Tetracarbonyl Ferrate Derivatives of (η^6-arene)Cr(CO)$_3$: New Reagents for Carbon–Carbon Bond Formation

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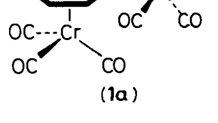
The reaction of $Na_2[Fe(CO)_4]$ and (η^6-ClC_6H_5)$Cr(CO)_3$ in tetrahydrofuran/*N*-methylpyrrolidinone (THF/NMP) produces Na[(η^6-{$(CO)_4Fe$}C_6H_5)$Cr(CO)_3$], while various (η^6-*o*-$LiXC_6H_4$)$Cr(CO)_3$ derivatives react with $Fe(CO)_5$ to produce Li[(η^6-*o*-{$(CO)_4Fe(CO)$}XC_6H_4)$Cr(CO)_3$] complexes.

Arene π-complexes of chromium tricarbonyl substrates have been extensively used in synthetic transformations such as simple ring-forming reactions,[1] spirocyclization processes,[2] and stereo- and enantio-selective nucleophilic substitution reactions.[3] Despite the general ease of synthesis of (η^6-arene)$Cr(CO)_3$ complexes, the $Cr(CO)_3$ template can be incompatible with sensitive functional groups if it is introduced late in a synthetic scheme.[4] In addition, the site of $Cr(CO)_3$ addition to molecules containing several arene substituents frequently cannot be controlled.[5] For these reasons, new reagents capable of selectively delivering functionalized arene π-complexes to target molecules are clearly desirable. As one aspect of our efforts to achieve this goal, we report the preparation and preliminary studies of the reactivity of the first tetracarbonyl ferrate-substituted π-arene complexes.

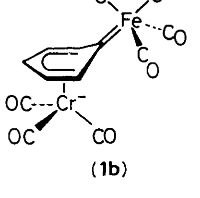
In the first such example of nucleophilic aromatic substitution, freshly prepared $Na_2[Fe(CO)_4]$[6] reacts with (η^6-ClC_6H_5)$Cr(CO)_3$[4a] in 1 : 1 tetrahydrofuran/*N*-methylpyrrolidinone (THF/NMP) to produce a 45% yield of Na[(η^6-{$(OC)_4Fe$}C_6H_5)$Cr(CO)_3$](**1**), as shown in equation (1).† Compound (**1**) can be isolated as a yellow crystalline solid by extraction into degassed water, followed by precipitation with aqueous tetra-alkyl ammonium halides. I.r. and ^{1}H n.m.r. spectroscopic data suggested that (**1**) adopts the η^6-arene structure (**1a**) as opposed to the alternative η^5-cyclohexadienyl carbene structure (**1b**).[7]

$$Na_2[Fe(CO)_4] + (\eta^6\text{-}ClC_6H_5)Cr(CO)_3 \xrightarrow[22\,°C,\ 12\,h]{1:1\ THF/NMP} \underset{(\mathbf{1})}{Na[(\eta^6\text{-}\{(OC)_4Fe\}C_6H_5)Cr(CO)_3]} + NaCl \quad (1)$$

Reactions between (η^6-*o*-$LiXC_6H_4$)$Cr(CO)_3$[1a] and $Fe(CO)_5$ at −35 °C in ether solutions, outlined in equation (2), result in the formation of Li[(η^6-*o*-{$(OC)_4Fe$-



(**1a**)



(**1b**)

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† Pertinent i.r. and n.m.r. data for (**1**): i.r. data for the CO stretching region (KBr pellets, cm^{-1}) 2017.8, 1947.5, 1023.3, 1892.7, 1877.0, 1853.8, 1831.4; ^{1}H n.m.r. data ([^{2}H$_6$] acetone, 22 °C) δ 5.69 (2H, d, J_{CH} 6.3 Hz, *o*-Ar), 5.26 (2H, t, J_{CH} 6.3 Hz, *m*-Ar), 5.08 (1H, t, J_{CH} 6.3 Hz, *p*-Ar), 3.49, 1.39 (Et_4N^+ counterion).

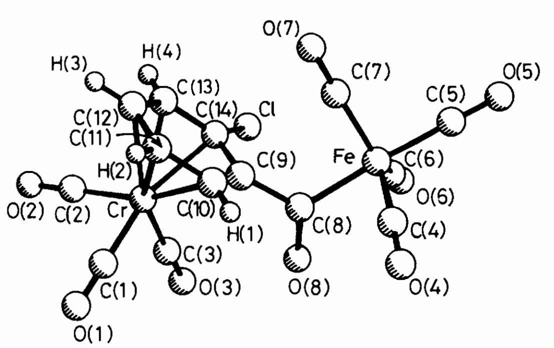


Figure 1. PLUTO depiction of the *X*-ray crystal structure of $[\text{Et}_4\text{N}][(\eta^6\text{-}o\text{-}\{(\text{OC})_4\text{Fe(CO)}\}\text{ClC}_6\text{H}_4)\text{Cr(CO)}_3]$ (**2a**). Selected bond distances (Å) and angles: Fe–C(7) 1.777(7), Fe–C(4) 1.777(6), Fe–C(6) 1.779(7), Fe–C(5) 1.780(6), Fe–C(8) 1.991(6), Cr–C(13) 2.202(5), Cr–C(14) 2.202(6), Cr–C(12) 2.209(6), Cr–C(11) 2.211(5), Cr–C(10) 2.229(5), Cr–C(9) 2.250(5), Cl–C(14) 1.739(5), C(8)–O(8) 1.218(6), C(7)–Fe–C(4) 116.2(3), C(7)–Fe–C(6) 122.3(3), C(4)–Fe–C(6) 120.8(3), C(6)–Fe–C(8) 84.7(2), C(6)–Fe–C(5) 91.3(3), C(5)–Fe–C(8) 175.5(3), C(9)–C(8)–Fe 115.7(4), O(8)–C(8)–Fe 126.4(4), O(8)–C(8)–C(9) 117.9(5), C(8)–C(9)–Cr 134.6(4), Cl–C(14)–Cr 129.0(3).

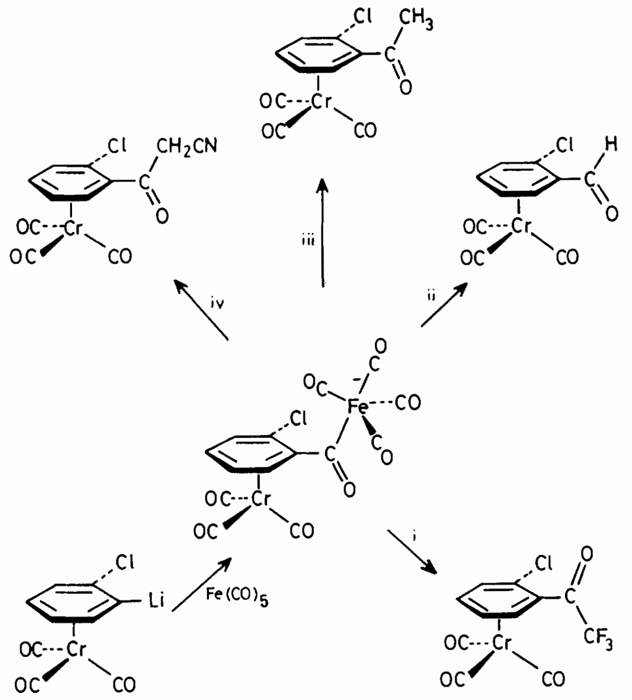
$(\text{CO})\}\text{XC}_6\text{H}_4)\text{Cr(CO)}_3]$ (**2**).‡ These molecules are the first examples of metal–acyl-substituted π-arene reagents. The products are moderately air-stable and also can be isolated as yellow-orange crystalline tetra-alkylammonium salts. Typical yields of crystalline (**2a**; X = Cl) vary between 40 and 80%.

$$(\eta^6\text{-}o\text{-LiXC}_6\text{H}_4)\text{Cr(CO)}_3 + \text{Fe(CO)}_5 \xrightarrow{\text{THF, }-35\,^\circ\text{C}} \text{Li}[(\eta^6\text{-}o\text{-}\{(\text{OC})_4\text{Fe(CO)}\}\text{XC}_6\text{H}_4)\text{Cr(CO)}_3] \quad (2)$$

(2)

(X = Cl, F, OMe, H)

A PLUTO depiction of the *X*-ray crystal structure of $[(\eta^6\text{-}o\text{-}\{(\text{OC})_4\text{Fe(CO)}\}\text{ClC}_6\text{H}_4)\text{Cr(CO)}_3]^-$ is shown in Figure 1.§ The structure confirms the regiospecificity of acyl substitution at the arene. The acryl unit lies perpendicular to the arene plane [torsional angles: Fe–C(8)–C(9)–C(10) 89.0° and Fe–C(8)–C(9)–C(14) 86.0°] and *anti* with respect to the Cr(CO)_3 fragment [torsional angle: Cr–C(9)–C(8)–O(8) 2.3°] to minimize steric interactions. The Cr(CO)_3 unit shows only a slight distortion from symmetrical bonding to the arene, as expected, slipping away from the sterically crowded C(9) and C(10) centres of the 'vinyl acyl' unit of the arene by 0.027 and 0.048 Å, respectively. An Fe–C(8) bond distance of 1.991 Å and C(8)–O(8) bond distance of 1.218 Å are nearly identical to the distances found for corresponding bonds in a recently characterized acyl pivaloyl ferrate complex.[8a] The acyl unit apparently shows some carbene character through a slight shortening of the $\text{Fe–C}_{\text{acyl}}$ bond and a corresponding lengthening of the C–O_{acyl} bond. The $\text{Fe–C}_{\text{carbene}}$ bond in a *bona-fide* oxy-carbene complex is 1.819(3) Å, significantly shorter than that observed in (**2a**).[8b]



Scheme 1. *Reagents*: i, $(\text{CF}_3\text{CO})_2\text{O}/\text{CH}_2\text{Cl}_2$; ii, $\text{HBF}_4\cdot\text{OEt}_2/\text{CO}/\text{THF}$; iii, MeI or $\text{Me}_3\text{OBF}_4/\text{CH}_2\text{Cl}_2$; iv, $\text{NCCH}_2\text{I}/\text{THF}/\text{CO}$.

Preliminary studies of the reactivity of (**1**) and (**2a**) are outlined in Scheme 1. Compound (**1**) has, thus far, shown no evidence of carbonyl insertion into the Fe–C(Ar) bond under CO pressure or in the presence of phosphine ligands. Like other alkyl tetracarbonyl ferrate derivatives, (**1**) is completely converted to its parent hydrocarbon, in this case $(\eta\text{-C}_6\text{H}_6)\text{Cr(CO)}_3$, on acidification.[9] Complex (**2a**) reacts at room temperature with a variety of electrophiles to produce $(\eta\text{-}o\{\text{ROC}\}\text{ClC}_6\text{H}_4)\text{Cr(CO)}_3$ derivatives. The reaction of (**2a**) with HBF_4 in non-protic solvents leads to formation of a 1 : 1 mixture of $(\eta^6\text{-}o\text{-}\{\text{HOC}\}\text{ClC}_6\text{H}_4)\text{Cr(CO)}_3$ and $(\eta\text{-ClC}_6\text{H}_5)\text{Cr(CO)}_3$. An identical protonation performed under CO pressure (1 atm) nearly eliminates the decarbonylation by-product, resulting in formation of the aldehyde in >80% yield.

The convenient preparative route to these iron–acyl derivatives, together with their ability to participate in C–C bond forming reactions, suggests that they will be useful reagents for introducing functionalized (η-arene)Cr(CO)_3 fragments into complex molecules.

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‡ Pertinent analytical data for (**2a**): i.r. data for the CO stretching region (KBr pellet, cm^{-1}) 2023.6, 1900.1, 1877.0, 1868.7, 1591.5; ^1H n.m.r. data ([$^2\text{H}_6$]acetone, 22 °C) δ 5.58 (2H, m), 5.46 (1H, d, J_{HH} 6.3 Hz), 5.33 (1H, m), 3.49, 1.39 (Et_4N^+ counterion); ^{13}C n.m.r. data ([$^2\text{H}_6$]acetone, 23 °C) δ 234.3 [s, Cr(CO)_3], 220.3 [s, Fe(CO)_4], 252.3, 252.4 [s, $(\text{CO})\text{Fe(CO)}_4$], 132.7, 106.2 (s, ipso-Ar), 93.4, 92.2, 91.2, 90.7 (d, J_{CH} 161 Hz, Ar), 53.0, 7.6 (Et_4N^+ counterion).

§ *Crystal data* for (**2a**): (23 °C) M = 487.55, orthorhombic, a = 14.413(2), b = 29.253(3), c = 11.691(1) Å, Z = 8, D_c = 1.31 g cm^{-3}, space group *Pbca* (No. 61). All calculations were performed using the TEXSAN (© Molecular Structure Corporation) crystallographic software package. Of 3676 unique reflections collected (Mo-K_α, $6° \leq 2\theta \leq 45°$), the 2096 having $F > 3\sigma(F)$ were used in the final cycle of the least-squares refinement. Hydrogen atom positions were included in the structure factor calculation in idealized positions (d_{CH} = 0.95 Å), and were assigned isotropic thermal parameters which were 20% greater than the B_{eq} value of the atom to which they were bonded. Final residuals are: $R(F)$ = 0.037, $R_w(F)$ = 0.045. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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References

1 (a) M. F. Semmelhack, J. Bisaha, and M. Czarny, *J. Am. Chem. Soc.*, 1979, **101**, 768; (b) M. F. Semmelhack, Y. Thebtaranonth, and L. Keller, *ibid.*, 1977, **99**, 959.

2 M. F. Semmelhack and A. Yamashita, *J. Am. Chem. Soc.*, 1980, **102**, 5926.

3 M. F. Semmelhack, G. R. Clark, J. L. Harrison, Y. Thebtaranonth, W. Wulff, and A. Yamashita, *Tetrahedron*, 1981, **37**, 3957.

4 (a) B. Nicholls and M. C. Whiting, *J. Chem. Soc.*, 1959, 511; (b) G. R. Knox, D. G. Leppard, P. L. Paulson, and W. E. Watts, *J. Organomet. Chem.*, 1972, **35**, 347.

5 B. Deubzer, H. P. Fritz, C. G. Kreiter, and K. Ofele, *J. Organomet. Chem.*, 1967, **7**, 289.

6 H. Strong, P. J. Krusic, and J. San Fillippo, *Inorg. Synth.*, 1986, **24**, 157.

7 (a) M. F. Semmelhack, H. T. Hall, J. Farina, M. Yoshifuji, G. Clark, K. Airotsu, and J. Clardy, *J. Am. Chem. Soc.*, 1979, **101**, 3535; (b) M. Brookhart, W. Lamanna, and A. P. Pinhas, *Organometallics*, 1983, **2**, 638.

8 (a) K. H. Dotz, V. Wenicker, G. Muller, H. G. Alt, and D. Seyferth, *Organometallics*, 1986, **5**, 2570; (b) K. H. Dotz, H. Fischer, P. Hoffman, F. R. Kreissl, V. Schubert, and F. Weiss, 'Transition Metal Carbene Complexes,' Verlag Chemie, Weinheim, 1983.

9 J. P. Collman, *Acc. Chem. Res.*, 1975, **8**, 342.