Simple Organometallic Alcohols: Synthesis of (C₅H₄OH)Mn(CO)₃ (Hydroxycymantrene) and $(C_5H_4OH)W(CO)_3CH_3$

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Summary: The reaction of tert-butyldimethylsilyl triflate with cyclopent-2-enone and 3,4-dimethylcyclopentenone, respectively, gives siloxycyclopentadienes in yields > 90%, whose deprotonation and reaction with BrMn(CO)₃(py)₂ or W(CO)₃(CH₃CN)₃/MeI generates (CpOSi^tBuMe₂)- $Mn(CO)_3$ and $(CpOSi^tBuMe_2)W(CO)_3Me$. Cleavage of the organometallic silvl ether with NBu₄F results in the formation of the previously unknown alcohols (C₅H₄OH)- $Mn(CO)_3$ and $(C_5H_4OH)W(CO)_3Me$ in 80–90% yield, from which the corresponding ethers can be synthesized.

Cyclopentadienyl ligands continue to be most important in organometallic chemistry, and consequently an enormous number of such compounds with different substituents have been synthesized.¹ However, cyclopentadienes and cyclopentadienyls substituted with heteroatoms of high electronegativity are not very common^{2,3} and even simple aminometallocenes and hydroxymetallocenes used to be available only via multistep reactions.⁴

Aminocyclopentadienes in which a nitrogen atom is directly linked to the five-membered ring have become easily available lately via the enamine reaction of secamines with 3,4-diphenylcyclopentenone.⁵ Numerous η^5 -bound complexes such as aminoferrocenes,^{6,7} aminocobaltocenes,^{6,7} aminocymantrenes,⁸ or aminozirconocene dichlorides⁹ could thus be synthesized.

Very recently we have discovered that cyclopentenones can also serve as excellent starting materials for

(9) (a) Plenio, H.; Burth, D. J. Organomet. Chem. **1996**, *519*, 269. (b) Leino, R.; Luttikhedde, H.; Wilen, C. E.; Sillanpaa, R.; Nasman, J. H. Organometallics 1996, 15, 2450.

oxygen-substituted cyclopentadienes. The reactions of cyclopentenones with silvlating reagents result in the formation of the corresponding silyl enol ethers (=siloxycyclopentadienes) in almost quantitative yields, which can be easily transformed into the respective ferrocenyl silyl ethers.¹⁰

We wish to report on the synthesis of novel cyclopentadienyl-tert-butyldimethylsilyl ethers and (R₂CpO- $Si^{t}BuMe_{2}Mn(CO)_{3}$ (3a, R = H; 3b, R = Me) and $(R_2CpOSi^tBuMe_2)W(CO)_3Me$ (4a, R = H; 4b, R = Me) as well as the previously unknown alcohols (C₅H₄OH)- $Mn(CO)_3$ (5a) and $(C_5H_4OH)W(CO)_3Me$ (6a).

Trialkylsilyl groups are among the most popular protecting groups for alcohols. The stability of the silyl ethers crucially depends on the steric demand of the alkyl group ($-SiMe_3 < -SiEt_3 < Si^tBuMe_2 < Si^iPr_3$) and thus governs the yield of the desired product as well as the conditions for silvl ether cleavage.¹¹

The $-SiMe_3$ and $-SiEt_3$ protecting groups which work well for the synthesis of the siloxyferrocenes fail in the synthesis of (R₂CpOSiR₃)Mn(CO)₃ or (R₂CpOSiR₃)- $W(CO)_3Me$. A more robust choice for the siloxycyclopentadienes therefore was -Si^tBuMe₂ protection. The reactions of cyclopentenone (1a, R = H) and 3,4dimethylcyclopentenone (1b, R = Me) with CF_3SO_3 -Si^tBuMe₂ in petroleum ether (30-50 °C) and NEt₃ yielded the respective silvl enol ethers 2a,b in almost quantitative yields (Scheme 1) as a mixture of three isomers. 2b is a stable compound, whereas 2a is prone toward dimerization but can be stored for several weeks at -20 °C without significant decomposition. Deprotonation of **2a** or **2b** with BuLi at 0 °C and reaction with BrMn(CO)₃(py)₂ gave the respective cymantrenes **3a**,**b** in yields of 45-50%. For the synthesis of (R₂CpO-SiR₃)W(CO)₃Me the siloxycyclopentadienes 2a,b were reacted first with NaN(SiMe₃)₂ and then with W(CO)₃(CH₃CN)₃ and MeI, resulting in the formation of 4a,b in modest yields of 30-40% (Scheme 1). The manganese as well as the tungsten compound is very stable, and the silyl ether could not be cleaved in strongly acidic or basic media. However, treatment of solutions of 3a,b, and 4a,b in anhydrous THF with $NBu_4^+F^-\cdot 3H_2O$ cleaves the organometallic silvl ethers within 15 min at room temperature. After evaporation of the solvent the pure alcohol is isolated by simply filtering a 2:1 cyclohexane/ethyl acetate solution of the residue over a short silica plug. Evaporation of the

[†] E-mail: plenio@ruf.uni-freiburg.de. [®] Abstract published in *Advance ACS Abstracts,* October 15, 1996. (1) (a) Haltermann, R. Chem. Rev. 1992, 92, 965. (b) Okuda, J. Top. Curr. Chem. **1991**, *160*, 97. (c) Janiak, C.; Schumann, H. Adv. Organomet. Chem. **1991**, *33*, 291. (2) (a) Macomber, D. W.; Hart, W. P.; Rausch, M. D. Adv. Organomet.

Chem. 1982, 21, 1. (b) Jutzi, P.; Schwartzen, K.-H.; Mix, A. Chem. Ber. **1990**, *123*, 837. (c) Jutzi, P.; Schwartzen, K.-H. *Chem. Ber.* **1989**, *122*, 287. (d) Kohl, F. X.; Schwarzen, K.-H.; Jutzi, P. *Zh. Org. Khim.* **1988**, *24*, 1109. (e) Paprott, G.; Lentz, D.; Seppelt, K. *Chem. Ber.* **1984**, *117*, 1153

^{(3) (}a) Benson, R. E.; Lindsey, R. V. J. Am. Chem. Soc. 1957, 79, 5471. (b) Egger, H.; Nikiforov, A. Monatsh. Chem. 1969, 100, 1069. (c) Sünkel, K.; Blum, A. Z. Naturforsch. 1995, B50, 1307. (d) Klauck, A.; Seppelt, K. Angew. Chem., Int. Ed. 1994, 33, 93.

^{(4) (}a) Herberhold, M. In *Ferrocenes*; Togni, A., Hayashi, T., Eds.; VCH: Weinheim, Germany, 1995. (b) Kirchner, K.; Meriter, K.; Schmid, R.; Taube, H. *Inorg. Chem.* **1993**, *32*, 5553. (c) Sheats, J. E.; Hlatky, G.; Dickson, R. S. J. Organomet. Chem. **1979**, *173*, 107. (d) Kur, S. A.; Rheingold, A. L.; Winter, C. H. *Inorg. Chem.* **1995**, *34*, 414. (e) Han, Y. H.; Heeg, M. J.; Winter, C. H. Organometallics 1994, 13, 3009

⁽⁵⁾ Plenio, H.; Burth, D. Angew. Chem. **1995**, 107, 881; Angew. Chem., Int. Ed. Engl. **1995**, 34, 800.

⁽⁶⁾ Plenio, H.; Burth, D. Organometallics 1996, 15, 1151.
(7) Plenio, H.; Burth, D. Organometallics 1996, 15, 4054.
(8) Plenio, H.; Burth, D. Z. Anorg. Allg. Chem. 1996, 622, 225.

⁽¹⁰⁾ Plenio, H.; Aberle, C. J. Chem. Soc., Chem. Commun. 1996, 2123.

⁽¹¹⁾ Greene, T. W.; Wuts, P. G. M. Protective Groups in Organic Synthesis; J. Wiley & Sons: New York, 1991.



^a Reagents and conditions: (a) petroleum ether (30/50), 1.1 equiv of Et_3N , 0.98 equiv of $CF_3SO_3Si^{t}BuMe_2$, **2a**, R = H, **2b**, R = Me; (b) 1.0 equiv of BuLi, 1.0 equiv of BrMn(CO)₃(py)₂ or 1.0 equiv of NaN(SiMe_3)₂, 1.0 equiv of W(CO)₃(CH₃CN)₃, 1.5 equiv of MeI; (c) 1.5 equiv of NBu₄F in THF; **7** from **5a** + PhCH₂Br/Na₂CO₃.

volatiles gives the previously unknown alcohols as yellow crystalline materials (5a,b) or as almost colorless solids (6a) in >80% yield. Somewhat to our surprise none of these compounds is very stable, and after 24 h in the flask the alcohols have darkened significantly. Despite the sensitivity of 5a synthesis of the cymantrenyl benzyl ether 7 was possible in good yields.

One application of these systems could be the use as aqueous IR-active organometallic pH probes as described recently by Creaser, Stephenson, et al.¹² Preliminary tests have shown that upon changing the pH the ν (CO) varies between 1930, 2016 cm⁻¹ (pH = 1) and 1910, 2000 cm⁻¹ (pH = 13). The pK value of the alcohol which determines the useful range of such potential sensor molecules can be changed easily by using different cyclopentenones as starting materials for the synthesis of the cymantrenes.

We are currently exploring the synthetic potential of **3a** and **4a** with a view to the chemistry of the organic phenols and are attempting the synthesis of new organometallic alcohols.

Experimental Section

Commercially available solvents and reagents were purified according to literature procedures. All reactions were carried out in dry solvents under a nitrogen atmosphere. NMR spectra were recorded at 300 K with a Bruker AC200 F (¹H NMR 200 MHz, ¹³C NMR 50.3 MHz). ¹H NMR were referenced to residual ¹H impurities in the solvent and ¹³C NMR to the solvent signals: CDCl₃ (7.26 ppm, 77.0 ppm), C₆D₆ (7.16, 128.0 ppm), CD₃CN (1.93 ppm, 1.30 ppm). IR spectra: Bruker IFS-25 with solids as CHCl₃ solutions between KBr disks or in aqueous solution between CaF₂ plates. Elemental analyses: Mikroanalytisches Laboratorium der Chemischen Laboratorien, Universität Freiburg.

Siloxycyclopentadienes 2a,b. A solution of a cyclopent-2-en-1-one (0.05 mol) and Et_3N (7.07 g, 0.07 mol) in pentane (75 mL) was treated with *tert*-butyldimethylsilyl triflate (13.2 g, 0.05 mol). After being stirred for 15 min, the oily precipitate of $Et_3NH^+CF_3SO_3^-$ was removed with a syringe and the volatiles were removed in vacuo. Due to a possible Diels– Alder dimerization of the cyclopentadiene derived from cyclopentenone all workup was performed without delay. The remaining oil, which may still contain small amounts of ammonium salt, was removed from the flask with a syringe. **2a** may be distilled (only data of main isomer listed), yield >90%: ¹H NMR (CDCl₃) $\delta = 0.19$ (s, SiCH₃, 6H), 0.95 (s, C₄H₉, 9H), 2.90–2.93 (m, CH₂, 2H), 5.22–5.25 (m, CH, 1H), 6.24–6.38 (m, CH, 2H). **2b**: yield >90%, complex isomer mixture.

Silvl Cymantrenyl Ethers 3a,b. An ice-cooled solution of the siloxycyclopentadiene (2 mmol) in THF (25 mL) was treated with BuLi (2 mmol, 0.8 mL). After 10 min BrMn-(CO)₃(py)₂ (2 mmol, 754 mg) was added and the reaction mixture stirred for 4 h. The volatiles were evaporated in vacuum, and the remaining solid was extracted with cyclohexane. The extract was filtered over a silica plug (5 cm) and extracted with cyclohexane. The filtrate was evaporated and dried in vacuum yielding pale-yellow oils, which slowly crystallize. 3a: ¹H NMR (C₆D₆) & 0.00 (s, SiCH₃, 6H), 0.84 (s, C₄H₉, 9H), 3.74 (br, CpH, 2H), 3.86 (br, CpH, 2H); ¹³C NMR $(C_6D_6) \delta$ -5.03, 17.98, 25.39, 69.35, 76.82, 137.21, 225.45; IR ν (CO) = 1935, 2019 cm⁻¹. Yield: 48%. Anal. Calcd for C₁₄H₁₉-MnO₄Si (335.24): C, 50.16; H, 5.71. Found: C, 49.88; H, 5.85. **3b**: Yield 45%; ¹H NMR (C₆D₆) δ 0.63 (s, SiCH₃, 6H), 0.89 (s, C₄H₉, 9H), 1.45 (s, CH₃, 6H), 3.95 (s, CpH, 2H); ¹³C NMR (C₆D₆) δ -4.87, 11.60, 18.07, 25.47, 69.77, 92.41, 135.24, 226.1; IR ν (CO) = 1921, 2012 cm⁻¹. Anal. Calcd for C₁₆H₂₃MnO₄Si (363.29): C, 52.90; H, 6.38. Found: C, 52.50; H, 6.31.

(Siloxycyclopentadienyl)tungsten Tricarbonyl Methyls 4a,b. An ice-cooled solution of the siloxycyclopentadiene (2 mmol) in THF (25 mL) was treated with NaN(SiMe₃)₂ (2.2 mmol, 403 mg). After 10 min W(CO)₃(CH₃CN)₃ (782 mg, 2 mmol) was added and stirring continued at room temperature. After 2 h CH₃I (3 mmol, 429 mg) was added and 30 min later the reaction mixture evaporated to dryness. The solid residue was extracted with cyclohexane. The solution was filtered over a silica plug (5 cm) and extracted with cyclohexane. The filtrate was evaporated and dried in vacuum yielding yellow solids that are pure products. 4a: Yield 37%; ¹H NMR (CDCl₃) δ 0.23 (s, SiMe₂, 6H), 0.95 (s, C₄H₉, 9H), 4.83 ("t", 2.4 Hz, CpH, 2H), 5.00 ("t", 2.4 Hz, CpH, 2H). ¹³C NMR (CDCl₃) -20.71, -4.43, 18.22, 25.51, 77.99, 78.05, 141.82, 216.74, 229.62; IR ν (CO) = 1920, 2011 cm⁻¹. Anal. Calcd for C₁₅H₂₂O₄SiW (478.28): C, 37.67; H, 4.64. Found: C, 37.54; H, 4.62. 4b: Yield 33%; ¹ H NMR (C₆D₆) δ 0.00 (s, SiCH₃, 6H), 0.56 (s, WCH3, 3H), 0.85 (s, C4H9, 9H), 1.61 (s, CH3, 6H), 4.56 (s, CpH, 2H); ¹³C NMR (C₆D₆) δ -21.27, -4.70, 11.95, 18.16, 25.51, 30.16, 78.81, 96.72, 137, 218.74, 232.51. IR ν (CO) = 1916, 2005 cm⁻¹. Anal. Calcd for C₁₇H₂₆O₄SiW (506.33): C, 40.33; H, 5.18. Found: C, 39.89; H, 5.30.

Organometallic Alcohols 5a,b and 6a. One equivalent of the silvl ethers 3a,b or 4a was dissolved in anhydrous THF and 1.5 equiv of $NBu_4^+F^-\cdot 3H_2O$ added. After the mixture was stirred at room temperature for 15 min, the volatiles were evaporated. The residue was dissolved in cyclohexane/ethyl acetate (2:1) and filtered over a silica plug. The filtrate was evaporated to dryness with the alcohols staying behind in good purity but may be purified further by chromatography. Yields were between 80 and 90%. 5a: ¹H NMR (C_6D_6) δ 3.59–3.65 (m, CpH, 4H); 13 C NMR (C₆D₆) δ 66.45, 76.74, 138.05, 225.4; IR $\nu(CO) = 1925$, 2017 cm⁻¹. Anal. Calcd for C₈H₅MnO₄ (220.07): C, 43.66; H, 2.29. Found: C, 43.12; H, 2.25. 5b: ¹H NMR (C₆D₆) δ 1.40 (s, CH₃, 6H), 3.71 (s, CpH, 2H); IR ν(CO) = 1924, 2010 cm⁻¹. Anal. Calcd for $C_{10}H_9MnO_4$ (248.10): C, 48.41; H, 3.66. Found: C, 48.29; H, 3.69. **6a**: ¹H NMR (C₆D₆) δ 0.49 (s, WCH₃, 3H), 3.98 ("t", 2.2 Hz, CpH, 2H), 4.29 ("t", 2.2 Hz, CpH, 2H); ¹³C NMR (C₆D₆) δ –20.50, 74.38, 77.59, 142.74, 217.61, 230.05; IR ν (CO) = 1914, 2010 cm⁻¹. Anal. Calcd for C₉H₈O₄W (364.01): C, 29.69; H, 2.22. Found: C, 29.26; H, 2.15

Cymantrenyl Benzyl Ether (7). A mixture of **5a** (48 mg, 0.22 mmol), benzyl bromide (42 mg, 0.24 mmol), and Na_2CO_3 (50 mg) in CH₃CN (20 mL) was heated under reflux for 10 h. After evaporation of the volatiles the remaining solid was

⁽¹²⁾ Anson, C. E.; Baldwin, T. J.; Creaser, C. S.; Fey, M. A.; Stephenson, G. R. *Organometallics* **1996**, *15*, 1451.

purified by chromatography (cyclohexane/ethyl acetate = 5:1). Yield: 50 mg (73%) of yellow crystals, mp 92 °C. ¹H NMR (C₆D₆): δ 3.78 (br, 2H, CpH), 3.87 (br, 2H, CpH), 4.23 (s, 2H, CH₂), 7.12–7.21 (m, 5H, C₆H₅). ¹³C NMR (C₆D₆): δ 65.54, 72.64, 76.90, 128.29, 128.62, 128.74, 135.60, 141.34, 225.3 (CO). IR: ν (CO) = 2020, 1936. Anal. Calcd for C₁₅H₁₁MnO₄ (310.19): C, 58.08; H, 3.57. Found: C, 57.67; H, 3.69.

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