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Halogenophilic pathway in the reactions of transition metal carbonyl anions with [(η^6-iodobenzene)Cr(CO)$_3$]

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Electronic supplementary information

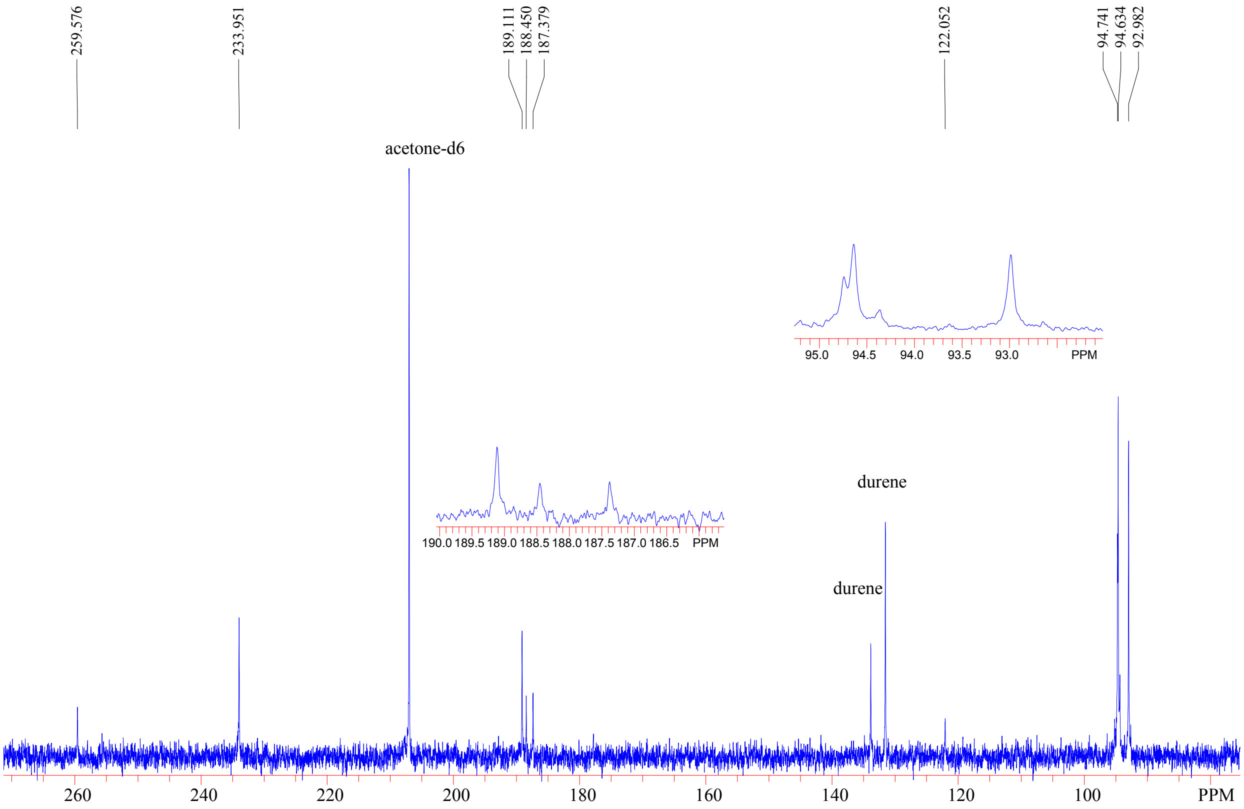

Figure S1. The ^{13}C NMR spectrum of Na[(η^6-C_6H_5CORe(CO)$_4$I)Cr(CO)$_3$] formed in the reaction of [(η^6-C_6H_5I)Cr(CO)$_3$] with Na[Re(CO)$_5$] (THF, 100.6 MHz).

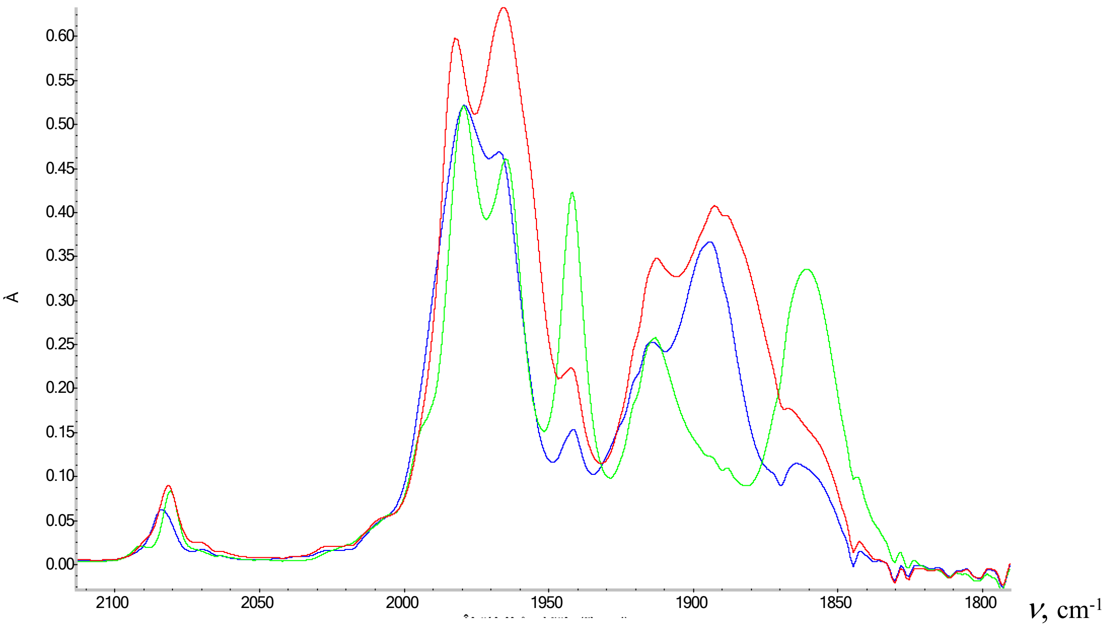

Figure S2. The IR spectra of rhenate anions in THF (superimposed for comparison):
the iodo(acyl)rhenate Na[(η^6-C_6H_5CORe(CO)$_4$I)Cr(CO)$_3$] (blue);
the same iodo(acyl)rhenate in the presence of 18-crown-6 (red);
the iodo(aryl)rhenate [Et$_4$N][(η^6-C_6H_5Re(CO)$_4$I)Cr(CO)$_3$ (green).
Weak bands at 1942 and 1865 cm^{-1} in the spectra of iodo(acyl)rhenate belong to a small impurity of iodo(aryl)rhenate.

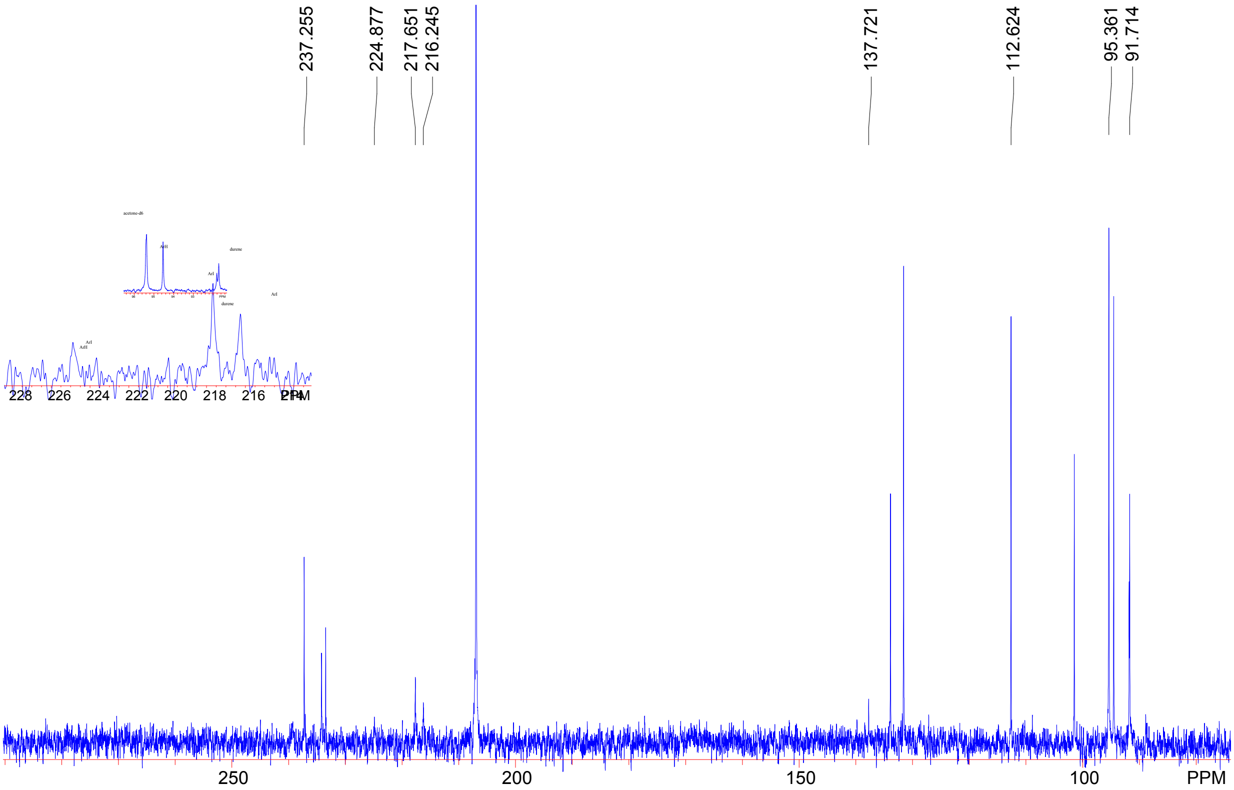

Figure S3. The ^{13}C NMR spectrum for the completed reaction of $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ with $K[Mn(CO)_5]$ at r.t. in the presence of 18-crown-6 (THF, 100.6 MHz).
The main component is $K[(\eta^6\text{-}C_6H_5Mn(CO)_4I)Cr(CO)_3]$ (its peaks are labeled), also present are the starting $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ (labeled “ArI”) and its dehalogenation product, $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$, (labeled “ArH”).

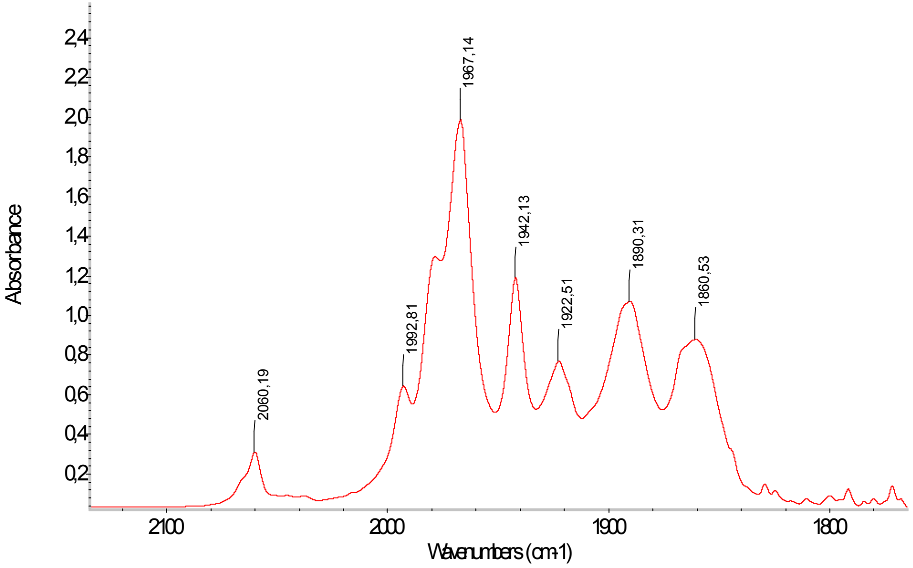

Figure S4. The IR spectrum for the completed reaction of $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ with $K[Mn(CO)_5]$ at r.t. in the presence of 18-crown-6 in THF.

The spectrum is mainly that of $K[(\eta^6\text{-}C_6H_5Mn(CO)_4I)Cr(CO)_3]$, except for the bands at 1890 cm^{-1} and 1967 cm^{-1} belonging to $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$ and a weak band at 1993 cm^{-1} and shoulder at 2066 cm^{-1} belonging to $K[Mn(CO)_4I_2]$[1].

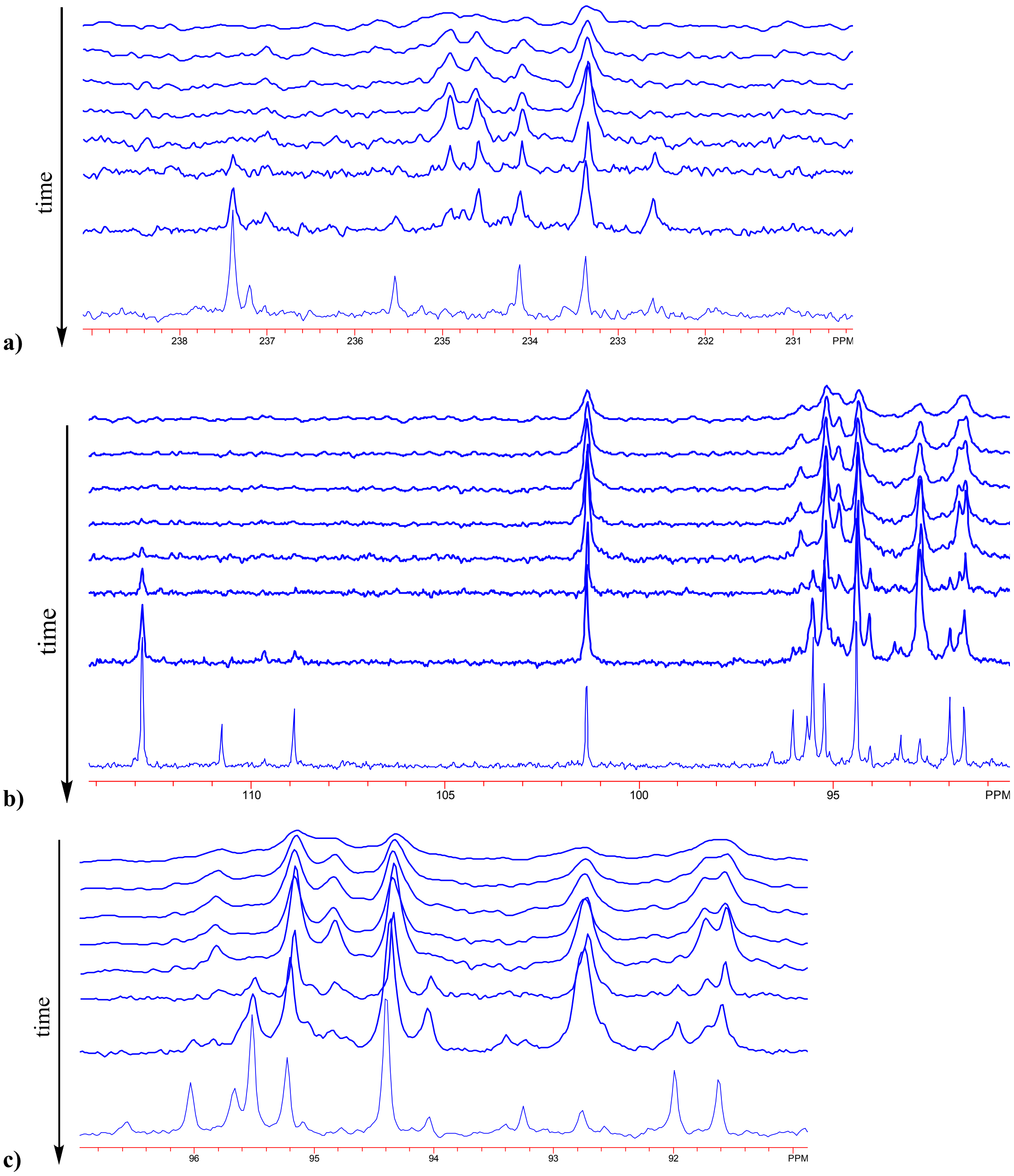

Figure S5. Time dependence of the ^{13}C NMR spectra for the reaction of $[(\eta^{6}\text{-}C_6H_5I)Cr(CO)_3]$ (0.19 mmol) with $K[Mn(CO)_5]$ (0.15 mmol) in THF (0.6 ml) at r.t.

The spectra (from top to bottom) were taken after 13 min (1); 16 min (2); 19 min (3); 22 min (4), 26 min (5); 33 min (6); 70 min (7) and 25 hr (8, at the bottom), the last one corresponds to the reaction completion.

a) Signals in the $Cr(CO)_3$ region. The signals of two intermediates appear at 234.6 and 235 ppm (signal at 234.1 belongs to $[(\eta^{6}\text{-}C_6H_6)Cr(CO)_3]$).

b, c) Signals of the arene ligands. The signals assigned to the $K[(\eta^{6}\text{-}C_6H_5C(O)Mn(CO)_4I)Cr(CO)_3]$ intermediate can be seen at 95.8, 94.8 and 91.7 ppm, they decay already after 30 min (6 th spectrum). The second intermediate manifested by the signal at 92.7 ppm (actually two signals as seen in other experiments with better resolution) continues to build up till 70 min, but disappears towards the end of the reaction.

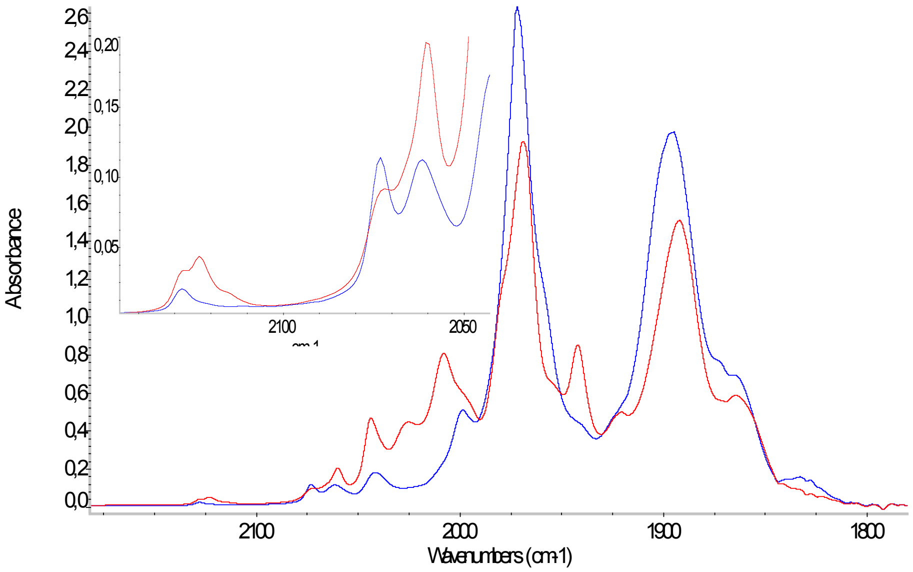

Figure S6. Time dependence of the IR spectra for the reaction of $[(\eta^{6\text{-}}C_6H_5I)Cr(CO)_3]$ with $K[Mn(CO)_5]$ in THF at r.t.

The first spectrum (blue) was taken 20 min after the start of the reaction, and shows the band at 2073 cm^{-1} attributed to iodo(acyl)manganate intermediate $K[(\eta^6\text{-}C_6H_5C(O)Mn(CO)_4I)Cr(CO)_3]$, which almost disappears in the second spectrum (red, taken after 4 hr), while the bands at 2060 and 1942 cm^{-1} belonging to $K[(\eta^6\text{-}C_6H_5Mn(CO)_4I)Cr(CO)_3]$ appear, as well as the bands of other products – 2123 and 2027 cm^{-1} of $[(\eta^6\text{-}C_6H_5Mn(CO)_5)Cr(CO)_3]$, 2044 and 2008 of $[Mn_2(CO)_{10}]$.

Strong bands at 1890-1900 and 1965-1970 cm^{-1} visible in both spectra are mainly composed of the overlapping bands belonging to $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ (main component in the first spectrum) and $[(\eta^6\text{-}C_6H_6)Cr(CO)_3]$. In the first spectrum (blue) one can also see bands at 1830 and 1865(sh) belonging to $K[Mn(CO)_5]$[2].

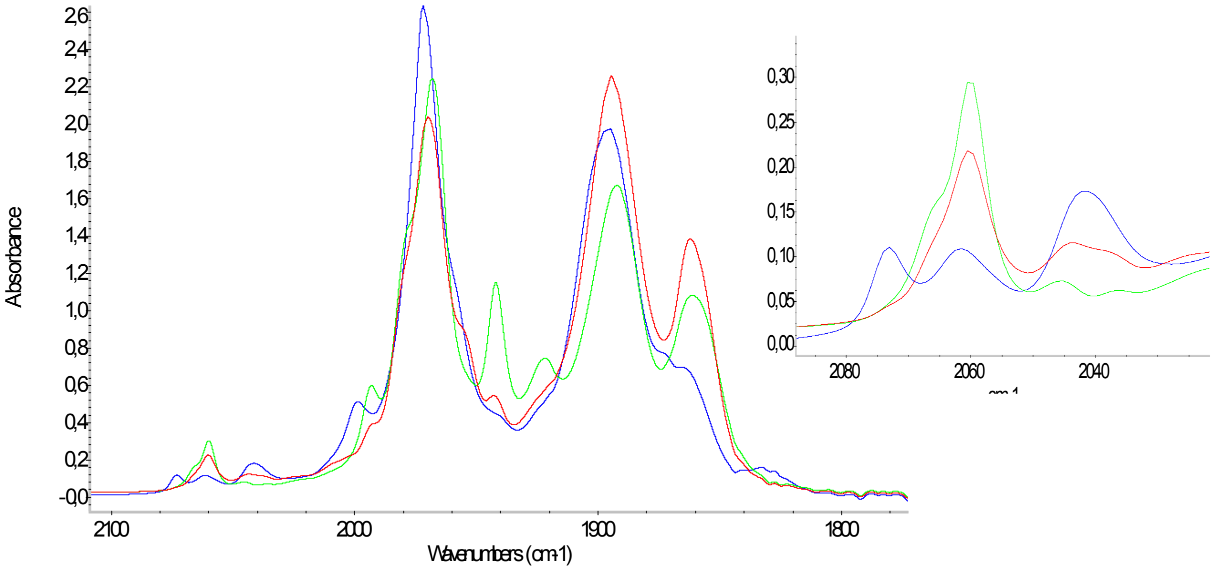

Figure S7. The effect of 18-crown-6 addition on the IR spectra of the reaction of $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ with $K[Mn(CO)_5]$ in THF at r.t..

The first spectrum (blue) was taken 20 min after the start of the reaction (it's the same as in Fig. S6). On the addition of 18-crown-6 to this reaction solution (red spectrum) the band at 2073 cm^{-1} attributed to the $K[(\eta^6\text{-}C_6H_5C(O)Mn(CO)_4I)Cr(CO)_3]$ disappears, and at 2060 cm^{-1} a new band appears, coinciding with the highest frequency band of iodo(aryl)manganate (Fig. S4). However, it cannot belong to iodo(aryl)manganate because at the moment its band at 1942 cm^{-1} is very weak. The band at 2060 cm^{-1} must then belong to the iodo(acyl)manganate intermediate. The large difference in the position of this band in the presence of 18-crown-6 (2060 cm^{-1}) and in THF alone (2073 cm^{-1}) can be attributed to the formation of contact ion pairs by $K[(\eta^6\text{-}C_6H_5C(O)Mn(CO)_4I)Cr(CO)_3]$ in THF, which are transformed into crown-separated ion pairs upon the addition of 18-crown-6. The Na cation is better solvated by THF than K [2], and the corresponding iodo(acyl)rhenate $Na[(\eta^6\text{-}C_6H_5CORe(CO)_4I)Cr(CO)_3]$ forms solvent-separated ion pairs, which is evidenced by a small shift of the corresponding band (from 2084 to 2082 cm^{-1}) upon the addition of 18-crown-6 (Figure S2).

The iodo(aryl)metallate anions do not have a localized hard donor center (acyl oxygen) for cation coordination and form solvent-separated ion pairs in THF, and the position of their highest frequency CO-band coincides with that for the corresponding acylmetallates in the presence of 18-crown-6 (2060 cm^{-1} for manganates and 2081-2082 cm^{-1} for rhenates).

The third spectrum (green) was taken from the same reaction mixture 4 hr after the 18-crown-6 addition. The band of iodo(aryl)manganate at 1942 cm^{-1} is now seen in the spectrum as well as weak band at 1993 cm^{-1} and sholder at 2066 cm^{-1} belonging to $[K\cdot 18\text{-crown-}6][Mn(CO)_4I_2]$ [1].

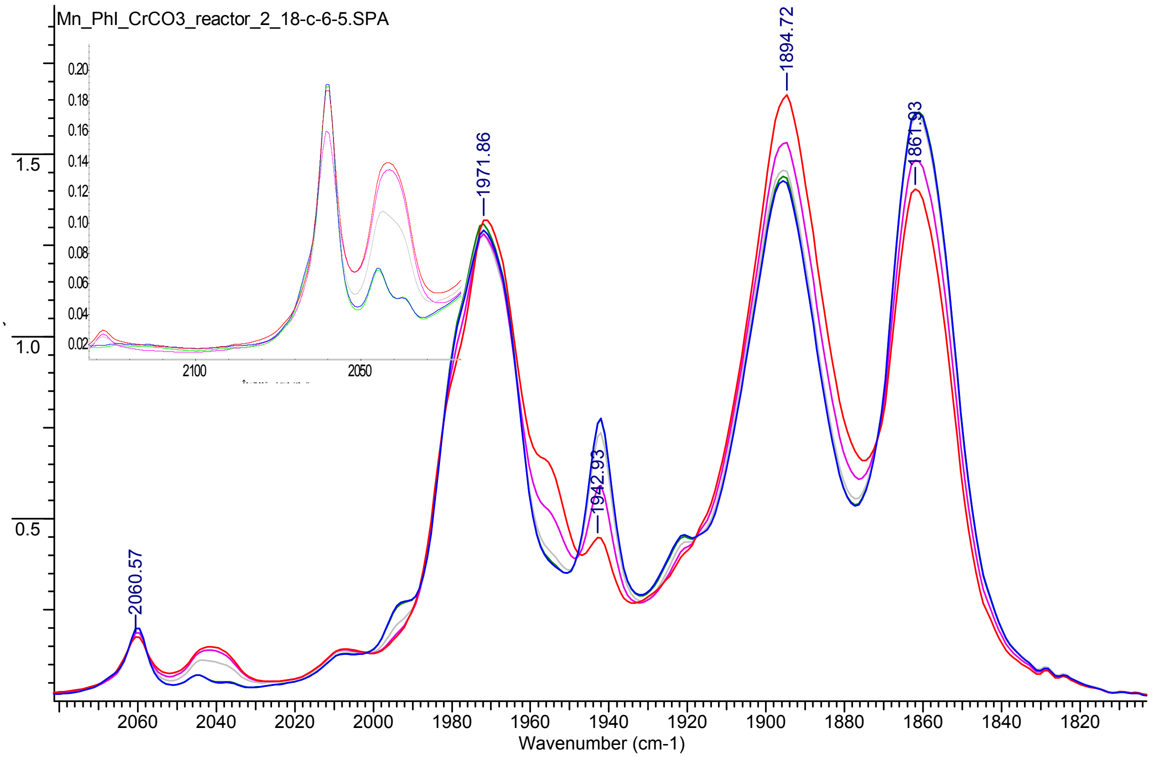

Figure S8. Time dependence of the IR spectra for the reaction of [(η^{6-}C$_6$H$_5$I)Cr(CO)$_3$] with K[Mn(CO)$_5$] in the presence of 18-crown-6 in THF at r.t.

The probe of reaction mixture was taken after 15 min, diluted to ~2·10^{-2} mol·l^{-1} and transferred to IR-cell (red line), the following spectra were recorded after 7 min (magenta), 23 min (grey), 67 min (green), 130 min (blue). The growth of the band at 1942 cm^{-1} corresponds to the buildup of iodo(aryl)manganate, K[(η^6-C$_6$H$_5$Mn(CO)$_4$I)Cr(CO)$_3$] and the decay of weak bands at 2040 and 2128 cm^{-1} corresponds to the disappearance of the small amount of [Mn(CO)$_5$I] formed as intermediate.

The band at 2060 cm^{-1} is already present in the first spectrum and grows only slightly, which means that it is a superposition of bands belonging to iodo(aryl)manganate product and the intermediate, K[(η^6-C$_6$H$_5$C(O)Mn(CO)$_4$I)Cr(CO)$_3$] (see also comments to Fig. S7).

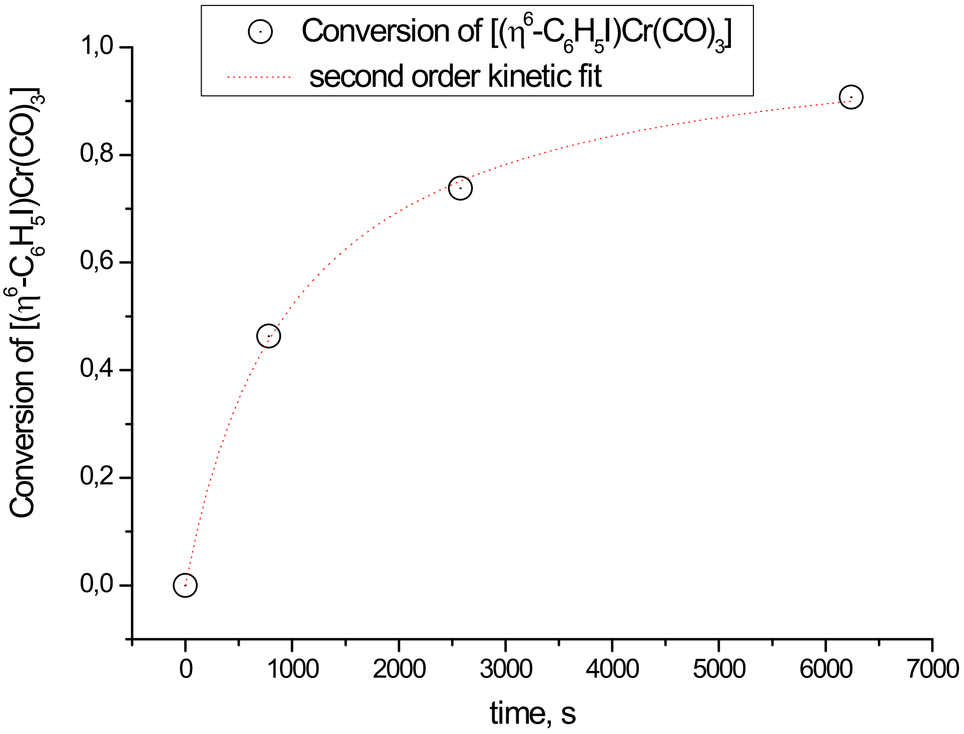

Figure S9. The rate plot for the reaction of $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ with $K[Mn(CO)_5]$ in the presence of *t*-BuOH. The conversion was determined by ^1H NMR spectroscopy using durene as internal standard.

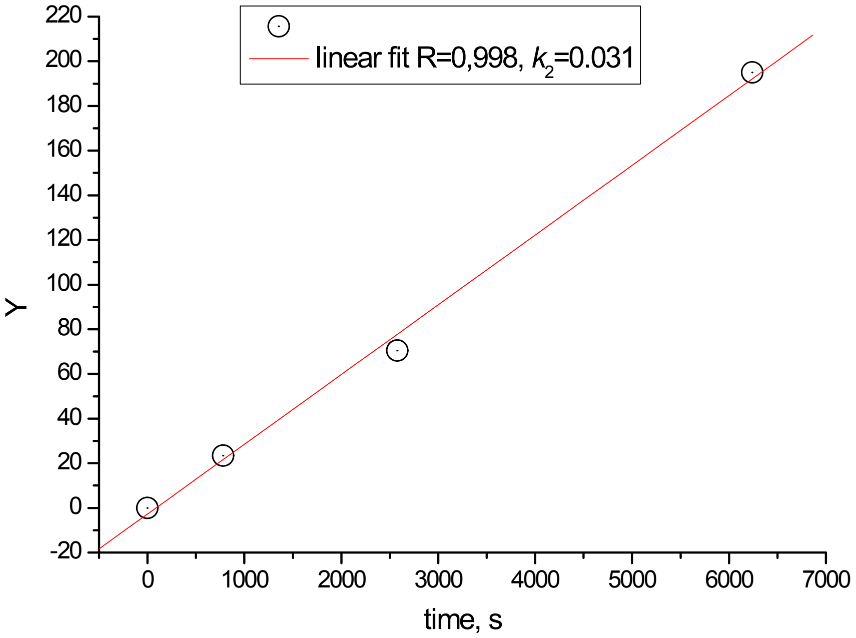

Figure S10. The linearization of kinetic curve (anamorphosis) for the reaction of $[(\eta^6\text{-}C_6H_5I)Cr(CO)_3]$ with $K[Mn(CO)_5]$ in the presence of *t*-BuOH. The Y-coordinate corresponds to the second order kinetic law: $Y=\frac{1}{([ArI]_0-[KMn(CO)_5]_0)}\cdot\frac{[KMn(CO)_5]_0\cdot[ArI]}{[KMn(CO)_5]\cdot[ArI]_0}$

References

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[2] M. Y. Darensbourg, D. J. Darensbourg, D. Burns, D. A. Drew, *J. Am. Chem. Soc.* **1976**, *98*, 3127.