ORGANOMETALLICS

Volume 9, Number 11, November 1990

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Communications

Preparation and Reactivity of (Phenylsilatrane)manganese Tricarbonyl **Perchlorate**

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Summary: The reaction of [Mn(CO)₅ClO₄] with N(CH₂C- $H_2O_3Si-C_6H_5$ produces $[N(CH_2CH_2O)_3Si-C_6H_5Mn(CO)_3]$ -CIO₄ (1). Compound 1 undergoes a highly regioselective reaction with RMgX to give $[\eta^5-1-(N(CH_2CH_2O)_3Si-6-(R) C_6H_5$]Mn(CO₃, (2a, R = Ph; 2b, R = Me) and with R⁻ to yield $[\eta^5-3-(N(CH_2CH_2O)_3Si)-6-(R)-C_6H_5]Mn(CO)_3$ (3c, R = H; 3d, R = CH₂CO₂CMe₃). However, 1 does not react regioselectively with the carbanion of acetone or sodium cyanide. The crystal structure of 3d (space group $P2_12_12_1$; unit cell parameters a = 6.5359 (8) Å, b =11.157 (1) Å, c = 33.298 (4) Å, and V = 2428.1 (5) Å³; R = 4.67%, $R_{w} = 5.01\%$) has been determined.

The particular structure and the chemical properties of silatranes (silatrane = 2,8,9-trioxa-5-aza-1-silabicyclo-[3.3.3]undecane) have been investigated by using various methods.1 However, the silatrane derivatives have not been used as π -coordinating ligands for transition metals. We have, therefore, attempted to establish the coordinating ability of phenylsilatrane.

Recently, we prepared the Cr(CO)₃ derivative of phenylsilatrane and determined its molecular structure.² The Cr(CO)₃ derivative of phenylsilatrane undergoes photochemical substitution reactions with PR₃, in analogy with

(arene)Cr(CO)₃ complexes. However, no reaction occurred between (phenylsilatrane)Cr(CO)3 and carbanions, although (arene)Cr(CO)₃ complexes readily reacted with carbanions. This was ascribed to the low electrophilicity of the phenylsilatrane attached to the neutral metal center. In order to gain insights into the relationship between the reactivity of the coordinated phenylsilatrane and its electrophilicity, we have investigated the reactivities of (arene)manganese tricarbonyl cations, which are more electrophilic than (arene)Cr(CO)₃.3 In this communication we report the reactions of compound 1 with PhMgBr, MeMgBr, NaBH₄, LiCH₂CO₃CMe₃, LiCH₂C(O)CH₂, and NaCN.

Phenylsilatrane (0.754 g, 3 mmol) was added to a solution of Mn(CO)₅OClO₃ (0.883 g, 3 mmol) in CH₂Cl₂ (50 mL).4 The reaction mixture was refluxed under nitrogen for 24 h. The product (1.32 g, 90%) was isolated by evaporation of the solvent, followed by precipitation with diethyl ether.⁵ Another compound containing the same cation as the compound 1 could be synthesized by reaction with Mn(CO)₅BF₄ and was obtained in low yield (35%). Compound 1 is stable in the solid state, is soluble in polar organic solvents such as acetone and CH₂Cl₂, and can be handled for several hours under air.

Treatment of compound 1 with PhMgBr in an ice bath led to the isolation of a dienyl-Mn(CO)₃ complex in 56% yield.6 The 200-MHz ¹H NMR spectrum of the dienyl

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Sil = Si (OCH2CH2)3N

complex indicated that the compound was formed by an ortho-addition reaction. This is rather surprising because steric hindrance to the ortho addition of the phenyl group is generally thought to be substantial. The X-ray crystallographic study of compound 2a is in progress.8 The reaction of compound 1 with MeMgBr gave a 73% yield of 2b for the ortho addition. Treatment of compound 1 with NaBH₄ in THF at -5 °C led to the isolation of a solid that was a mixture of para and meta adducts (76% yield).9

(6) A typical procedure is as follows. The compound 1 (245 mg, 0.50 mmol) was stirred in dry dichloromethane (50 mL) under N_2 at 0 °C while the Grignard reagent (2 equiv, commercially available solution) was added dropwise. After 40 min the excess Grignard reagent was quenched by dropwise addition of 0.1 N HCl solution, and the mixture was warmed to room temperature. The solution was dried (MgSO₄) and evaporated to dryness, yielding a brown residue. Extraction into diethyl ether (100 mL) and chromatography on a silica gel column with diethyl ether as eluent gave a yellow solution. Evaporation to dryness gave the product as a yellow crystalline solid (2a, R = Ph, 56.7% yield; 2b, R = Me, 72.5% yield). 2a: mp 178-179 °C; ¹H NMR (CDCl₃) δ 7.2-6.9 (m, 6 H, Ph), 5.72 (t, J = 5.0 Hz, 1 H, H³), 5.17 (d, J = 5.0 Hz, 1 H, H²), 4.84 (m, J = 5.0, 6.0 Hz, 1 H, H⁴), 4.03 (d, J = 6.0 Hz, 1 H, H⁶), 3.70 (t, J = 5.9 Hz, 6 H, 6.0 Hz, 1 H, H⁶), 2.24 (t, J = 5.0 Hz, 6 H, J = 5.0 Hz, 6 Hz, J = 5.0 Hz, J = 5.0 Hz, 6 Hz, J = 5.0 Hz, JOCH₂), 3.24 (t, J = 6.0 Hz, 1 H, H⁵), 2.76 (t, J = 5.9 Hz, 6 H, NCH₂) ppm; IR (CH₂Cl₂) ν (CO) 2009, 1930, 1908 cm⁻¹. MS m/z 467 (M⁺), 439 (M⁺ – CO), 383 (M⁺ – 3CO), 382 (M⁺ – 3CO – H), 327 (M⁺ – Mn(CO)₃ – H), 74 (Si(OCH₂CH₂)₃N). Anal. Calcd for $C_{21}H_{22}MnNO_6Si$: C, 53.97; H, 4.74; N, 3.00. Found: C, 53.97; H, 5.00; N, 3.09. 2b: mp 160 °C; IR (CH₂Cl₂) ν (CO) 2000, 1920 cm⁻¹; ¹H NMR (CDCl₃) δ 5.74 (t, J = 5.6 Hz, 1 H, H³), 4.95 (d, J = 5.3 Hz, 1 H, H²), 4.69 (t, 1 H, H⁴), 3.78 (t, J = 5.6 Hz, 6 H, OCH₂), 3.05 (t, 1 H, H⁴), 2.80 (t, J = 5.6, 6 H, NCH₂), 2.59 (m, riz, o ri, UCh₂), 3.05 (t, 1 H, H°), 2.80 (t, J = 5.6, 6 H, NCH₂), 2.59 (m, 1 H, H°), 0.43 (d, J = 6.4 Hz, 3H, Me) ppm (the signals of H⁴ and H⁵ were observed as broad triplets, but accurate coupling constants were not accessible); MS m/z 467 (M*), 439 (M* – CO), 383 (M* – 3CO), 382 (M* – 3CO – H), 327 (M* – Mn(CO)₃ – H), 174 (Si(OCH₂CH₂)₃N). Anal. Calcd for C₂₁H₂₂MnNO₆Si: C, 53.97; H, 4.74; N, 3.00. Found: C, 53.97; H, 5.00; N, 3.09.

H, 5.00; N, 3.09.

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(9) To a stirred suspension of 1 (245 mg, 0.50 mmol) in 30 mL of THF at -5 °C was added a slight excess of NaBH4. After it was stirred for 1 h, the solution was evaporated to dryness and extracted with diethyl ether (100 mL). Evaporation of the ether gave a yellow crystalline solid of a mixture of the para and meta adducts (76% yield). The ratio of para and meta adducts was determined to be 16:1 by comparing the integration of H² and H⁴ of the para adduct with that of H³ of the meta adduct of ¹H NMR spectrum. The mixture has the following properties: mp 184–186 dec; IR (CH₂Cl₂) ν (CO) 2000, 1912 cm⁻¹; MS m/z 391 (M⁺), 335 (M⁺ – 2CO), 307 (M⁺ – 3CO), 251 (M⁺ – Mn(CO)₃ – H), 174 (Si(OCH₂-CH₂)₃N). Anal. Calcd for Cl₃H₁₃MnN0₂Si: C, 46.04; H, 4.64; N, 3.58. Found: C, 46.67; H, 4.59; N, 3.63. 3e: ¹H NMR (CDCl₃) δ 5.03 (d, 5.03 (d, 5.03 (d, 14.74), 3.91 (t, J = 5.8 Hz, 6 H, OCH₂), 2.96 (t, J = 5.8 Hz, 8 H, NCH₂ and H¹.5), 2.56 (m, 1 H, H³-ando), 2.09 (d, J = 12.7, 1 H, H³-ando) ppm. Meta adduct: ¹H NMR (CDCl₃) δ 6.0 (d, 1 H, H³), 4.8 (m, 1 H, H⁴), 3.82 (t, 6 H, OCH₂), 3.2 (d, 1 H, H¹), 2.86 (t, 6 H, NCH₂) ppm. The signals of H⁵, H³-ando, and H³-ando were overlapped with other signals and obscured. meta adducts was determined to be 16:1 by comparing the integration

The ¹H NMR pattern showed that the para- and metaaddition adducts were formed in a ratio of 16:1. Treatment of compound 1 with lithium tert-butylacetate in THF at -78 °C led to the isolation of a dienyl complex in 62% vield.10 The structure (Figure 1) obtained by the spectroscopic and X-ray crystallographic studies indicates that the carbanion tert-butylacetate added to the phenyl ring at the position para to the silatrane moiety. To the best of our knowledge, this is the first example of the exclusive para addition of the carbanion to the (arene) manganese cation (Scheme I). The cyclohexadienyl ring is symmetrical across a mirror plane, which coincides with a pseudo mirror plane of the entire molecule. The dienyl carbon atoms C11, C12, C13, C14, and C15 define a nearly perfect plane with a deviation of 0.013 (7) Å. The cyclohexadienyl ring is folded about C11-C15 with an angle of 39.2 (7)°. The introduction of Mn(CO)₃⁺ and the addition of the carbanion tert-butylacetate to phenylsilatrane do not affect the silatrane ring geometry appreciably. The bond length of N-Si (2.127 (6) Å) and the bond length of Si-C13 (1.898 (6) A) in compound 3d are similar to those (2.108 (5) and 1.907 (6) Å, respectively) in (phenysilatrane)Cr(CO)₃. However, the bond length N-Si in compound 3d is shorter than that (2.193 (5) Å) in phenylsilatrane and the bond length Si-C13 in compound 3d is similar to that (1.882 (6) Å) in phenylsilatrane.11

Treatment of compound 1 with the carbanion of acetone led to the isolation of the corresponding adducts in 57%

⁽¹⁰⁾ The preparation of 3d is as follows. To a dry ice/acetone cooled solution of diisopropylamine (0.40 mL, 3.0 mmol) in 15 mL of dry THF was added 1.2 mL of n-butyllithium (3.0 mmol, 2.5 M in hexane) dropwise over 30 min. To the LDA solution was added dropwise 0.41 mL of tert-butyl acetate (3.0 mmol). The alkyllithium reagent was added dropwise to compound 1 (245 mg, 0.50 mmol) in dry THF (30 mL) under N_2 at -78 °C. The reaction mixture was stirred for 1 h at -78 °C. Then the reaction mixture was poured into water and extracted three times the reaction mixture was poured into water and extracted three times with diethyl ether. The ether extracts were dried (MgSO₄) and evaporated to dryness, yielding the product (62%): mp 189–190 °C dec; ¹H NMR (CDCl₃) δ 5.02 (dd, J = 7.0, 2.0 Hz, 2 H, H^{2.4}), 3.89 (t, J = 5.8 Hz, 6 H, OCH₂), 3.25 (t, J = 7.0, 2 H, H^{1.5}), 2.93 (t, J = 5.8, 6 H, NCH₂), 2.86 (m, 1 H, H^{6-sido}), 1.63 (d, J = 6.8 Hz, 2 H, H₂), 1.38 (s, 99 H, MMe) ppm; IR (CH₂Cl₂) ν (CO) 2007, 1920, 1716 cm⁻¹; MS m/z 505 (M⁺), 449 (M⁺ = 3CO), 421 (M⁺ = 3CO) = 20 H, 3.83 (M⁺ = 3CO) = CM. 2CO), 421 (M⁺ – 3CO), 391 (M⁺ – 3CO – 2CH₃), 383 (M⁺ – 3CO – CMe₃ – H), 319 (M⁺ – 3CO – CO₂CMe₃ – H). Anal. Calcd for $C_{21}H_{28}MnNO_{8}Si$: C, 49.90; H, 5.58; N, 2.77. Found: C, 49.67; H, 5.65; N, 2.65. Crystal structure of 3d: Crystals grown by evaporation of the methylene chloride solution at room temperature; orthorhombic; a=6.5359 (8) Å, b=11.157 (1) Å, c=33,298 (4) Å; V=2428.1 (5) Å³; space group $P2_12_12_1$ (No. 19); Z=4; $D_{calcd}=1.38$ g/cm³; 2514 independent reflections (3° $\leq 2J \leq 54^\circ$, Mo K α radiation, Enraf-Nonius CAD4 diffractometer); solution of the structure by the conventional heavy-atom method (SHELX-76); hydrogen positions calculated according to ideal geometry with a C-H bond lengths of 1.08 Å. Refinement by use of SHELX-76 with anisotropic temperature factors for all non-hydrogen atoms gave R=0.0467 and $R_w=0.0501$ ($w=0.3135/(\sigma^2(F)+0.001600F^2)$ for 1720 unique reflections with $I\geq 3\sigma(I)$. (11) Turley, J. W.; Boer, F. B. J. Am. Chem. Soc. 1968, 90, 4026.

Figure 1. ORTEP drawing of $[\eta^5-3-(N(CH_2CH_2O)_3Si)-6-(Me_3CCO_2CH_2)-C_6H_5]Mn(CO)_3$ with thermal ellipsoids shown at the 50% probability level. Selected bond distainces (Å): C1-Mn, 1.810 (9); C2-Mn, 1.788 (8); C3-Mn, 1.811 (8); C11-Mn, 2.211 (7); C12-Mn, 2.132 (7); C13-Mn, 2.152 (7); C14-Mn, 2.132 (7); C15-Mn, 2.221 (7); N-Si, 2.127 (6); C13-Si, 1.898 (6); C15-C16, 1.498 (12); C11-C16, 1.513 (10). Selected bond angles (deg): C2-Mn-C1, 94.4 (4); C3-Mn-C1, 87.5 (3); C3-Mn-C2, 94.9 (3); C13-Si-N, 176.9 (3).

yield.¹² However, the products were obtained as a mixture of 2e and 3e in the ratio 1:1.5. When compound 1 was treated with NaCN in wet THF, the mixture of 2f and 3f was obtained in the ratio 1:1.7 (combined yield 56%).¹⁴

(12) The product was prepared in a manner identical with that used for 3d. Reaction of 245 mg (0.50 mmol) of 1 in 30 mL of dry THF with 3.0 mmol of acetone enolate gave a yellow solid (57%), as a 1:1.5 mixture of 2e and 3e. Purification by chromatography on a silica gel column (8:1 THF/diethyl ether) afforded 2e (R_f) 0.72) and 3e $(R_f$ 0.46). 3e was contaminated by a small amount of meta-addition product. However, we failed to separate a meta-addition product from 3e. 3e: mp 153 °C; 'H NMR (CDCl₃) δ 5.00 (d, J = 6.9 Hz, 2 H, H^{2.4}), 3.89 (t, J = 5.8 Hz, 6 H, OCH₂), 3.23 (t, J = 6.9 Hz, 2 H, H^{1.5}), 3.13 (m, 1 H, H⁶), 2.93 (t, t, J = 5.8 Hz, 6 H, NCH₂), 1.95 (s, 3 H, Me), 1.89 (d, J = 6.4 Hz, 2 H, CH₂) ppm; IR (CH₂Cl₂) ν (CO) 2000, 1914, 1705 cm⁻¹; MS m/z 390 (M⁺ – 2CO – H), 363 (M⁺ – 3CO), 319 (M⁺ – 3CO – CH₃C(O) – H), 307 (M⁺ – Mn(CO)₃ – Ch₂C(O)-CH₃). Anal. Calcd for C₁₈H₂₂MnNO₇Si: C, 48.32; H, 4.96; N, 3.13. Found: C, 48.20; H, 5.24; N, 2.93.

(13) To a stirred suspension of 1 (245 mg, 0.50 mmol) and a slight excess of NaCN in 30 mL of THF at room temperature was added 2 mL of water. After it was stirred for 30 min, the solution was concentrated and extracted with diethyl ether (100 mL). The ether extracts were dried (MgSO₄) and evaporated to give a yellow solid (56%), as a 1:1.7 mixture of 2f and 3f. The mixture has the following properties: IR (CH₂Cl₂) ν (CO) 2018, 1929 cm⁻¹, ν (CN) 2220 cm⁻¹; mp 156 °C dec. Anal. Calcd for C₁₆H₁₇MnN₂O₆Si: C, 46.16; H, 4.12; N, 6.73. Found: C, 46.04; H, 3.71, N, 6.21. 2f: ¹H NMR (CDCl₃) δ 5.89 (t, J = 5.3 Hz, 1 H, H³), 5.16 (d, J = 5.3, 1 H, H²), 4.97 (t, J = 5.3 Hz, 1 H, H⁴), 3.78 (t, J = 5.8 Hz, 6 H, OCH₂), 2.83 (t, J = 5.8 Hz, 6 H, NCH₂) ppm. The signals of H⁵ and H⁶ were overlapped with other signals and obscured. 3f: ¹H NMR (CDCl₃) δ 5.25 (d, J = 6.8 Hz, 2 H, H^{2.4}), 3.88 (t, J = 5.8 Hz, 6 H, OCH₂), 3.56 (t, J = 5.8 Hz, 1 H, H⁶), 3.00 (m, J = 5.8, 6.8 Hz, 2 H, H^{1.5}), 2.89 (t, J = 5.8 Hz, 6 H, NCH₂) ppm.

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When compound 1 was treated with the sodium salt of dimethyl malonate, the corresponding cyclohexadienyl compound was formed. However, the yield was poor. There might be an equilibrium between product and reactants in polar solvent. While the ¹H NMR spectrum was taken in CDCl₃, the cyclohexadienyl compound decomposed readily. We failed to characterize the cyclohexadienyl compound in detail.

The cyclohexadienylmanganese compounds obtained in the present study can be subjected to column chromatography.

It is known that methoxy substituents on (arene)Mn-(CO)₃+ complexes deactivate the ortho and para positions, leading to nucleophilic attack predominantly at the meta position.¹² At first we expected that the inductive effect of the silatrane moiety would be similar to that of the methoxy group and the nucleophilic attack would occur at the meta position. However, the nucleophiles attack at the para or ortho position. The directing effect of the silatrane moiety did not follow that of the methoxy group. The attacking sites of the nucleophile in compound 1 showed some special trends. For the addition of PhMgBr and MeMgBr, ortho adducts were obtained. For the addition of NaBH₄ or LiCH₂CO₂CMe₃, para adducts were obtained predominantly. These results indicated that the regioselectivity of nucleophile addition to compound 1 is dependent upon the nature of the nucleophile. We expect that the electronic effect of the silatrane moiety on the cation plays an important role in the addition of nucleophiles and the oxygen atoms in the silatrane moiety seem to affect the Grignard reagent addition. It is difficult at this stage to completely rationalize the observations, but it would seem that further information is desirable. Further studies of nucleophilic addition to 1 are in prog-

In conclusion, with the appropriate nucleophile, either type of adducts 2 and 3 can be obtained in a reasonable yield. It has also been demonstrated that nucleophilic addition to an activated phenylsilatrane is a synthetically useful procedure.

Acknowledgment. Financial support from the Korea Science and Engineering Foundation (Grant No. 87-03-04-03) is gratefully acknowledged.

Registry No. 1, 129619-20-1; **2a**, 129619-23-4; **2b**, 129619-24-5; **2e**, 129619-28-9; **2f**, 129619-30-3; **3c**, 129619-25-6; **3c** (meta adduct), 129619-26-7; **3d**, 129619-27-8; **3e**, 129619-29-0; **3f**, 129619-31-4; $[N(CH_2CH_2O)_3Si-C_6H_5Mn(CO)_3]BF_4$, 129619-22-3; phenyl-silatrane, 2097-19-0.

Supplementary Material Available: Tables of crystal and experimental details, atomic coordinates and thermal parameters, bond distances and angles, and least-squares planes for $[\eta^5$ -3- $(N(CH_2CH_2O)_3Si)$ -6- $(Me_3CCO_2CH_2)$ - $C_6H_5]Mn(CO)_3$ (3d) (7 pages); a listing of observed and calculated structure factors for 3d (9 pages). Ordering information is given on any current masthead page.