Tricarbonyl-η⁶-[(2-thiophenyl)arene]- and -η⁶-[(2-thiophenyl)carbonylarene]-chromium Complexes: Preparation and Conformational Study

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The cross coupling reaction of (*p*-chloroanisole)tricarbonylchromium complex (**1**) with thiophene derivatives under palladium-catalyzed conditions leads to the selective formation of tricarbonyl-η⁶-[(2-thiophenyl)arene]- or -η⁶-[(2-thiophenyl)carbonylarene]chromium complexes (**2** or **3**) depending on reaction conditions. The conformation of complexes **2** and **3** in the solid state as well as in solution are reported.

Introduction

Over the last three decades, cross-coupling reactions using Stille, Suzuki, or Negishi methodologies have attracted much attention.[1,2] The unique behaviour of organotin, boron, or zinc reagents with different halogenated aromatics (iodides, bromides, and more recently, chlorides[3]) under palladium catalysis has become one of the most powerful C_{sp2}–C_{sp2} bond formation methods.

It has been shown that the decrease of the electron density in an aromatic ring due to the presence of the $Cr(CO)_3$ moiety allows an easier oxidative addition of the carbon–halogen bond to the zero-valent palladium active species, which is the initial step of most of the palladium-catalyzed cross coupling processes. This ability allowed for the more frequent inclusion of aryl chloride among the electrophiles, thus enhancing the usefulness of these reactions.[4–6] Since then, palladium-catalyzed processes at π-bond ligands in the presence of $Cr(CO)_3$ groups have been developed.[7]

As part of our current studies on organochromium complexes[8,9] and on cross-coupling reactions,[10,11] we were interested in the preparation of tricarbonyl-η⁶-[(thiophenyl)arene- and -(thiophenyl)carbonylarene]chromium complexes by using a bimetallic activation. This paper describes how the judicious choice of reaction conditions can lead to exceptional selectivities in this class of bond-formation reactions. In particular, in taking advantage of CO insertion under a carbon monoxide atmosphere, exclusive access to carbonylation products can be achieved.

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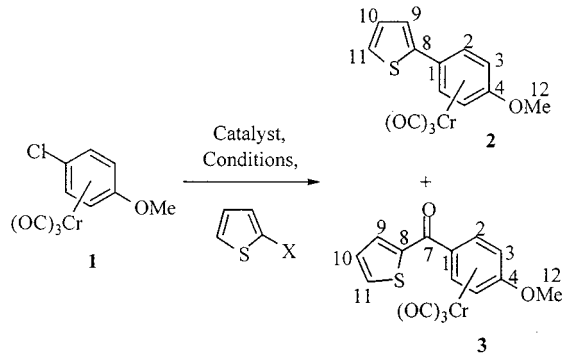
Results and Discussion

The reaction of *p*-chloroanisole tricarbonylchromium complex (**1**) with thiophene derivatives under palladium-catalyzed conditions (Scheme 1) leads to the formation of two new complexes: the expected thienyl complex **2** but also a second compound due to a carbonyl insertion into the newly formed carbon-carbon bond. We have examined the scope of this reaction with three different thienyl derivatives under several palladium-catalyzed procedures, and the results are presented in Table 1.



Scheme 1

We first tried the classical conditions: $PdCl_2(PPh_3)_2$ in refluxing THF (entry 1), complexes **2** and **3** were obtained in 54% yield in a 3:1 ratio.[12] The two complexes were easily separated by column chromatography, and their spectral data as well as their conformational study in solution and in the solid state will be discussed later (vide infra). If this reaction was performed with (2-thienyl)boronic acid (entry 2) and 2-thienyl zinc chloride[10] (entry 3) (prepared in situ from 2-thienyllithium and anhydrous zinc chloride in THF) complexes **2** and **3** were obtained in a 7:1 ratio (63% yield) and 3.5:1 ratio (19% yield), respectively after silica gel column chromatography. Under milder reaction conditions (room temperature) using Stille-coupling reaction conditions and a modified catalytic system[13] such as $Pd_2(dba)_3$

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Table 1. Preparation of complexes **2** and **3**

Entry	X	Catalyst	Conditions	Time [h]	2:3	Yield [%]
1	$SnBu_3$	$PdCl_2(PPh_3)_2$	THF, reflux	18	3:1	54
2	$B(OH)_2$	$Pd(PPh_3)_4$	Acetone, K_2CO_3, reflux	14	7:1	63
3	ZnCl	$Pd(PPh_3)_4$	DMF, 80°	18	3.5:1	19
4	$SnBu_3$	$Pd_2(dba)_3$, 4 $AsPh_3$	DMF, room temp.	20	1:0	82
5	$SnBu_3$	$PdCl_2(PPh_3)_2$	THF, CO, reflux	2	0:1	88

and $AsPPh_3$, where the arsane ligand has been shown to be a more effective dissociative ligand at the transmetallation stage (entry 4), we succeeded in selectively preparing complex **2** in good yield (82%). This selectivity is certainly due to the reaction conditions (room temperature) which inhibit the internal CO migration and therefore the formation of compound **3**. This reaction represents a significant improvement in the synthesis of such complexes. Indeed, the preparation of the [(2-thienyl)-η^6-benzene]tricarbonylchromium complex has already been reported[14] using thermal complexation of the $Cr(CO)_3$ entity to the six-membered ring of 2-phenylthiophene, but with a low yield of 7%. Moreover, if we carried out the coupling reaction under a CO atmosphere as reported in entry 5, we were able to isolate complex **3** as the sole product in high yield (88%).

Conformational Studies in Solution and in the Solid State of Complexes 2 and 3

Solution

The spectral data of complexes **2** and **3** were in good agreement with their respective structures. The IR spectrum of complex **3** showed one band typical for a keto group at 1635 cm^{-1}, besides the bands between 1900 and 1975 cm^{-1} due to CO ligands.

The ^{1}H-NMR data of complexes **2** and **3** are noteworthy to observe the influence by the coordination of the $Cr(CO)_3$ entity and by the conformation of the tripod in solution[15] on the chemical shifts of the protons of the arene. Indeed, protons H-2 and H-3 of complex **2** are privileged spectators vis-à-vis the $Cr(CO)_3$ conformation: they resonate at δ = 5.92 and 5.20 (Table 2, entry 1). Knowing

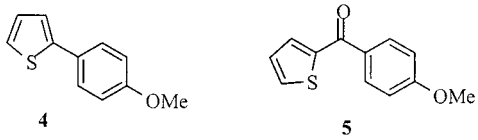

Figure 1. Free arenes

that the protons H-2 and H-3 of the free arene **4** (Figure 1) resonate at δ = 7.60 and 6.96 (Table 2, entry 2), we were able to calculate the shielding of these protons as Δδ = δ(free arene **4**) – δ(complex **2**). In this way we obtained the values of Δδ = 1.68 for H-2 and 1.76 for H-3 in complex **2** (Table 2, entry 3), a small difference of 0.08 ppm! In other words, the coordination of the tricarbonylchromium entity has the same shielding effect on the arene protons. These data are in good agreement with an almost staggered conformation of the $Cr(CO)_3$: indeed the two conformations eclipsing (**2E**, Figure 2) and *anti*-eclipsing the methoxy group (**2AE**, Figure 2), which are in equilibrium, are present in an almost 50:50 ratio.[16]

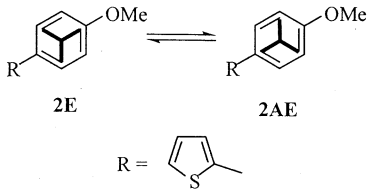

Figure 2. The two conformers of complex **2**

For complex **3**, the shielding of the two protons H-2 and H-3: Δδ = δ(free arene **5**) – δ(complex **3**) are 1.57 and 1.78 ppm, respectively, a difference of 0.21 ppm[17a]

Table 2. ^{1}H- and ^{13}C-NMR data for compounds **2**–**5**

Entry	Compound	H-2	H-3	δ(H-2) – δ(H-3)	Δδ(H-2) – Δδ(H-3)	C-2	C-3
1	2[a]	5.92	5.20	0.72	–	93.3	77.5
2	4[a]	7.60	6.96	0.64	–	127.3	114.1
3	$\Delta\delta^{[a]} = \delta(4) - \delta(2)$	1.68	1.76	–	0.08	34.0	36.6
4	2[b]	5.25	4.37	0.88	–		
5	4[b]	7.43	6.69	0.74	–		
6	$\Delta\delta^{[b]} = \delta(4) - \delta(2)$	2.18	2.32	–	0.14		
7	3[a]	6.32	5.19	1.13	–	95.8	76.6
8	5[a]	7.89	6.97	0.92	–	131.9	144.1
9	$\Delta\delta^{[a]} = \delta(5) - \delta(3)$	1.57	1.78	–	0.21	36.1	37.5
10	3[b]	5.82	4.23	1.59	–		
11	5[b]	7.80	6.59	1.21	–		
12	$\Delta\delta^{[b]} = \delta(5) - \delta(3)$	1.98	2.56	–	0.58		

[a] $CDCl_3$. – [b] C_6D_6.

(Table 2, entry 9). These data are no longer consistent with a mean staggered conformation of the tripod in solution. As the proton H-2 resonates at a lower field (δ = 6.32) with respect to the proton H-3 (δ = 5.19), the population of the conformation eclipsing the methoxy group should be favoured. This can be explained by the synergic effect of the electron-withdrawing keto group which favours an *anti*-eclipsed conformation and of the electron-donating methoxy group which favours the eclipsed conformation.[17b–17f]

Some of the ^{13}C-NMR data of compounds **2–5** are reported in Table 2. First of all, the spectrum of complex **3** displayed, among others, a signal at δ = 230.7 attributed to the carbonyl keto group, whereas carbons of carbonyl ligands appeared as a signal at δ = 232.2. The shielding of the aromatic carbons of the arene ring of complexes **2–5** are, as expected, between 34 and 37 ppm, except the quaternary carbons bearing the methoxy group which are shielded only by 17.1 and 19.8 ppm for complexes **2** and **3**, respectively (Table 2, entries 3 and 9). It is worthy to note that the quaternary carbons C-8 of the thiophene residues of complexes **2** and **3** are also shielded by 17.2 and 22.0 ppm, the other carbons C-9, C-10, C-11 resonating at almost the same field for couples **2**, **4** and **3**, **5**.

Solid State

In order to know more about the conformation of complexes **2** and **3**, they were both subjected to X-ray analysis. The ORTEP views showing the most important bond distances appear in Figure 3 and Figure 4. The conformation of the $Cr(CO)_3$ entities of complexes **2** and **3** are very similar, adopting an almost staggered conformation. The

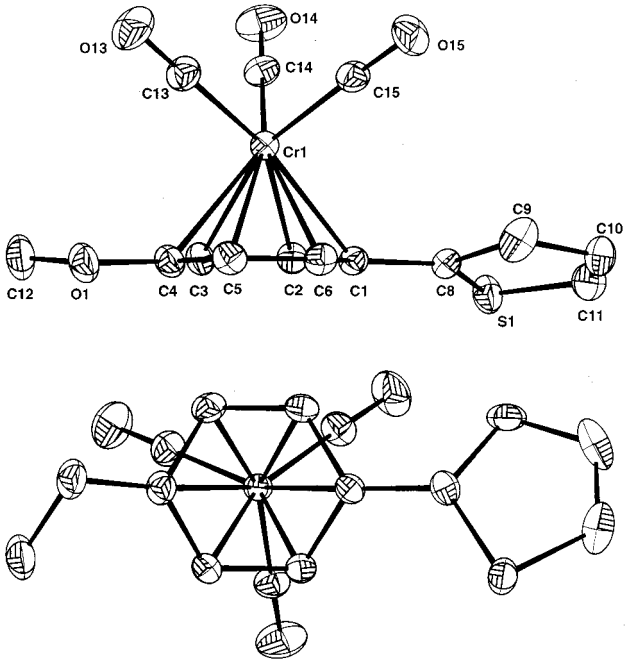

Figure 3. Two views of ORTEP diagram of complex **2**. Selected bond lengths [A]: Cr–C-1 2.233(3), Cr–C-2 2.201(3), Cr–C-3 2.251(3), Cr–C-4 2.289(3), Cr–C-5 2.221(3), Cr–C-6 2.203(3), C-8–C-9 1.46(2), C-10–C-11 1.326(2)

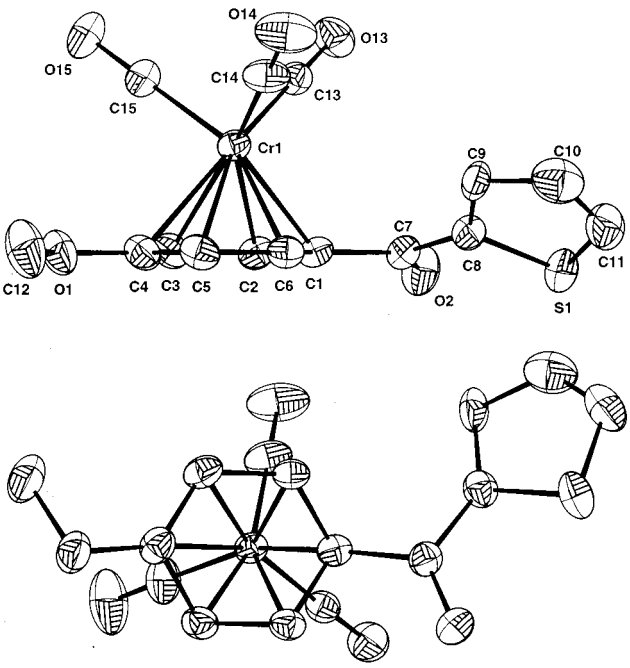

Figure 4. Two views of ORTEP diagram of complex **3**. Selected bond lengths [A]: Cr–C-1 2.181(4), Cr–C-2 2.206(4), Cr–C-3 2.238(4), Cr–C-4 2.282(4), Cr–C-5 2.242(4), Cr–C-6 2.181(4), C-8–C-9 1.52(3), C-10–C-11 1.326(7), C-7–O-2 1.216(5)

values of the torsion angles C-2–C-100–Cr–C-14, C-4–C-100–Cr–C-13, and C-6–C-100–Cr–C-15 for **2** (C-100 being the centre of the six-membered ring) are 22.73°, 22.41°, and 23.12°, respectively. The corresponding values C-2–Cr–C-100–C-13, C-6–Cr–C-100–C-14, and C-4–Cr–C-100–C-15 for **3** are 20.76°, 22.42°, and 21.76°, respectively. These data clearly show that the solid state and solution conformations of the $Cr(CO)_3$ entities are almost the same for complex **2**, but are different for complex **3**. It is interesting to point out that in the case of complex **2**, the thiophene plane is not parallel to the arene plane, the dihedral angle being 19°. In the case of complex **3**, the carbonyl function is not in the plane of the arene ring, the carbonyl pointing out in the direction opposite to the $Cr(CO)_3$ entity with dihedral angles of 14° (with the six-membered arene ring) and of 23° (with the thiophene ring). These features could partially explain why the carbonyl group does not play a complete electron-withdrawing effect in the solid state.

Conclusion

By using the same coupling reaction, we were able to selectively synthesise, in high yield, [(2-thiophenyl)-η⁶-arene]- and [(2-thiophenyl)oxo-η⁶-arene]tricarbonylchromium complexes by slightly modifying the reaction conditions. This methodology addresses the potentiality of this highly versatile bimetallic activation in the preparation of new arenechromiumtricarbonyl complexes.

Experimental Section

General: All experiments were protected at all times from exposure to light and oxygen. Workup procedures were done in air. Tetrahy-

drofuran (THF) used was distilled from sodium benzophenone ketyl under dry nitrogen. – ^{1}H- and ^{13}C-NMR spectra were obtained with Bruker 200 and ARX 400 spectrometers. – Infrared and UV/Vis spectra were recorded with Perkin–Elmer 1420 and Shimadzu 1420 spectrometers, respectively. – Elemental analyses were performed by Le Service de Microanalyses de l'Université Pierre et Marie Curie. – Melting points were measured with a Reichert apparatus. The coupling procedures using 2-thienylzinc chloride and thienylboronic acid had been reported in ref.[10] (4-Anisole)tricarbonylchromium complex was prepared according to ref.[18]

Coupling Reaction with 2-(Tributylstannyl)thiophene. – General Procedure: $Pd_2(dba)_3$ (0.025 g, 0.05 mmol) and $AsPh_3$ (0.06 g, 0.2 mmol) were added successively to complex **1** (0.280 g, 1 mmol) and 20 mL of anhydrous DMF. After 30 min at room temperature, 2-tributylstannylthiophene (0.355 g, 1 mmol) in 5 mL of DMF was added. The mixture was stirred at room temperature for 20 h, poured into 100 mL of ice cold water, and extracted twice with 50 mL of diethyl ether. The combined organic phases were dried on magnesium sulfate and evaporated under reduced pressure. The residue was then purified by flash chromatography on silica gel (petroleum ether/ethyl acetate 75:25) to afford complexes **2** (R_f = 0.36) and **3** (R_f = 0.27) as a yellow and an orange solid, respectively.

Complex 2: M.p. 189–190 °C (Et_2O/petroleum ether 1:1). – IR (CH_2Cl_2): $\tilde{\nu}$ = 1965 cm^{-1} ($Cr(CO)_3$), 1885 cm^{-1} ($Cr(CO)_3$). – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 334 nm (8860), 232 (3400). – ^{1}H NMR ($CDCl_3$): δ = 3.72 (s, 3 H, OCH_3), 5.20 (d, J = 7.1 Hz, 2 H, H-3), 5.92 (d, J = 7.1 Hz, 2 H, H-2), 6.94 (m, 1 H, H-10), 7.18 (d, J = 4.7 Hz, 1 H, H-11), 7.23 (d, J = 3.8 Hz, 1 H, H-9). – ^{1}H NMR (C_6D_6): δ = 2.88 (s, 3 H, OCH_3), 4.37 (d, J = 7.0 Hz, 2 H, H-3), 5.25 (d, J = 7.0 Hz, 2 H, H-2), 6.56 (m, 1 H, H-10), 6.66 (d, J = 4.7 Hz, 1 H, H-11), 6.77 (d, J = 3.4 Hz, 1 H, H-9). – ^{13}C NMR ($CDCl_3$): δ = 56.1 (C-12), 77.5 (C-3), 93.3 (C-2), 96.7 (C-1), 124.6 (C-11), 125.9 (C-9), 127.3 (C-8), 128.0 (C-10), 142.2 (C-4), 232.7 (CO). – MS (70 eV); *m/z* (%): 327 (14) [M^{+1}], 191 (100) [M^{+1} – $Cr(CO)_3$]. – $C_{14}H_{10}CrO_4S$ (326.3): calcd. C 51.33, H 3.09; found C 51.56, H 3.10.

Complex 3: M.p. 160–161 °C (Et_2O/petroleum ether 1:1). – IR (CH_2Cl_2): 1975 cm^{-1} ($Cr(CO)_3$), 1900 cm^{-1} ($Cr(CO)_3$), 1645 (CO). – UV/Vis (CH_2Cl_2): λ_{max} (ε) = 302 nm (39300), 230 (25100). – ^{1}H NMR ($CDCl_3$): δ = 3.78 (s, 3 H, OCH_3), 5.19 (d, J = 7.0 Hz, 2 H, H-3), 6.32 (d, J = 7.1 Hz, 2 H, H-2), 7.17 (m, 1 H, H-10), 7.70 (d, J = 4.9 Hz, 1 H, H-11), 7.84 (d, J = 3.7 Hz, 1 H, H-9). – ^{1}H NMR (C_6D_6): δ = 2.85 (s, 3 H, OCH_3), 4.23 (d, J = 7.1 Hz, 2 H, H-3), 5.82 (d, J = 7.1 Hz, 2 H, H-2), 6.55 (m, 1 H, H-10), 6.81 (d, J = 4.5 Hz, 1 H, H-11), 7.60 (d, J = 3.8 Hz, 1 H, H-9). – ^{13}C NMR ($CDCl_3$): δ = 56.1 (C-12), 76.6 (C-3), 93.3 (C-1), 121.9 (C-8), 128.2 (C-10), 133.2 (C-11), 134.1 (C-9), 144.1 (C-4), 230.7 (C-7), 232.2 (CO). – MS (70 eV); *m/z* (%): 355 (18) [M^{+1}], 219 (40) [M^{+1} – $Cr(CO)_3$]. – $C_{15}H_{10}CrO_5S$ (354.3): calcd. C 50.85, H 2.85; found C 50.67, H 2.70.

Crystal Structure of 2: $[(CO)_3Cr(C_{11}H_{10}OS)]$, M = 326.3, μ = 0.972 mm^{-1}; ρ = 1.59 gcm^{-3} orthorhombic, $P2_12_12_1$, Z = 4, a = 8.111(1), b = 11.196(1), c = 15.027(2) Å, V = 1364.6(3) Å^3, from 25 reflections (34° < 2θ < 34.6°). Cell dimensions and intensities were measured at 295 K on a Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å). ω/2θ scans, two standard reflections measured every two hours showed no significant variation 1° < θ < 30° (0 < h 11, 0 < k < 15, 14 < l < 21); 2293 measured reflections, 2268 unique reflections of which 2001 were observed {$[F_o]^2 > 3\sigma([F_o]^2)$}. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using SHELXS,[19] all other calculations used CRYSTALS.[20] Atomic scattering factors and anomalous dispersion terms were taken from ref.[21] Full-matrix least-squares refinement based on [F] and a Chebychev weighting scheme gave final values R = 0.0383, wR = 0.0432 and s = 1.04 for 201 variables and 2001 contributing reflections. The maximum shift/esd on the last cycle was 1.71. Non-hydrogen atoms were anisotropically refined. A disorder was observed on the thiophene group between the sulfur atom S(1) and the carbon atom C(9). The best solution was obtained by a model with two positions with an occupancy of approximately 0.63/0.37. Hydrogen atoms were introduced in calculated positions (except on the thiophene group) and only an overall isotropic thermal parameter was refined. The final difference electron density map showed a maximum of 0.27 and a minimum of –0.38 eÅ^{-3}.

Crystal Structure of 3: $[(CO)_3Cr(C_{12}H_{10}O_2S)]$, M = 354.3, μ = 0.892 mm^{-1}; ρ = 1.56 g.cm^{-3} triclinic, P –1, Z = 2, a = 7.355(5), b = 10.520(3), c = 10.665(6) Å, α = 109.56(3), β = 93.65(5), γ = 101.91(4)°, V = 752.9(7) Å^3, from 25 reflections (26° < 2θ < 28°). Cell dimensions and intensities were measured at 295 K on a Nonius CAD4 diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069Å). ω/2θ scans, two standard reflections measured every hour showed no significant variation 1° < θ < 28° (0 < h < 9, –13 < k < 13, 14 < l < 14); 3907 measured reflections, 3628 unique reflections of which 2311 were observed ($[F_o]^2 > 3\sigma([F_o]^2)$); R_{int} = 0.04 for equivalent reflections. Data were corrected for Lorentz and polarization effects. The structure was solved by direct methods using SHELXS,[19] all other calculations used CRYSTALS.[20] Atomic scattering factors and anomalous dispersion terms were taken from ref.[21] Full-matrix least-squares refinement based on [F] and a Chebychev weighting scheme gave final values R = 0.0587, wR = 0.0711 and s = 1.04 for 245 variables and 2311 contributing reflections. The maximum shift/esd on the last cycle was 1.75. Non-hydrogen atoms were anisotropically refined. A disorder was observed on the thiophene group between the sulfur atom S(1) and the carbon atom C(9). The best solution was obtained by a model with two positions with an occupancy of approximately 0.65/0.35. Hydrogen atoms (except on the thiophene group) were located on a difference Fourier map; their coordinates were refined with an overall isotropic thermal parameter. The final difference electron density map showed a maximum of 0.47 and a minimum of –0.58 eÅ^{-3}.

Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication n° CCDC 132984 and CCDC 132985. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1 EZ, UK (Fax: (internat.) +44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk).

Acknowledgments

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[12] To our knowledge, the CO inserted organometallic compound formation was reported in only one example under analogous conditions depending upon the nature of the *ortho*-substituent of the chromium complex (see refs. [7d], [7i]).

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