Simple Organometallic Alcohols: Synthesis of $(C_5H_4OH)Mn(CO)_3$ (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 $W(CO)_3(CH_3CN)_3/MeI$ generates $(CpOSi^tBuMe_2)Mn(CO)_3$ and $(CpOSi^tBuMe_2)W(CO)_3Me$. Cleavage of the organometallic silyl ether with NBu_4F results in the formation of the previously unknown alcohols $(C_5H_4OH)Mn(CO)_3$ 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 sec-amines with 3,4-diphenylcyclopentenone.[5] Numerous η^5-bound complexes such as aminoferrocenes,[6,7] aminocobaltocenes,[6,7] aminocymantrenes,[8] or aminozirconocene dichlorides[9] could thus be synthesized.

Very recently we have discovered that cyclopentenones can also serve as excellent starting materials for oxygen-substituted cyclopentadienes. The reactions of cyclopentenones with silylating 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 $(R_2CpOSi^tBuMe_2)Mn(CO)_3$ (**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 $(C_5H_4OH)Mn(CO)_3$ (**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 silyl 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 $(R_2CpOSiR_3)Mn(CO)_3$ or $(R_2CpOSiR_3)W(CO)_3Me$. A more robust choice for the siloxycyclopentadienes therefore was $-Si^tBuMe_2$ protection. The reactions of cyclopentenone (**1a**, R = H) and 3,4-dimethylcyclopentenone (**1b**, R = Me) with $CF_3SO_3Si^tBuMe_2$ in petroleum ether (30−50 °C) and NEt_3 yielded the respective silyl 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 $(R_2CpOSiR_3)W(CO)_3Me$ the siloxycyclopentadienes **2a**,**b** were reacted first with $NaN(SiMe_3)_2$ and then with $W(CO)_3(CH_3CN)_3$ 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 silyl 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

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(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.

(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.

(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.

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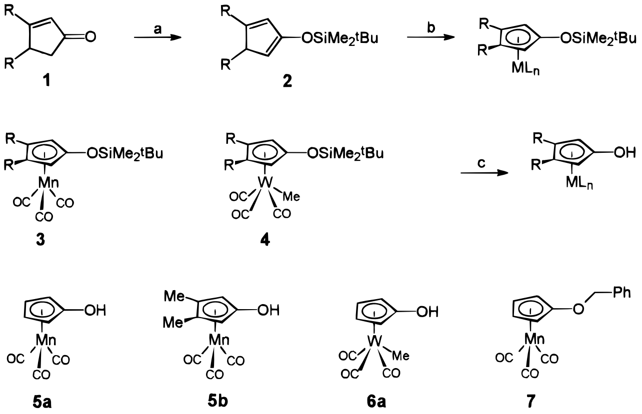
Scheme 1[a]



[a] Reagents and conditions: (a) petroleum ether (30/50), 1.1 equiv of Et_3N, 0.98 equiv of $CF_3SO_3Si^tBuMe_2$, **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 $W(CO)_3(CH_3CN)_3$, 1.5 equiv of MeI; (c) 1.5 equiv of NBu_4F in THF; **7** from **5a** + $PhCH_2Br/Na_2CO_3$.

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 p*K* 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, ^{13}C NMR 50.3 MHz). ^1H NMR were referenced to residual ^1H impurities in the solvent and ^{13}C NMR to the solvent signals: $CDCl_3$ (7.26 ppm, 77.0 ppm), C_6D_6 (7.16, 128.0 ppm), CD_3CN (1.93 ppm, 1.30 ppm). IR spectra: Bruker IFS-25 with solids as $CHCl_3$ solutions between KBr disks or in aqueous solution between CaF_2 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 ($CDCl_3$) δ = 0.19 (s, $SiCH_3$, 6H), 0.95 (s, C_4H_9, 9H), 2.90−2.93 (m, CH_2, 2H), 5.22−5.25 (m, CH, 1H), 6.24−6.38 (m, CH, 2H). **2b**: yield >90%, complex isomer mixture.

Silyl 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 (C_6D_6) δ 0.00 (s, $SiCH_3$, 6H), 0.84 (s, C_4H_9, 9H), 3.74 (br, CpH, 2H), 3.86 (br, CpH, 2H); ^{13}C NMR (C_6D_6) δ −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 $C_{14}H_{19}MnO_4Si$ (335.24): C, 50.16; H, 5.71. Found: C, 49.88; H, 5.85. **3b**: Yield 45%; ^1H NMR (C_6D_6) δ 0.63 (s, $SiCH_3$, 6H), 0.89 (s, C_4H_9, 9H), 1.45 (s, CH_3, 6H), 3.95 (s, CpH, 2H); ^{13}C NMR (C_6D_6) 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 $C_{16}H_{23}MnO_4Si$ (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 $NaN(SiMe_3)_2$ (2.2 mmol, 403 mg). After 10 min $W(CO)_3(CH_3CN)_3$ (782 mg, 2 mmol) was added and stirring continued at room temperature. After 2 h CH_3I (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 ($CDCl_3$) δ 0.23 (s, $SiMe_2$, 6H), 0.95 (s, C_4H_9, 9H), 4.83 ("t", 2.4 Hz, CpH, 2H), 5.00 ("t", 2.4 Hz, CpH, 2H). ^{13}C NMR ($CDCl_3$) −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 $C_{15}H_{22}O_4SiW$ (478.28): C, 37.67; H, 4.64. Found: C, 37.54; H, 4.62. **4b**: Yield 33%; ^1H NMR (C_6D_6) δ 0.00 (s, $SiCH_3$, 6H), 0.56 (s, WCH_3, 3H), 0.85 (s, C_4H_9, 9H), 1.61 (s, CH_3, 6H), 4.56 (s, CpH, 2H); ^{13}C NMR (C_6D_6) 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 $C_{17}H_{26}O_4SiW$ (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 silyl 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 (C_6D_6) δ 66.45, 76.74, 138.05, 225.4; IR ν(CO) = 1925, 2017 cm^{-1}. Anal. Calcd for $C_8H_5MnO_4$ (220.07): C, 43.66; H, 2.29. Found: C, 43.12; H, 2.25. **5b**: ^1H NMR (C_6D_6) δ 1.40 (s, CH_3, 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 (C_6D_6) δ 0.49 (s, WCH_3, 3H), 3.98 ("t", 2.2 Hz, CpH, 2H), 4.29 ("t", 2.2 Hz, CpH, 2H); ^{13}C NMR (C_6D_6) δ −20.50, 74.38, 77.59, 142.74, 217.61, 230.05; IR ν(CO) = 1914, 2010 cm^{-1}. Anal. Calcd for $C_9H_8O_4W$ (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 CH_3CN (20 mL) was heated under reflux for 10 h. After evaporation of the volatiles the remaining solid was

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[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. ^{1}H NMR (C_6D_6): δ 3.78 (br, 2H, CpH), 3.87 (br, 2H, CpH), 4.23 (s, 2H, CH_2), 7.12−7.21 (m, 5H, C_6H_5). ^{13}C NMR (C_6D_6): 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 $C_{15}H_{11}MnO_4$ (310.19): C, 58.08; H, 3.57. Found: C, 57.67; H, 3.69.

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