

Reactions of Cyclopentadienyl-(tributylphosphine)copper(I) and Nickelocene with Some α -Bromo Acids

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In contrast to most transition metal cyclopentadienyl complexes, cyclopentadienyl(tributylphosphine)copper(I) (CpCuPBu_3) and nickelocene (Cp_2Ni) react with a variety of organic halides under mild and neutral conditions to form new C—C bonds.^{1,2} They are useful alternatives to lithium and sodium cyclopentadienyls as sources of a reactive cyclopentadienyl group, particularly when the desired products contain acidic hydrogens, since CpCuPBu_3 and Cp_2Ni do not undergo metal-hydrogen exchange easily. We have now investigated their reactions with some α -bromo acids.

Results and discussion. Cp_2Ni is more reactive than CpCuPBu_3 towards α -bromo acids. It reacts smoothly with α -bromophenylacetic acid in the presence of triphenylphosphine to give cyclopentadienylphenylacetic acid (Scheme 1). The phosphine is not essential, but increases the rate of the reaction. α -Bromophenylmalonic acid reacts rapidly with Cp_2Ni even in the absence of triphenylphosphine, whereas 2-bromopropionic acid reacts slowly with Cp_2Ni and triphenylphosphine (70% conversion after three days). The rate of the reaction is increased considerably when the solvent is changed from diethyl ether to diglyme. Only trace amounts of cyclopentadienylacetic acid (NMR evidence) were observed from the reaction between Cp_2Ni and bromoacetic acid.

To gain some information on the mechanism of these reactions we have reacted CpCuPBu_3 and Cp_2Ni with (–)- α -bromophenylacetic acid. The latter reaction was carried out both in the presence and absence of triphenylphosphine. In no case did the product, cyclopentadienylphenylacetic acid, show any optical activity

(within the accuracy of the Zeiss OLD 5 polarimeter). However, some recovered starting material from the reaction with Cp_2Ni retained its optical activity ($\alpha_{578} - 78.4^\circ$). Thus, a reasonable conclusion is that both reactions occur with complete racemisation. Previously, oxidative-addition mechanisms have been considered for CpCuPBu_3 and Cp_2Ni reactions.^{3,4} Such mechanisms should have resulted in inversion or, possibly, retention of the configuration at the asymmetric carbon rather than in complete racemisation. Alternative mechanisms, such as one-electron transfer processes, seem more likely from the present results.

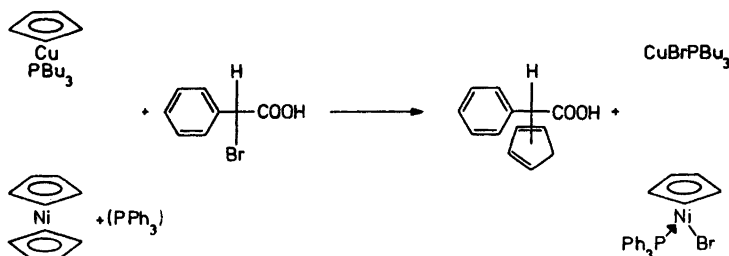
At room temperature, cyclopentadienylphenylmalonic acid decarboxylates slowly in solution to give cyclopentadienylphenylacetic acid and one isomer of (2-cyclopentenyldiene)-phenylacetic acid (the *E* isomer, Scheme 2). This can be rationalised by assuming a normal decarboxylation of the 1-isomer of cyclopentadienylphenylmalonic acid and a stereospecific decarboxylation of the 2-isomer by a concerted 6-electron process (Scheme 2).

Experimental. NMR spectra were recorded on a Varian A 60 or a Bruker WH 270 spectrometer, UV spectra on a Beckman DK-2A, IR spectra on a Beckman IR 9 and MS on an AEI MS 902 spectrometer.

All reactions with CpCuPBu_3 and Cp_2Ni were performed under dry, oxygen-free nitrogen in dry diethyl ether (Mallinckrodt, AR). CpCuPBu_3 was prepared from alkali-free cyclopentadienylthallium and copper(I) iodide tributylphosphine⁵ and Cp_2Ni from sodium cyclopentadienide and hexaamminenickel(II) chloride.⁶

General procedure. An ether solution of the bromo acid was added dropwise to an ether solution of CpCuPBu_3 or Cp_2Ni . The temperature was kept at 0 and 25°C, respectively. When the organometallic reagent had been consumed, according to TLC, the reaction mixture was filtered and the filtrate extracted with aqueous NaOH (0.1 M, 3 × 50 ml). The aqueous phase was filtered, acidified with HCl, and extracted with ether (3 × 50 ml). The ether solution was dried and the solvent evaporated to give the product as a yellow oil.

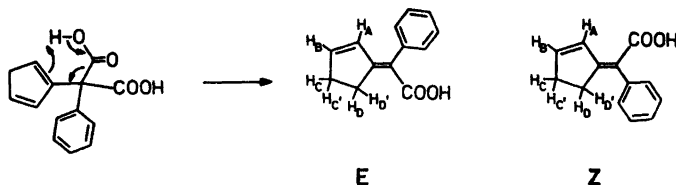
Cyclopentadienylphenylacetic acid. CpCuPBu_3 (10 mmol) in ether (60 ml) and bromophenyl-



Scheme 1.

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Scheme 2.

acetic acid (100 mmol) in ether (20 ml) gave crude cyclopentadienylphenylacetic acid (1.47 g, 73 %). The crude product was chromatographed on silica gel with methanol–chloroform as eluent to give a light yellow oil which slowly solidified (1.35 g, 67 %). NMR (CDCl_3): δ 10.3 (1 H, s, acid proton), 7.2 (5 H, m, aromatic protons), 6.5–6.1 (3 H, m, olefinic protons), 4.7 (1 H, m, methine proton), and 2.9 (2 H, m, methylene protons). IR (film): 1710 cm^{-1} (carbonyl). UV (ethanol): 247 nm (ϵ 3100). MS (70 eV): m/e 200 (M^+ , 32 %), 172 (42), 170 (32), 155 (100), 154 (66), 153 (79), 152 (45), 140 (48), 130 (42), 129 (79), 128 (86), 118 (34), 116 (34), 115 (100), 107 (66), and 105 (93). Abs. mass 200.107; calc. for $\text{C}_{13}\text{H}_{12}\text{O}_2$, 200.084.

Cp_2Ni (10 mmol) and triphenylphosphine (10 mmol) in ether (70 ml) and α -bromophenylacetic acid (10 mmol) in ether similarly gave cyclopentadienylphenylacetic acid (1.96 g, 98 %).

2-Cyclopentadienylpropionic acid. Cp_2Ni (10 mmol) and triphenylphosphine (10 mmol) in ether (70 ml) and 2-bromopropionic acid (10 mmol) in ether (30 ml) gave after three days 2-cyclopentadienylpropionic acid (0.98 g, 71 %). The product was purified by chromatography on silica gel with methanol as eluent. NMR (270 MHz, CDCl_3): δ 10.5 (1 H, s, acid proton), 6.55, 6.42, 6.35, and 6.25 (3 H, m, olefinic protons), 3.61 (1 H, dq, methine proton), 3.01 and 2.98 (2 H, m, methylene protons), 1.43 and 1.42 (3 H, dd, methyl protons). IR (film): 1705 cm^{-1} (carbonyl). UV (CH_2Cl_2): 249 nm (ϵ 3200). MS (70 eV): m/e 138 (M^+ , 25 %), 93 (100), 91 (84), 79 (29), 78 (24), 77 (86), and 65 (31). Abs. mass 138.057; calc. for $\text{C}_9\text{H}_{10}\text{O}_2$, 138.068.

Cyclopentadienylphenylmalonic acid. Cp_2Ni (10 mmol) and bromophenylmalonic acid (10 mmol) in ether (70 ml) gave after 2 h cyclopentadienylphenylmalonic acid (0.87 g, 36 %), m.p. 125–140 $^\circ\text{C}$ (dec.), as pale yellow crystals from CH_2Cl_2 . NMR (270 MHz, acetone- d_6): δ 9.35 (2 H, s, acid protons), 7.44 (2 H, m, aromatic protons), 7.31 (3 H, m, aromatic protons), 6.55–6.35 (3 H, m, olefinic protons), 3.13 and 3.06 (2 H, q, methylene protons). IR (KBr): 1675 cm^{-1} (carbonyl). UV (ethanol): λ_{max} 246 nm (ϵ 2900). MS (70 eV): m/e 200 (37 %, $\text{M}^+ - \text{CO}_2$), 156 (29, $\text{M}^+ - 2\text{CO}_2$), 155 (100), 154 (24), 153 (22), 152 (14), 128 (14), 115 (16), 91 (33), and 77 (21). The molecular ion at m/e 244 was not observed.

CpCuPBu_3 (5.6 mmol) in ether (100 ml) and bromophenylmalonic acid (4.6 mmol) in ether (15 ml) gave cyclopentadienylphenylmalonic acid (18 %, spectroscopic yield) and phenylmalonic acid (49 %, spectroscopic yield) after 15 h.

On standing in solution at room temperature, cyclopentadienylphenylmalonic acid slowly decarboxylates to give 42 % of cyclopentadienylphenylacetic acid as a mixture of 1- and 2-isomers and 58 % of (*E*)-(2-cyclopentenyldene)phenylacetic acid. NMR (270 MHz): δ 7.41–7.17 (5 H, m, aromatic protons), 6.56 (1 H, dt, H_A), 6.09 (1 H, dt, H_B), 3.11 (2 H, m, H_D) and 2.62 (2 H, m, H_C). The following coupling constants were determined from decoupling experiments: J_{AB} 5.5 Hz, J_{AC} 2.2 Hz and J_{BC} 3.0 Hz. IR (KBr): 1650 cm^{-1} (carbonyl). MS (70 eV): m/e 200 (88 %, M^+), 182 (17), 156 (16), 155 (100), 154 (78), 153 (41), 152 (26), 129 (16), 128 (27), 115 (28) and 77 (35). Abs. mass 200.084; calc. for $\text{C}_{13}\text{H}_{12}\text{O}_2$, 200.084. The three acids were isolated in pure state by reverse phase HPLC on an RP 18 column with a methanol–water–acetic acid (80:20:0.5) solvent system. On an attempted chromatographic purification (silica gel with benzene–dioxane as eluent of cyclopentadienylphenylacetic acid, the compound rearranged to a mixture of the (*Z*) and (*E*) isomers of (2-cyclopentenyldene)phenylacetic acid. NMR of the (*Z*) isomer (270 MHz): δ 7.48 (1 H, m, H_A), 6.68 (1 H, m, H_B), and 2.43 (4 H, m, H_C and H_D).

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