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First Sonogashira coupling reactions with the chlorobenzeneCr$(CO)_2PPh_3$ complex

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Abstract

Alkynylated benzeneCr$(CO)_2PPh_3$ complexes **4** are readily synthesized in moderate to good yields by Sonogashira couplings of the chlorobenzeneCr$(CO)_2PPh_3$ complex **2** with terminal alkynes **3**. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Alkynes; Arene complexes; Chromium; Catalysis; Coupling reactions

1. Introduction

The advent of palladium-catalyzed cross-coupling reactions [1] has not only had a significant impact on the synthesis of complex natural compounds [2] but has also gained considerable importance in the development of new organometallic structures with extended π-conjugation [3], especially for future opto-electronical and electrical applications [4]. In terms of synthetic efficiency, highly convergent strategies have emerged from cross-coupling methodologies of bromo and iodoarenes, heteroarenes and numerous organometallics [1,5]. However, the less expensive chloroarenes have been notorious for a long time and even the recently prepared Herrmann–Beller catalyst [6] still requires higher temperatures for efficient coupling rates. Interestingly, the complexation of chloroarenes with the $Cr(CO)_3$ fragment activates the arene chlorine bond considerably towards the oxidative addition [7]. Thus, $Cr(CO)_3$ complexed chloroarenes react about 15 times faster than iodoarenes in palladium-catalyzed cross-coupling reactions [8,9] under mild reaction conditions, in particular Sonogashira couplings [10] in refluxing THF and/or tertiary amines [11]. However, the introduction of the electronically donating phosphane ligands in the coordination sphere of the chromium atom should render the metal more electron rich and thus more or less reluctant in cross-coupling reactions. Here we wish to communicate our first findings on Sonogashira couplings of the chlorobenzeneCr$(CO)_2PPh_3$ complex **2** with terminal alkynes **3**.

2. Results and discussion

According to a standard procedure [12] we synthesized the chlorobenzeneCr$(CO)_2PPh_3$ complex by irradiating a benzene solution of the chlorobenzeneCr$(CO)_3$ complex (**1**) in the presence of 1.1 equivalents of triphenylphosphane for 5 h (Scheme 1). This photochemical ligand exchange reaction can be monitored by TLC as a spot-to-spot transformation indicating the formation of a less polar orange chlorobenzene dicarbonyl phosphane complex **2**.

Due to the increased acid sensitivity of **2** chromatography on silica gel leads to rapid decomplexation. Therefore, the purification was achieved by filtration and recrystallization from diethyl ether. The complex **2** could be isolated as a pure orange crystalline material in 50% yield.

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The chlorobenzene$Cr(CO)_2PPh_3$ complex **2** can be coupled with different terminal alkynes in THF/triethylamine with $Pd(PPh_3)_2Cl_2$ and CuI to furnish the complexed alkynes **4** (Scheme 2). Most importantly, even with the reduced acceptor capacity of the chromiumdicarbonyl-PPh_3 fragment the chloroarene complex **2** still can be successfully coupled with alkynes. The cross-coupling products **4** are isolated in moderate to excellent yields after purification by chromatography on silica gel. Deprotection of the silylated alkyne **4d** with TBAF in THF furnishes the phenylacetylene complex **4e** in excellent yield as pure orange crystals.

The structure of the complexes **4a**–**4e** is fully supported by NMR, IR and elemental analysis. In the ^{1}H-NMR spectra the signals of the complexed arene protons appear in the expected region between $\delta = 4.5$ and 5.1. In the ^{13}C-NMR spectra the signals of the complexed arene are found between $\delta = 87.7$ and 109.6. The alkyne carbon resonances appear between $\delta = 79$ and 86. They are slightly shifted to high field in comparison to those of the tricarbonylchromium complexes. Most significantly, the CO resonances appear between $\delta = 239.8$ and 240.4, i.e. shifted to downfield by 6–8 ppm compared to the related tricarbonylchromium complexes [11] due to the strong electron donating nature of the phosphane ligand. Analogously, the two carbonyl stretching vibrations in the IR spectra are shifted to lower wavenumbers (1881–1903 and 1831–1842 cm^{-1}), indicating an increase in the electron density on the metal and thus an enhanced backbonding to the carbonyl ligands.

Although the substitution of a CO ligand by a phosphane decreases the propensity of the complexes towards the oxidative addition of the palladium(0) species into the carbon–chlorine bond, cross-couplings are still efficiently possible. Nevertheless, for a complete conversion of the coupling reaction of the chlorobenzene-$Cr(CO)_2PPh_3$ complex **2** the reaction time has to be extended to 24 h in a refluxing mixture of THF and triethylamine. The coupling of the chlorobenzene-$Cr(CO)_3$ complex [11] **1** with terminal alkynes is complete within 3 h.

3. Conclusions

Since these novel examples of organometallic alkynes and propargyl alcohols are easily accessible via the Sonogashira coupling of phosphane dicarbonylchromium arene complexes, the application to other cross-coupling reactions like the Suzuki [13], Stille [14] and Heck [15] couplings lies at hand. Using this versatile tool, the syntheses 2of novel organometallic NLO chromophores and interesting organometallic building blocks for extended π-systems are currently under way.

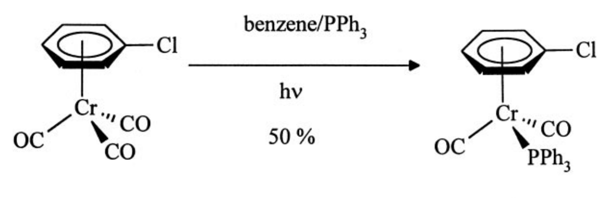
4. Experimental

All reactions involving tricarbonylchromium complexes were carried out in flame-dried Schlenk flasks under nitrogen by using septum and syringe techniques. Solvents were dried and distilled according to standard procedures [16]. Column chromatography: silica gel 60 (0.063–0.2 mm/70–230 mesh, Firma Merck Darmstadt). TLC: silica gel plates (60 F_{254} Merck, Darmstadt). Melting points (uncorrected values): Reichert-Jung Thermovar. The chlorobenzene complex **1** was synthesized according to standard conditions [17]. The alkynes and catalysts were purchased from Merck, Aldrich or Fluka and used without further purification; 4-nitrophenylacetylene was synthesized according to literature procedure [10]. ^{1}H- and ^{13}C-NMR spectra: Bruker WM 300, Bruker AC 300, Bruker ARX 300 or Varian VXR 400S; DMSO-d_6. IR: Perkin–Elmer FT-IR spectrometer 1000 or Perkin–Elmer FT-IR Paragon 1000 PC. The samples were pressed into KBr pellets and recorded on NaCl plates. UV–vis: Beckman DK-2-a or Beckman UV 5240. UV–vis: Perkin–Elmer model Lambda 16. MS: Finnigan MAT 311-A/100MS, Finnigan MAT 90 and MAT 95 Q. Elemental analysis were carried out in the Microanalytical Laboratories of the Institut für Organische Chemie, Ludwig-Maximilians-Universität München.

4.1. (η^6-C_6H_5Cl)$Cr(CO)_2(PPh_3)$ (**2**)

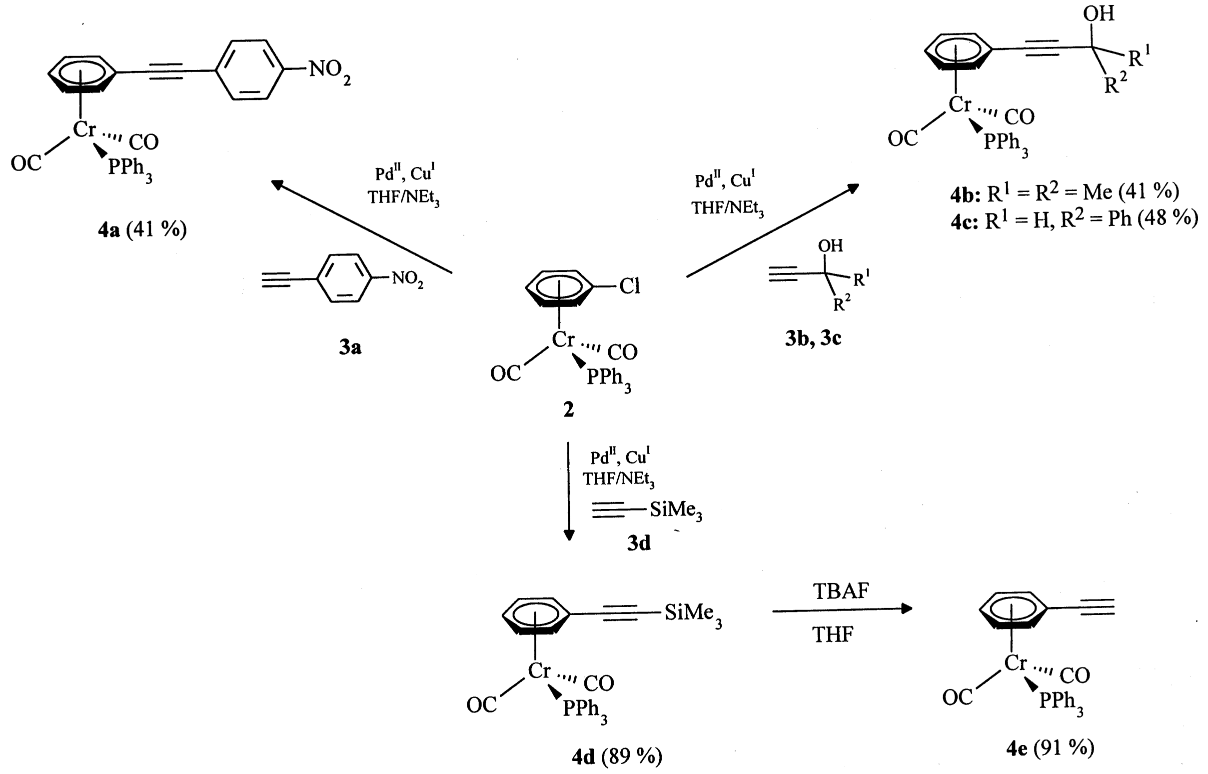
The chlorobenzene complex **1** (1.00 g, 4.02 mmol) and 1.13 g (4.42 mmol) of triphenylphosphane were dissolved in 150 ml benzene and the solution was irradiated for 8 h under a continuous flow of nitrogen in a reaction vessel equipped with a water-cooled cold finger and a mercury steam lamp (HPK 125W, Philips, quartz glass). The dark red–brown reaction mixture was then filtered and the solvent was evaporated in vacuo. Recrystallization of the crude product from diethyl ether furnishes 1.96 g (50%) of the chlorobenzene complex **2** as orange crystals, m.p. 158–160°C.

^{1}H-NMR (DMSO-d_6, 300 MHz): $\delta = 4.58$ (t, $J = 5.9$ Hz, 1 H), 4.82–4.96 (m, 4 H), 7.32–7.43 (m, 15 H). ^{13}C-NMR (DMSO-d_6, 75 MHz): $\delta = 87.78$ (CH), 88.27 (CH), 91.51 (CH), 109.65 (C_{quat}), 128.28 (CH, $J_{P,C} = 8.6$ Hz), 129.45 (CH, $J_{P,C} = 1.3$ Hz), 132.60 (CH, $J_{P,C} = 10.6$ Hz), 138.60 (C_{quat}, $J_{P,C} = 33.8$ Hz), 239.83 (C_{quat}, $J_{P,C} = 20.5$ Hz). MS (70 eV, EI), m/z (%): 482 (M^+, 8),



1 2

Scheme 1.



Scheme 2.

426 (M$^+$ 2CO, 19), 314 ([Cr(PPh$_3$)]$^+$, 100), 262 ([PPh$_3$]$^+$, 42), 52 (Cr$^+$, 16). IR (KBr): $\tilde{\nu} = 1903$ cm^{-1}, 1836, 1629, 1585, 1571, 1479, 1434, 1403, 1308, 1281, 1184, 1159, 1137, 1089, 1073, 1027, 1011, 998, 989, 844, 802, 746, 697, 684, 640, 607, 573, 522, 467, 428. UV–vis (DMSO): λ_{max} (ε) = 326 nm (9800). $C_{26}H_{20}ClCrO_2P$ (482.86): Calc.: C: 64.67, H: 4.17, Cl: 7.34, Found: C: 64.78, H: 4.16, Cl: 7.06.

4.2. *Sonogashira coupling of the chlorobenzene complex* **2**

To a degassed solution of 1.00 g (2.07 mmol) of **2**, 30 mg (0.04 mmol) of bis(triphenylphosphane) palladium dichloride and 9 mg (0.04 mmol) of copper(I)iodide in a mixture of 40 ml of THF and 20 ml of triethylamine was added dropwise over a period of 1 h a solution of the corresponding terminal alkyne (Table 1) in 10 ml of THF. The reaction mixture was then heated to reflux temperature for 24 h. After cooling to room temperature, 50 ml of diethyl ether was added, the mixture was filtered and the filtrate was evaporated in vacuo. The residue was chromatographed on silica gel with diethyl ether and pentane as eluent to give the coupling products **4** as crystalline solids (Table 1).

4.3. p-$O_2NC_6H_4C{\equiv}C(\eta^6$-$C_6H_5)Cr(CO)_2(PPh_3)$ (**4a**)

^{1}H-NMR (DMSO-d_6, 300 MHz): $\delta = 4.82$ (m, 2 H), 4.96 (m, 1 H), 5.10 (m, 2 H), 7.37 (m, 15 H), 7.66 (d, $J = 8.4$ Hz, 2 H), 8.23 (d, $J = 8.4$ Hz, 2 H). ^{13}C-NMR (DMSO-d_6, 75 MHz): $\delta = 81.77$ (C$_{quat}$), 86.31 (C$_{quat}$), 89.21 (CH), 90.52 (CH), 93.03 (CH), 93.87 (C$_{quat}$), 124.08 (CH), 128.24 (CH, $J_{P,C} = 8.6$ Hz), 128.89 (C$_{quat}$), 129.42 (CH, $J_{P,C} = 2.0$ Hz), 132.56 (CH), 132.69 (CH, $J_{P,C} = 10.6$ Hz), 138.41 (C$_{quat}$, $J_{P,C} = 34.5$ Hz), 146.86 (C$_{quat}$), 240.28 (C$_{quat}$, $J_{P,C} = 21.2$ Hz). ^{31}P-NMR (DMSO-d_6, 121 MHz): $\delta = 86.71$. MS (70 eV, EI), m/z (%): 314 ([Cr(PPh$_3$)]$^+$, 4), 277 (100), 223 (M$^+$ Cr(CO)$_2$PPh$_3$, 35), 52 (Cr$^+$, 2). IR (KBr): $\tilde{\nu} = 2214$ cm^{-1}, 1898, 1841, 1629, 1593, 1515, 1480, 1433, 1340, 1310, 1286, 1176, 1106, 1089, 1027, 998, 856, 829, 807, 747, 720, 696, 635, 604, 569, 522, 427. UV–vis (DMSO): λ_{max} (ε) = 310 nm (25470), 472 (5010). $C_{34}H_{24}CrNO_4P$ (593.53): Calc.: C: 68.80, H: 4.07, N: 2.36, Found: C: 68.56, H: 4.26, N: 2.49. m.p.: 133–135°C.

Table 1
Experimental details of the coupling reactions of **2** with **3**

Alkyne **3**	Yield
334 mg (2.28 mmol) 4-nitrophenylacetylene	0.50 g (41%) **4a**
0.25 ml (2.50 mmol) 3-methyl-but-1-yn-3-ol	0.45 g (41%) **4b**
314 mg (2.50 mmol) 1-phenyl propyn-1-ol	0.58 g (48%) **4c**
0.59 ml (4.14 mmol) trimethylsilyl acetylene	1.00 g (89%) **4d**

4.4. $(H_3C)_2C(OH)C{\equiv}C(\eta^6\text{-}C_6H_5)Cr(CO)_2(PPh_3)$ (**4b**)

^{1}H-NMR (DMSO-d_6, 300 MHz): $\delta = 1.41$ (s, 6 H), 4.59–4.81 (m, 5 H), 5.41 (s, 1 H), 7.39 (m, 15 H). ^{13}C-NMR (DMSO-d_6, 75 MHz): $\delta = 31.84$ (CH$_3$), 63.68 (C$_{quat}$), 78.71 (C$_{quat}$), 85.30 (C$_{quat}$), 89.71 (CH), 90.03 (CH), 91.90 (CH), 94.75 (C$_{quat}$), 128.20 (CH, $J_{P,C} = 8.6$ Hz), 129.30 (CH, $J_{P,C} = 1.3$ Hz), 132.67 (CH, $J_{P,C} = 10.6$ Hz), 138.88 (C$_{quat}$, $J_{P,C} = 33.8$ Hz), 240.45 (C$_{quat}$, $J_{P,C} = 22.8$ Hz). MS (70 eV, EI), m/z (%): 530 (M$^+$, 1), 474 (M$^+$ 2 CO, 5), 314 ([Cr(PPh$_3$)]$^+$, 82), 262 ([PPh$_3$]$^+$, 100), 52 (Cr$^+$, 18). IR (KBr): $\tilde{\nu} = 3436$ cm^{-1}, 1895, 1842, 1633, 1480, 1434, 1270, 1163, 1089, 961, 903, 745, 696, 636, 605, 574, 522, 429. UV–vis (DMSO): λ_{max} (ε) = 336 nm (8900). $C_{31}H_{27}CrO_3P$ (530.52): Calc.: C: 70.18, H: 5.13, Found: C: 69.19, H: 5.13. m.p.: 66–71°C.

4.5. $H_5C_6CH(OH)C{\equiv}C(\eta^6\text{-}C_6H_5)Cr(CO)_2(PPh_3)$ (**4c**)

^{1}H-NMR (DMSO-d_6, 300 MHz): $\delta = 4.67$–4.99 (m, 5 H), 5.56 (d, $J = 5.8$ Hz, 1 H), 6.16 (d, $J = 5.8$ Hz, 1 H), 7.34–7.59 (m, 20 H). ^{13}C-NMR (DMSO-d_6, 75 MHz): $\delta = 63.00$ (CH), 82.87 (C$_{quat}$), 84.27 (C$_{quat}$), 89.29 (CH), 89.34 (CH), 89.76 (C$_{quat}$), 90.81 (CH), 92.06 (CH), 92.24 (CH), 126.75 (CH), 127.79 (CH), 128.14 (CH), 128.31 (CH, $J_{P,C} = 8.6$ Hz), 129.29 (CH, $J_{P,C} = 1.3$ Hz), 132.64 (CH, $J_{P,C} = 10.6$ Hz), 138.76 (C$_{quat}$, $J_{P,C} = 33.8$ Hz), 142.00 (C$_{quat}$), 240.37 (C$_{quat}$, $J_{P,C} = 21.2$ Hz). MS (70 eV, EI), m/z (%): 314 ([Cr(PPh$_3$)]$^+$, 15), 262 (PPh$_3$, 100), 52 (Cr$^+$, 6). IR (KBr): $\tilde{\nu} = 3058$ cm^{-1}, 2924, 1968, 1894, 1842, 1637, 1479, 1452, 1433, 1382, 1309, 1285, 1185, 1158, 1089, 1026, 1000, 956, 918, 809, 745, 696, 636, 605, 572, 522, 428. UV–vis (DMSO): λ_{max} (ε) = 336 nm (10000). $C_{35}H_{27}CrO_3P$ (578.56): Calc.: C: 72.65, H: 4.70, Found: C: 72.43, H: 4.91. m.p.: 55–60°C.

4.6. $(H_3C)_3SiC{\equiv}C(\eta^6\text{-}C_6H_5)Cr(CO)_2(PPh_3)$ (**4d**)

^{1}H-NMR (DMSO-d_6, 300 MHz): $\delta = 0.17$ (s, 9 H), 4.72 (m, 2 H), 4.83–4.89 (m, 3 H), 7.39 (m, 15 H). ^{13}C-NMR (DMSO-d_6, 75 MHz): $\delta = 0.07$ (CH$_3$), 83.58 (C$_{quat}$), 89.38 (CH), 89.91 (CH), 92.39 (CH), 92.91 (C$_{quat}$), 103.82 (C$_{quat}$), 128.16 (CH, $J_{P,C} = 8.6$ Hz), 129.34 (CH, $J_{P,C} = 1.3$ Hz), 132.68 (CH, $J_{P,C} = 10.6$ Hz), 138.66 (C$_{quat}$, $J_{P,C} = 33.8$ Hz), 240.20 (C$_{quat}$, $J_{P,C} = 20.5$ Hz). MS (70 eV, EI), m/z (%): 544 (M$^+$, 6), 488 (M$^+$ 2 CO, 39), 314 ([Cr(PPh$_3$)]$^+$, 100), 262 (PPh$_3^+$, 77), 226 (M$^+$ 2 CO–PPh$_3$, 5), 52 (Cr$^+$, 32). IR (KBr): $\tilde{\nu} = 2158$ cm^{-1}, 1972, 1900, 1842, 1667, 1586, 1572, 1512, 1480, 1448, 1308, 1249, 1218, 1185, 1158, 1119, 1089, 1069, 1027, 998, 844, 744, 721, 696, 633, 604, 570, 540, 521, 463, 427. UV–vis (DMSO): λ_{max} (ε) = 333 nm (7600). $C_{31}H_{29}CrO_2PSi$ (544.62): Calc.: C: 68.36, H: 5.36, Found: C: 68.46, H: 5.36. m.p.: 58–61°C.

4.7. $HC{\equiv}C(\eta^6\text{-}C_6H_5)Cr(CO)_2(PPh_3)$ (**4e**)

To a degassed solution of 1.00 g (1.83 mmol) of **4d** in 50 ml of THF was added 0.57 g (1.83 mmol) of tetrabutylammonium fluoride trihydrate. The mixture was stirred for 1 h at room temperature, diethylether was added and the solution was filtered through a short plug of silica gel. The orange solution was evaporated in vacuo to give 0.79 g (91%) of essentially pure **4e**. Recrystallization from pentane affords 0.60 g (69%) **4e** with a melting point of 135–140°C.

^{1}H-NMR (DMSO-d_6, 300 MHz): $\delta = 3.98$ (s, 1 H), 4.68 (m, 2 H), 4.84 (m, 1 H), 4.98 (d, $J = 6.0$ Hz, 2 H), 7.35 (m, 15 H). ^{13}C-NMR (DMSO-d_6, 75 MHz): $\delta = 79.17$ (C$_{quat}$), 82.06 (CH), 83.00 (C$_{quat}$), 89.59 (CH), 91.10 (CH), 92.03 (CH), 128.22 (CH, $J_{P,C} = 8.6$ Hz), 129.36 (CH), 132.63 (CH, $J_{P,C} = 11.2$ Hz), 138.71 (C$_{quat}$, $J_{P,C} = 34.5$ Hz), 240.14 (C$_{quat}$, $J_{P,C} = 20.5$ Hz). MS (70 eV, EI), m/z (%): 314 ([Cr(PPh$_3$)]$^+$, 7), 262 (PPh$_3^+$, 100), 52 (Cr$^+$, 5). IR (KBr): $\tilde{\nu} = 1896$ cm^{-1}, 1881, 1831, 1637, 1478, 1432, 1183, 1089, 997, 814, 744, 695, 638, 606, 572, 522, 513, 421. UV–vis (DMSO): λ_{max} (ε) = 333 nm (8320). $C_{28}H_{21}CrO_2P$ (472.44): Calc.: C: 71.18, H: 4.48, Found: C: 71.33, H: 4.58.

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