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The Reaction of Tertiary Phosphines with Tropylium Chromium Tricarbonyl Tetrafluoroborate

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The recent communication by Deganello *et al.*[1] on the reaction of PPh_3 with the tropylium molybdenum tricarbonyl cation prompts us to report some contrasting observations made by us on the chromium analogue.

Treatment of $[C_7H_7Cr(CO)_3]BF_4$ (I) with the strongly nucleophilic phosphines PEt_2Ph and PBu_3, leads to direct attack on the 7-membered ring only, rather than attack at the metal. The products are the red crystalline air-stable phosphonium salts $[R'_2R''PC_7H_7Cr(CO)_3]BF_4$ (II) ($R' = Et$, $R'' = Ph$; $R' = R'' = Bu^n$). This is similar to the reported reaction of phosphines with tricarbonyl iron cyclopentadienyl systems[2] and with $[C_7H_9Mo(CO)_3]^+$.[3] Although PPh_3 did not undergo reaction with I on prolonged stirring in CH_2Cl_2, addition of PPh_3 to an acetone solution of I caused an immediate colour change from orange to red. The I.R. spectrum of the mixture showed, besides peaks due to the starting material at 2064 and 2023 cm^{-1}, peaks at 1989, 1929 and 1899 cm^{-1} (*cf.* 1986, 1925 and 1895 cm^{-1} for $[Et_2PhPC_7H_7Cr(CO)_3]BF_4$). Increasing the molar excess of PPh_3 also increased the relative intensity of the lower frequency peaks. But even with a 50-fold excess of PPh_3, some tropylium salt still remained in solution. These data indicate that in acetone solution the following equilibrium is set up

$$[C_7H_7Cr(CO)_3]BF_4 + PPh_3 \rightleftharpoons [Ph_3PC_7H_7Cr(CO)_3]BF_4$$

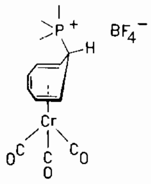
However addition of ether to these mixtures resulted in precipitation of the starting material only.

We were unsuccessful in attempts to prepare $[C_7H_7Cr(CO)_2PPh_3]BF_4$ (III) even by applying the same procedure used by Deganello *et al.*[1] for the Mo analogue. However, a ring substituted analogue of III, prepared by another route, has been reported.[4]

Evidently, the 7-membered ring in the chromium compound is more electrophilic than that in its molybdenum analogue. The higher carbonyl stretching frequencies of the Mo compound[5] may indicate less metal-to-ring back bonding in the Cr compound. Thus more charge is drained out of the tropylium ring in the Cr compound than in its Mo analogue with the result that the incoming nucleophile (PPh_3) is directed towards the ring, rather than the metal, in I.

Tropylium molybdenum tricarbonyl tetrafluoroborate also reacted rapidly with PEt_2Ph in CH_2Cl_2, but the only isolable product was *fac*-$(Et_2PhP)_3Mo(CO)_3$.[6]

The ^1H NMR spectra of II bear a striking resemblance to that of $C_7H_8Cr(CO)_3$ (IV). Assuming similar molecular geometries for II and IV, then the triorganophosphorus group would appear to be in an exo position with respect to the metal as shown in the diagram.



This is to be expected from the work of Pauson.[7]

Treatment of the phosphonium salts II with Ph_3CBF_4 gave quantitative regeneration of I.

Attempts to induce the salts II to undergo proton abstraction and subsequent Witting reaction have not so far been successful. The products of such a reaction would be the known coordinated heptafulvenes.[4]

Experimental

$C_7H_7Cr(CO)_3BF_4$[7] and $C_7H_7Mo(CO)_3BF_4$[8] were prepared by literature methods. Other chemicals were commercial samples.

Preparation of II

To a suspension of I (1 mmol) in 10 ml CH_2Cl_2 at room temperature was added with stirring 1 mmol

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of the appropriate phosphine. After 10 min the deep red solutions were filtered. Then 50 ml pentane was added with stirring and the resultant red oils were washed thoroughly with pentane and dried *in vacuo* to give *the products* as red crystalline solids in 89 - 96% yields.

II (R′ = Et, R″ = Ph) m.p. = 140 - 141 °C, Found: C, 50.4; H, 4.73. Calc. for $C_{20}H_{22}CrPBO_3F_4$: C, 50.0; H, 4.58. I.R. (acetone): 1986, 1925, 1895 cm^{-1}. ^{1}H NMR, τ (d_6-acetone): 2.26 (5H, m), 4.00 (2H, dd, *J* 5.0 Hz, 4.7 Hz), 4.84 (3H, m), 6.26 (2H, dt, *J* 8.0 Hz), 7.35 (4H, m) and 8.75 (6H, dt, *J* 18.5 Hz, 8.8 Hz).

II (R′ = R″ = Bu^n) m.p. [124 - 125 °C, Found: C, 51.8; H, 6.64. Calc. for $C_{22}H_{34}CrPBO_3F_4$: C, 51.2; H, 6.60. I.R. (acetone): 1990, 1929, 1899 cm^{-1}. ^{1}H NMR, τ (d_6-acetone): 3.52 (2H, dd, *J* 5.0 Hz, 4.2 Hz), 4.71 (2H, m), 4.99 (1H, dt, *J* 12.5 Hz, 7.8 Hz), 6.19 (2H, dt, *J* 7.8 Hz, 3.2 Hz), 7.94 (2H, m), 8.50 (4H, m) and 9.09 (3H, t, *J* 8.2 Hz).

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