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CYCLOPENTADIENYL RING METALATION IN CYCLOPENTADIENYLIRON CARBONYL COMPLEXES

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Summary

The cyclopentadienyl ligands in $Cp(CO)_2FePh$, $Cp(CO)_2FeCH_2Ph$ and $[Cp(CO)_2Fe]_2$ were metalated by BuLi in THF at −78°C. With $Cp(CO)_2FePh$ it was possible to employ the reaction for the synthesis of cyclopentadienyl carbonyl complexes substituted on the Cp ligands.

Cyclopentadienyliron carbonyl complexes $[Cp(CO)_2Fe]_2$ or $Cp(CO)_2FeR$ (where R is a σ-bonded alkyl or aryl group) are known since 1955 [1,2], but practically no date are available on substitution reactions of the Cp ligands of these complexes, the single exception being the communication on the $[Cp(CO)_2Fe]_2$ acetylation reaction giving rise to a monoacyl derivative [3]. During this study another report appeared concerning Cp ligand metalation in $Cp(CO)_2FeSiMe_3$ [4].

We had previously investigated the reactivity of the cyclopentadienyliron carbonyl complexes using the hydrogen isotope exchange method and found that hydrogen atoms of Cp ligands in $Cp(CO)_2FePh$ (I), as well as in $Cp(CO)_2FeCH_2Ph$ (II) and $[Cp(CO)_2Fe]_2$ (III) [5,6] underwent hydrogen exchange under conditions favouring protophilic substitution. The C–H acidity of Cp ligands estimated from hydrogen exchange constants turned out to be rather high: close to the acidity of the Ph_3CH methyne group (pK_a 29) for I and to that of Ph_2CH_2 methylene group for II and III ($pK_a 30$) [7].

Taking these data into account we examined the possibility of metalation of cyclopentadienyliron carbonyl complexes.

Results and discussion

We found that metalation of Cp ligands takes place when I–III are treated with n-butyllithium in THF solution at −78°C. Treatment of lithium derivatives with D_2O affords the corresponding deuterated complexes $DC_5H_4(CO)_2FePh$ (IV),

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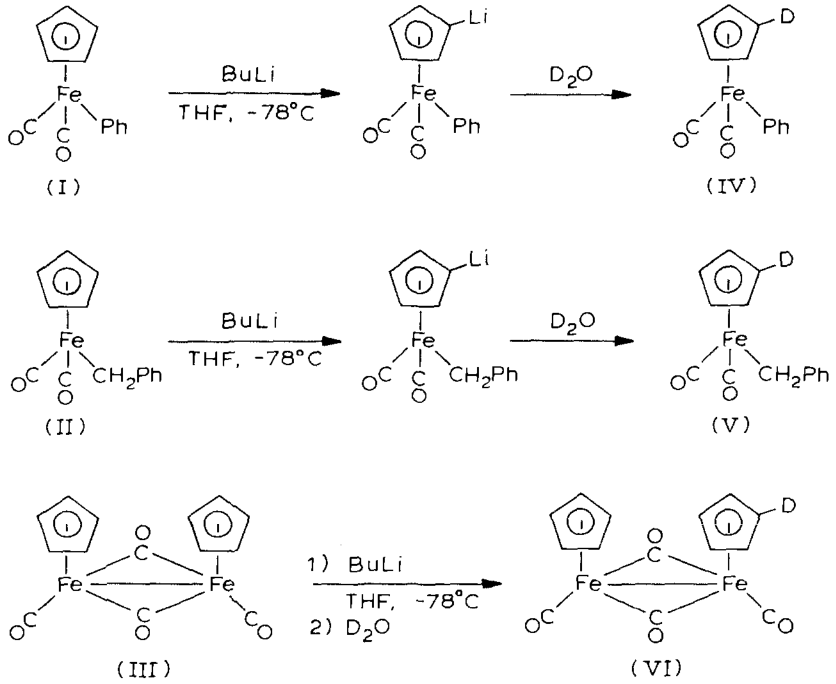
$DC_5H_4(CO)_2FeCH_2Ph$ (V) and $DC_5H_4Cp(CO)_4Fe_2$ (VI). The mass spectra of IV–VI include ions at m/z 122 ($C_5H_4DFe^+$); those of IV and V also include ions at m/z 77 ($C_6H_5^+$) and m/z 91 ($CH_2C_6H_5^+$), respectively. So these data show that deuterium is present in a Cp ligand only. Besides, from the mass spectra it transpires that as a result of metalation not only mono-, but also di- and tri-deuterated derivatives form, which indicates the possibility of introducing several lithium atoms into a molecule. Yields and spectral characteristics of complexes IV–VI are given in Table 1.



The ability of the Cp ligand in complexes I–III to be metalated allows the introduction of a variety of substituents onto the Cp ring, and hence the preparation of new derivatives of these systems.

TABLE 1

YIELDS AND IR, NMR AND MASS SPECTRAL DATA FOR COMPLEXES IV–VI

Complex	Yield (%)	IR: ν(CO) (cm^{-1}) (in CCl_4)	^1H NMR (δ, ppm) (in CCl_4)	M^+ (m/z)
IV	70	1969, 2021	4.6(s,4,Cp) 6.8(m,3,Ph) 7.4(m,2,Ph)	255
V	80	1951, 2021	2.8(s,2,CH_2) 4.6(s,4,Cp) 7.1(m,5,Ph)	269
VI	40	1788, 1965, 2009	4.7(s,Cp)	355

For the example of $Cp(CO)_2FePh$ we have shown that Cp ring-substituted complexes $RC_5H_4(CO)_2FePh$ can be obtained in good yields. Thus, treatment of the reaction mixture containing $LiC_5H_4(CO)_2FePh$ with an excess of Me_3ECl (E = Si, Sn) or RX (R = Me, Et; X = I, Br) gives rise to the complexes $Me_3SiC_5H_4(CO)_2FePh$ (VII), $Me_3SnC_5H_4(CO)_2FePh$ (VIII) $MeC_5H_4(CO)_2FePh$ (IX) and $EtC_5H_4(CO)_2FePh$ (X).

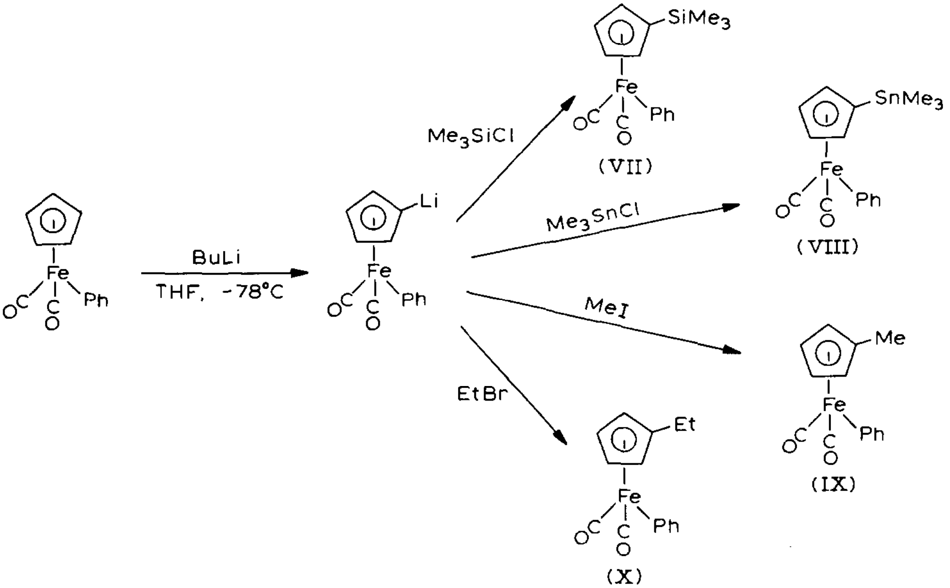


TABLE 2

YIELDS, ANALYTICAL DATA AND IR, ^1H NMR AND MASS SPECTRAL DATA FOR COMPLEXES VII–X

	Yield (%)	Analyses: Found(calcd) (%)				IR ν(CO) (cm^{-1}) (in hexane)	^1H NMR (δ, ppm) (in CCl_4)	M^+ (m/z)
		C	H	Si	Fe			
VII	90	59.4 (59,40)	5.8 (5.53)	8.3 (8.6)	16.6 (17.15)	1968 2019	0.1(s,9,Me) 4.6(s,4,Cp) 6.7(m,3,Ph) 7.2(m,2,Ph)	326
VIII	35					1975 2025	0.1(s,9,Me) 4.4(s,4,Cp) 6.9(m,3,Ph) 7.2(m,2,Ph)	403 [a]
IX	50	62.6 (62.60)	4.8 (4.48)		21.2 (20.90)	1970 2020	1.7(s,3,Me) 4.5(m,2,Cp) 4.7(m,2,Cp) 6.9(m,3,Ph) 7.2(m,2,Ph)	268
X	85					1958 2010	0.9(m,3,Me) 1.4(m,2,CH_2) 4.7(m,2,Cp) 4.9(m,2,Cp) 7.2(m,5,Ph)	282

[a] m/z 403 corresponds to $[M\text{-Me}]^+$ [8].

Complexes VII, VIII and X are viscous liquids; complex IX is a crystalline solid, m.p. 35°C. Yields, analytical data and IR, PMR and mass spectral data are given in Table 2.

Experimental

Experiments were carried out under an argon atmosphere. THF was distilled from $LiAlH_4$ before use. $Cp(CO)_2FePh$ was obtained from $[Cp(CO)_2Fe]Na$ and Ph_2IBF_4 [9], and $Cp(CO)_2FeCH_2Ph$ was obtained from $[Cp(CO)_2Fe]Na$ and $PhCH_2Cl$ [10].

IR spectra were taken on a UR-20 spectrometer, PMR spectra were recorded with a Perkin-Elmer R-20 spectrometer (60 MHz). Mass spectra were measured with MS-30 and Finigan-4000 mass spectrometers.

Lithiation of $Cp(CO)_2FePh$, $Cp(CO)_2FeCH_2Ph$ and $[Cp(CO)_2Fe]_2$; synthesis of $DC_5H_4(CO)_2FePh$, $DC_5H_4(CO)_2FeCH_2Ph$, $DC_5H_4Cp(CO)_4Fe_2$, $Me_3SiC_5H_4(CO)_2FePh$, $Me_3SnC_5H_4(CO)_2FePh$, $MeC_5H_4(CO)_2FePh$ and $EtC_5H_4(CO)_2FePh$

3.5 ml (3–4 mmol) of 0.8–0.9 *N* n-butyllithium solution in hexane were added at -78°C to 0.2 g (1 mmol) $Cp(CO)_2FeR$ ($R = Ph$ or CH_2Ph) or 0.3 g (1 mmol) $[Cp(CO)_2Fe]_2$ in 20 ml THF. The reaction mixture was stirred for 10–15 min and then a 10–50 fold excess of D_2O, Me_3SiCl, Me_3SnCl, MeI or EtBr was added. The mixture was stirred until it reached room temperature. Solvent was removed under reduced pressure and residue was chromatographed on Al_2O_3, the reaction product being eluted with hexane or a hexane benzene (1/1) mixture.

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