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# The Electrophilic Reactivity of Homotropylium Chromium Tricarbonyl Hexafluorophosphate[1]

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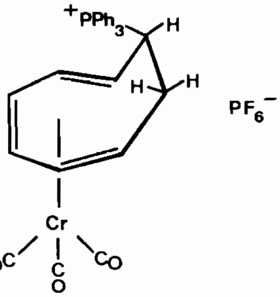
In a previous communication[2] we reported the reaction of alkylphosphines with tropylium compounds of molybdenum and tungsten and of triphenylphosphine ($PPh_3$) with the homotropylium molybdenum tricarbonyl cation. At low temperatures only nucleophilic addition to the ring system is observed. The resultant compounds are however not stable in room temperature solutions.

As the addition of alkylphosphines to $[C_7H_7Cr(CO)_3]BF_4$ gives a stable compound,[3] we investigated the analogous reaction of $[C_8H_9Cr(CO)_3]PF_6$ with $PPh_3$. Even at low temperatures a ready reaction is observed between equimolar amounts of the starting materials in $CH_2Cl_2$. The orange powder, that precipitates on addition of ether, analyses as $[C_8H_9PPh_3Cr(CO)_3]PF_6$ (I). The IR spectrum (in $CH_2Cl_2$) shows resonances at 1930, 1945 and 2002 $cm^{-1}$. As no decomposition was observed in room temperature solutions, we recorded the $^{13}C$ NMR spectrum to determine whether the phosphonium ligand was coordinated as a 1,3,5- or as a 1,3,6-cyclooctatriene.

The $^{13}C$ spectrum supports the assignment of a cycloocta-1,3,5-triene structure to the organic moiety.

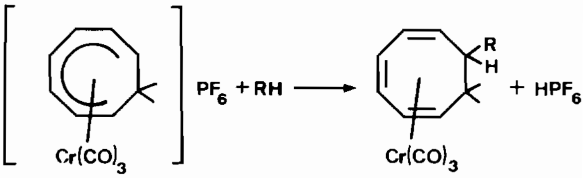


(I)

Molecular models indicate that under the assumption of an *exo*-position of the $PPh_3$ group, which is to be expected from the work of Pauson,[4] a 1,3,6-configuration in the complexed ligand would not be sterically feasible due to strong transannular hindrance.

The reduction of $[C_8H_9M(CO)_3]PF_6$ (M = Cr, Mo) with $NaBH_4$ also leads exclusively to 1,3,5-$C_8H_{10}M(CO)_3$, although we have recently been able to synthesize 1,3,6-$C_8H_{10}M(CO)_3$ for M = Cr, Mo by another route.[5]

As the work of Kane-Maguire has shown[6] that cationic dienyl iron compounds as well as $[C_7H_7Cr(CO)_3]BF_4$ can act as electrophilic reagents on aromatic compounds and β-diketones, we also reacted $[C_8H_9Cr(CO)_3]PF_6$ with indole, acetylacetone and dimedone. In all cases a rapid reaction was observed and the addition products could be isolated and fully characterised.



(II), R = indole
(III), R = acetylacetone
(IV), R = dimedone

$[C_8H_9Cr(CO)_3]PF_6$ appears to be a stronger electrophile than $[C_7H_7Cr(CO)_3]BF_4$, as reaction of indole with the former is rapid and complete even with equimolar amounts.

## Experimental

$[C_8H_9Cr(CO)_3]PF_6$ was prepared by literature methods.[7] The organic chemicals were commercial samples.

### *Preparation of I*

$[C_8H_9Cr(CO)_3]PF_6$ (2 mmol) was suspended in 4 ml $CH_2Cl_2$ and 2 mmol of $PPh_3$ was added. The resultant clear red solution was slowly dropped into 75 ml ether, giving a pale orange powder, yield 95%. *Anal.* $C_{29}H_{24}CrF_6O_3P_2$ requires C 53.72, H 3.73, F 17.57. Found: C 53.88, H 3.78, F 17.49. $^{13}C$ NMR (ppm, relative to internal TMS, $d_3$-nitromethane): phenylic carbons: 136, 134 (d, $J_{C-P}$ 10 Hz), 131 (d, 12 Hz), 118 (d, 82 Hz); olefinic carbons: 107, 101, 98, 97, 95 (d, 23 Hz), 81 (d, 4,5 Hz); aliphatic carbons: 44 (d, 31 Hz), 24.

### *Preparation of II, III and IV*

$[C_8H_9Cr(CO)_3]PF_6$ was dissolved in 5 ml acetone and the organic reagent (1 equivalent) was added.

After stirring for 2 minutes 50 ml of water was added. III and IV separate as a fine orange powder, which is dried. No further purification is necessary. II separates as a red oil, which is recrystallised from hexane/ether 20/80 at – 70 °C. Yield 70–80%.

(II) *Anal.* $C_{19}H_{16}CrNO_3$ requires C 63.68, H 4.49, Cr 14,50. Found: C 63.74, H 4.47, Cr 14.55. IR ($CH_2Cl_2$): 1890, 1916, 1981 $cm^{-1}$.

(III) *Anal.* $C_{16}H_{17}CrO_5$ requires C 56.30, H 5.01, Cr 15.23. Found: C 56.32, H 4.84, Cr 15.13. IR ($CH_2Cl_2$): 1715, 1900, 1926, 1987 $cm^{-1}$.

(IV) *Anal.* $C_{19}H_{21}CrO_5$ requires C 59.84, H 5.54, Cr 13.63. Found: C 59.57, H 5.47, Cr 13.43. IR ($CH_2Cl_2$): 1713, 1890, 1919, 1985 $cm^{-1}$.

## Acknowledgements

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