso*), 237.8 (s, CO), 336.8 (s, carbene); ^{29}Si NMR (C_6D_6/hexanes, (1/3) (v/v) (external $SiMe_4$ reference)): δ 33.6.

Results and discussion

Synthesis of (η^5-C_5H_4Me)Mn(CO)$_2$[C(Ph)(OSiMe$_2$R)]

Siloxycarbene complexes in the methylcyclopentadienylmanganese system can be prepared as indicated in Scheme 1. The anionic acyl complex, **3**, was prepared according to the method of Fischer and co-workers [7]. Addition of one equivalent of chlorotrialkylsilane to a suspension of **3** in methylene chloride results in the



(**3**)

(**1a**, R = CH_3 ;
1b, R = vinyl ;
1c, R = allyl)

SCHEME 1

TABLE 1

^{29}Si CHEMICAL SHIFTS FOR **1a–c**, **2**, AND SOME SILANE AND SILOXANE MODELS

Compound	Chemical shift [a]	Reference
1a	16.2	this work
1b	3.2	this work
1c	13.0	this work
2	33.6	this work
$Et_3Si(OMe)$	18.8	8d
$Me_3Si(OPh)$	19.7	8d
$(EtO)(Me)Si(CH_2)_4$	29.9	8c
$CH_2{=}CHSi(Me)_2OEt$	4.1	8b
$(\eta^2\text{-}CH_2{=}CHSi(Me)_2OEt)_2Rh(acac)$	11.1	8b
$CH_2{=}CHCH_2SiMe_3$	0.39	8b
$(\eta^2\text{-}CH_2{=}CHCH_2SiMe_3)_2Rh(acac)$	−1.39	8b

[a] Chemical shifts are relative to $SiMe_4$.

gradual formation of a dark red solution of $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2[C(Ph)(OSiMe_2R)]$ as LiCl precipitates. Evaporation of the CH_2Cl_2 solvent followed by extraction into hexane, filtration, and evaporation yields **1** as an air sensitive, viscous red oil.

The infrared spectrum of **1** shows a typical dicarbonyl pattern with nearly equal intensity bands at 1960 and 1890 cm^{-1}. The dicarbonyl pattern observed for analogous alkoxycarbenes, e.g. $(\eta^5\text{-}C_5H_4Me)Mn(CO)_2[C(Ph)(OMe)]$, is about 20 cm^{-1} higher in energy than that of **1**, suggesting that the :C(R)(OSiMe$_2$R) ligand is a weaker π acid than :C(R)(OR). Furthermore, for alkoxycarbenes an additional pair of less intense bands at 1985 and 1925 cm^{-1} is observed. Fischer has suggested that alkoxycarbenes exhibit isomerism due to different orientations of the alkoxy alkyl group with respect to the metal [7]. No such additional IR absorptions have been observed for **1**.

In the ^{1}H NMR spectrum of **1a** the four cyclopentadienyl ring protons are so close in chemical shift that they appear as a broad singlet. For **1b–c** the cyclopentadienyl protons are more clearly differentiated and appear as two closely spaced pseudo-quartets. The ^{1}H NMR spectra of **1b–c** indicate that a plane of symmetry is maintained in each case since the methyl groups on silicon appear as a singlet near 0 ppm. In **1b–c** the olefinic protons resonate between 5 and 6 ppm. The ^{13}C NMR spectra of **1a–c** are as anticipated with the signals near 340 ppm confirming the carbene formulation. The ^{29}Si NMR chemical shifts observed for **1a–c** are compatible with expectations based on comparisons with silane and siloxane models (see Table 1).

The dicarbonyl siloxycarbene complexes were examined by low resolution mass spectrometry (Table 2). In each case a weak parent ion peak is observed while ions corresponding to loss of both carbon monoxide ligands constitute the principal ions in the high molecular weight region of the spectra. A silicon isotope envelope attends both the parent ion signals and the $(P^+ - 2(CO))$ signals. The $(P^+ - [2(CO) + \text{carbene}])$ ion is also observed for **1a–c**.

The dicarbonyl siloxycarbene complexes were sent for microanalysis, but the results reflect the poor storage properties of these compounds (see Table 2). Significant deterioration of **1a–c** can be detected by IR and ^{1}H NMR after storage for 48 h at ca. −10 °C.

TABLE 2

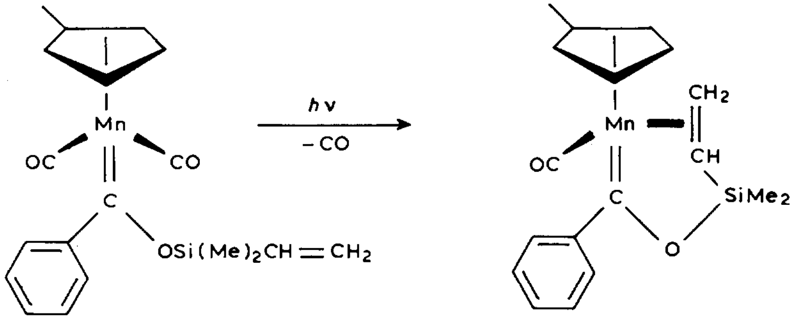
SELECTED MASS SPECTRAL AND ANALYSIS DATA FOR DICARBONYL SILOXYCARBENE COMPLEXES

Compound	m/z (peak assignments)	Relative intensity [a]	Analysis (Found (calc)(%))	
			C	H
1a	368 (P^+)	5.9	57.86	5.70
	312 ($P^+ - 2(CO)$)	90.9	(58.68)	(5.76)
	134 ($P^+ - \{2(CO)+\text{carbene}\}$)	34.3		
1b	380 (P^+)	3.0	59.14	6.15
	324 ($P^+ - 2(CO)$)	45.4	(59.98)	(5.57)
	134 ($P^+ - \{2(CO)+\text{carbene}\}$)	23.1		
1c	394 (P^+)	5.3	57.78	6.18
	338 ($P^+ - 2(CO)$)	48.1	(60.89)	(5.89)
	134 ($P^+ - \{2(CO)+\text{carbene}\}$)	31.8		

[a] Relative to the largest peak in the spectrum, which for **1a** is an ion with m/z equaling 144, while for **1b–c** is an ion with m/z equaling 208.

Photolysis of manganesesiloxycarbenes

Photolysis of a hexane solution of (η^5-C_5H_4Me)Mn(CO)$_2$[C(Ph)(OSi(Me)$_2$CH=CH$_2$)] using a mercury vapor lamp and a pyrex filter causes loss of carbon monoxide and formation of a chelated vinyl(dimethyl)siloxycarbene-alkene complex of manganese, **2** (eq. 1).



(1)

(1b) (2)

Filtration of the reaction solution followed by evaporation of the solvent yields **2** as a very air sensitive, viscous orange oil. Like the dicarbonyl siloxycarbene complexes, **2** exhibits poor storage properties, entirely decomposing in 48 h at ca. −10 °C.

The IR spectrum of **2** shows a single intense band at 1900 cm^{-1}. NMR spectra of **2** are similar to spectra obtained for (η^5-C_5H_4Me)Mn(CO)[C(Ph)(η^2-N(H)CH$_2$-CH=CH$_2$)] [6a]. Coordination of the alkene moiety shifts the ^1H resonances for the olefinic protons several ppm upfield; they appear between 1.2 and 2.2 ppm. Alkene coordination to the metal is also indicated in the ^{13}C NMR spectrum where the bound olefinic carbons resonate about 90 ppm upfield relative to those of dangling olefin in the dicarbonyl vinylsiloxycarbene complex, **1b**. Chelate formation generates a center of chirality at the manganese atom. The metal centered chirality is reflected by the observation of four separate cyclopentadienyl ring proton resonances (3.54, 3.66, 3.76, 4.02 ppm); likewise all five cyclopentadienyl carbons are differentiated in the ^{13}C NMR spectrum. Furthermore, in the carbene-alkene complex, **2**, the geminal methyl groups are diastereotopic, giving rise to two signals in both ^{1}H and ^{13}C NMR spectra. The ^{13}C NMR resonance for the carbene carbon of **2** occurs at 336.8 ppm. The difference in chemical shift between the carbene carbons of **1b** and **2** is less than one ppm which indicates a 16-electron metallacyclobutane resonance structure is unimportant in describing the ground state of **2**. The ^{29}Si resonance for **2** is observed at 33.6 ppm, a shift of 30 ppm downfield relative to its dicarbonyl precursor. Pannell et al. have established that a 6–11 ppm downfield shift in the ^{29}Si signal for vinylsilanes attends π-complexation to a single metal center [8a,b]. Moreover, ^{29}Si resonances for silacyclopentanes occur several ppm downfield from those of related acyclic siloxane models (see Table 1) [8c,d]. The combination of these two factors, i.e., π-complexation of the vinyl group and ring formation, suffices to rationalize the surprisingly low field ^{29}Si signal in **2**. Note that in $(\eta^5\text{-}C_5H_4Me)Mn(CO)[C(Ph)(\eta^2\text{-}N(H)CH_2CH{=}CH_2)]$ the ^{13}C resonance for the methylene carbon, β to the carbene carbon, is also shifted downfield relative to its dicarbonyl precursor, albeit by only 5 ppm.

Photolysis of a hexane solution of the dicarbonyl allyldimethylsiloxycarbene complex, **1c**, under conditions similar to those which produced **2** from **1b** did not lead to isolation of a chelated siloxycarbene-alkene complex. IR monitoring of the reaction solution indicated rapid decay of the starting material. Although a small amount of $(\eta^5\text{-}C_5H_4Me)Mn(CO)_3$ was observed in the IR spectrum of the reaction mixture, no other metal carbonyl species were detected. The decomposition of **1c** was accompanied by the precipitation of an intractable white solid. Examination of the reaction solution in search of cyclopropane products by thin layer chromatography (silica gel with hexane/ethyl acetate mixtures for the mobile phase) showed a farrago of spots upon development with UV light. Attempts to isolate and identify products by NMR after chromatography failed.

Conclusion

The methodology used to prepare chelating aminocarbene-alkene manganese complexes has been extended to one siloxycarbene-alkene complex, $(\eta^5\text{-}C_5H_4Me)Mn(CO)[C(Ph)(\eta^2\text{-}OSi(Me)_2CH{=}CH_2)$, isolated as an oil, but led to uncharacterized decomposition products when applied to **1c**. Metallacycle-derived chemistry anticipated from these manganese complexes has proven difficult to realize experimentally, and no further studies are planned.

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