Electronic Supplementary Material (ESI) for RSC Advances

Supporting Information for:

Role of basic sites of substituted ferrocenes in interaction with the trinuclear 3,5-bis(trifluoromethyl)pyrazolates: thermodynamics and structure of complexes

Alexey A. Titov[†], *Oleg A. Filippov*[†], *Ekaterina A. Guseva*[†], *Alexander F. Smol'yakov*[†], *Fedor M. Dolgushin*[†], *Lina M. Epstein*[†], *Vitaly K. Belsky*[‡], *Elena S. Shubina*[†]*

[†]A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences, Vavilov str. 28, 119991 Moscow, Russia

[‡]L.Ya. Karpov Institute of Physical Chemistry, Vorontsovo Pole St. 10, 103064, Moscow, Russia

IR spectroscopy

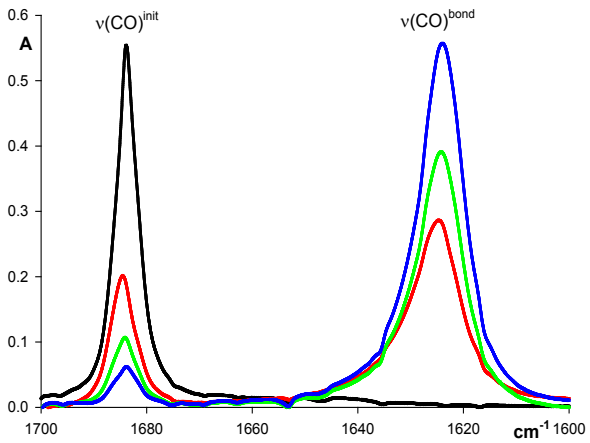


Figure S1: IR spectra in the ν(CO) range $FcC(O)CH_3$ (0.001 M, 230 K, black) and in the presence of $[AgL]_3$ (0.001 M) in hexane at different temperatures: 290 K (red line), 260 K (green line), 240 K (blue line), d= 0.12 cm.

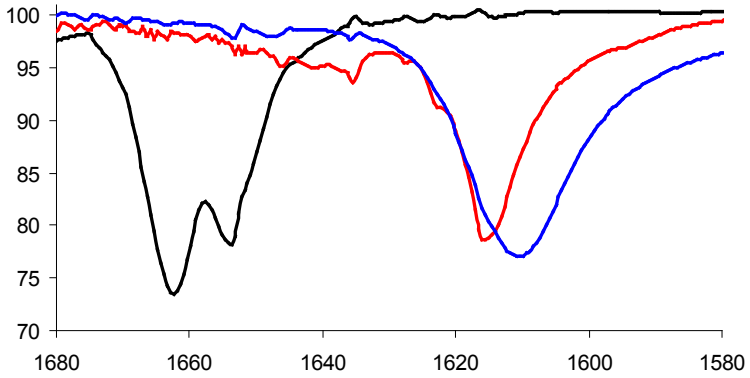


Figure S2 : The solid IR spectra in the ν(CO) range of the of $FcC(O)CH_3$ (black line) and it's crystals with $[AgL]_3$ (red), with $[CuL]_3$ (blue), nujol.

Table S1: IR spectral characteristics of the two bands in the range ν(CO) of $FcC(O)CH_2Ph$.

ν cm^{-1}	Hexane	THF	CH_2Cl_2	CH_3CN
ν_1	1688	1680	1672	1673
ν_2	1674	1667	1660	1661
D_2/D_1	2.15 (290K)	1,56(290K) 1,34(190K)		

NMR spectoscopy

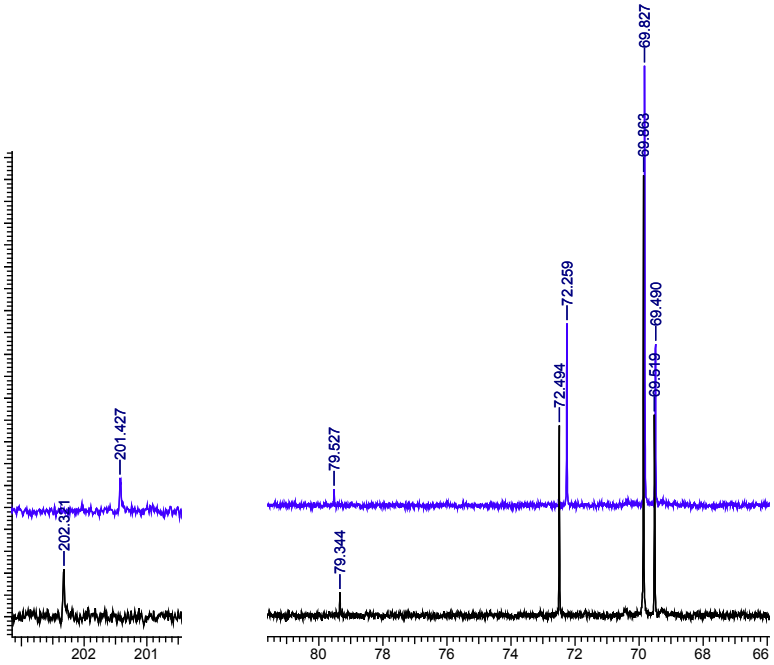


Figure S3: ^{13}C NMR spectra of $FcC(O)CH_3$ (297K blue line) and in the presence of $[AgL]_3$ (black line), DCM.

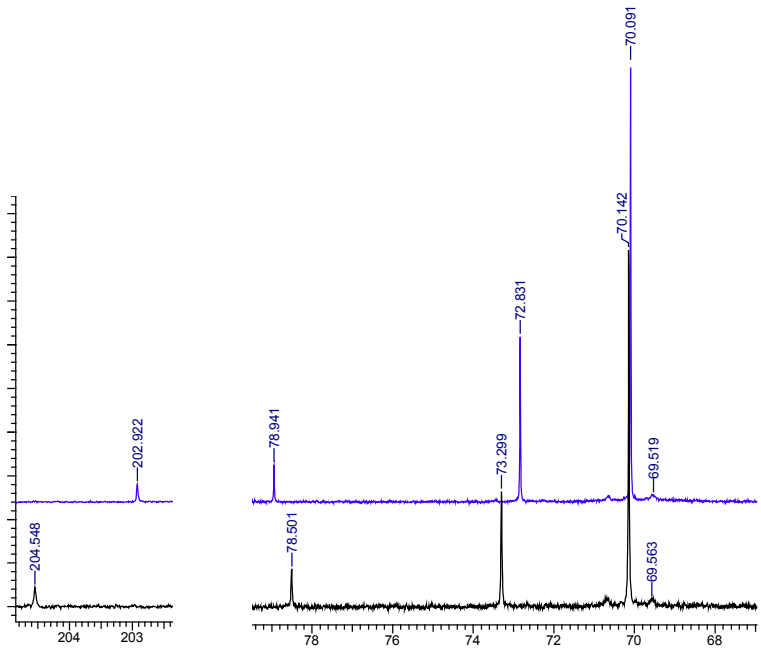


Figure S4: ^{13}C NMR spectra of $FcC(O)CH_3$ (213K blue line) and in the presence of $[AgL]_3$ (black line), DCM.

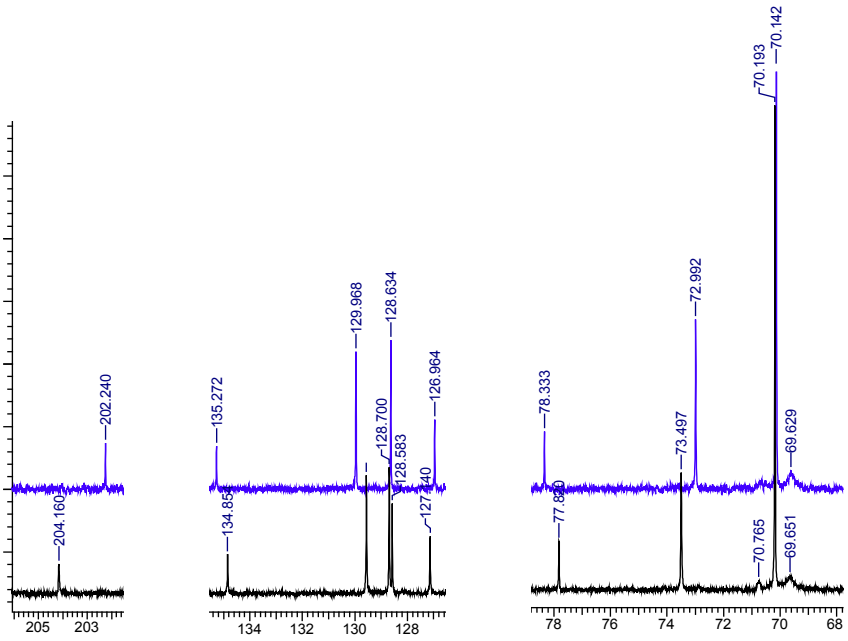
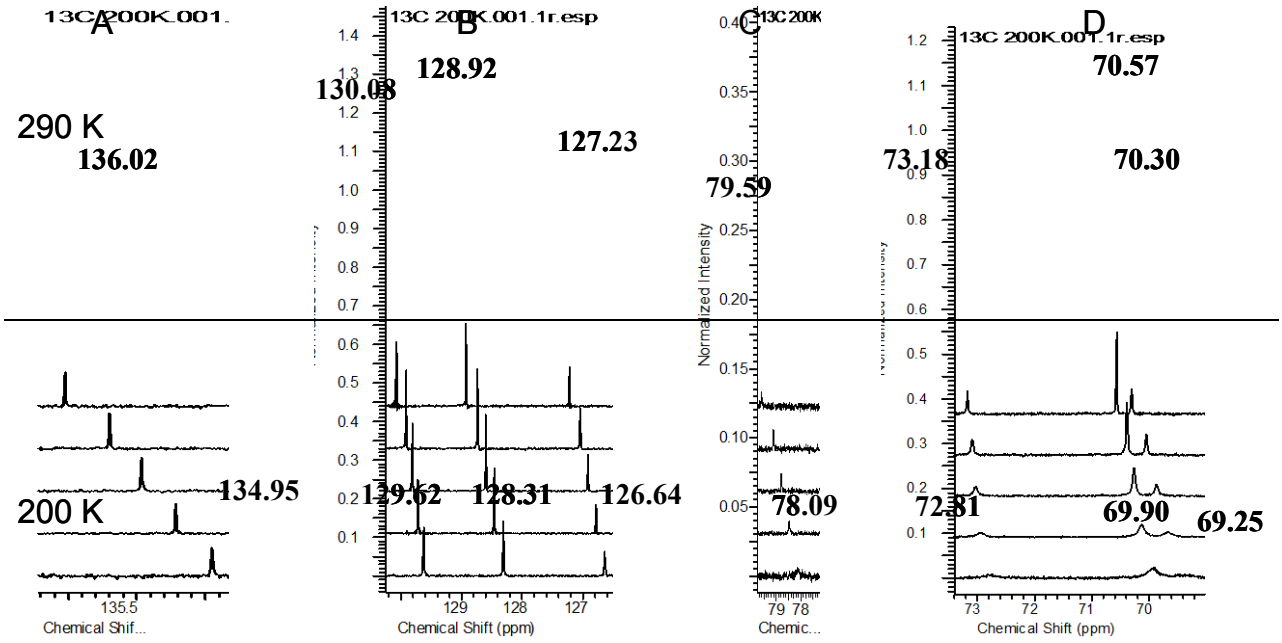


Figure S5: ^{13}C NMR spectra of $FcC(O)CH_2Ph$ (213K, blue line) and in the presence of $[AgL]_3$ (black line), DCM.



FigureS6: ^{13}C NMR of **2** at different temperature in CD_2Cl_2 , (Ph (A,B) and Cp (D,C) ranges), DCM.

Procedure for formation constants calculation from UV-vis spectra.

The absorbance at band maximum (463 nm) was expressed as:

$$D^{463} = \left(\varepsilon^{ketone} \cdot [ketone] + \varepsilon^{compl} \cdot [compl]\right) \cdot d \qquad (1)$$

Where D is absorbance, ε^{ketone} and ε^{compl} is extinction coefficients at given wavelength of nonbonded ketone and complex correspondingly, [ketone] and [compl] equilibrium concentrations of nonbonded ketone and ketone binded with macrocycle.

$\varepsilon^{ketone} = 284$ (l/(mol*cm)) was measured directly form UV experiment, while for ε^{compl} determination the value of formation constant from IR experiment at 290K was used. Taking into account mass balance and formation constant equations:

$$[ketone] + [compl] = C_{CO}$$

$$[[ML]_3] + [compl] = C_{[ML]_3}$$

$$K^f_{290} = \frac{[compl]}{[ketome] \cdot [[ML]_3]}$$

the values of equilibrium concentrations at 290 K were calculated and from equitation 1 the ε^{compl} value was obtained ($\varepsilon^{compl} = 802$ (l/(mol*cm)) for $\{1 \cdot [ML]_3\}$)

Because of negligible change of phenylacetylferrocene E values from temperature we assume same behaviour of complexes and use ε^{compl} values for formation constants calculation assuming that changes of absorbance at 463 nm caused by change of [ketone] and [compl] in the same extent:

$$\Delta D^{463} = \left(\varepsilon^{ketone} \cdot -\Delta[ketone] + \varepsilon^{compl} \cdot \Delta[compl]\right) \cdot d = \Delta C \cdot d \cdot (\varepsilon^{compl} - \varepsilon^{ketone})$$

$$K^f_T = \frac{[compl]_{290} + \Delta C_T}{([ketone]_{290} - \Delta C_T) \cdot ([[ML]_3]_{290} - \Delta C_T)}$$

where ΔC_T is change of complex concentration between given temperature T and 290K.