Synthesis and Chemical Reactivity of 2-Chlorohexafluorocyclopentenylcopper Reagent

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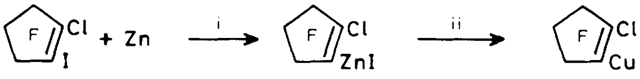
2-Chlorohexafluorocyclopentenylcopper reagent is readily produced *in situ* from 1-chloro-2-iodohexafluorocyclopentene under mild conditions and can be directly utilised in the synthesis of previously inaccessible substituted polyfluorocyclopentenes.

Although vinylcopper reagents derived from linear polyfluoro olefins have been the centre of attention recently,[1] the analogous copper derivatives of alicyclic perfluoro olefins have no chemical precedent. These copper derivatives play an invaluable role in synthesis of previously inaccessible compounds.

We report herein the preliminary results of a novel, high yield preparation of stable 2-chlorohexafluorocyclopentenyl copper (**1**) *via* a cuprous bromide metathesis reaction of the corresponding zinc reagent.†

Compound (**1**)‡ exhibits excellent stability at room temperature in the absence of oxygen and/or moisture, and in DMF under a nitrogen atmosphere showed a 3% loss of activity after 1 day at room temperature, with a loss of only 10% activity after 7 days at room temperature. Compound (**1**) participates in a variety of alkylation, coupling, and acylation reactions illustrated in Table 1.

To demonstrate the synthetic utility of (**1**), we prepared a number of previously unreported compounds through treatment of (**1**) with acid halides. Accordingly, acylation of (**1**)

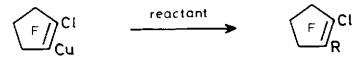


(**1**)

96 %

Reagents and conditions: i, DMF, room temp.; ii, CuBr, room temp.

Table 1. Reactions of (**1**) with various reactants.[a]



Reactant	Product[b] R =	Yield[c] /%	B.p. /°C (mmHg)
aq. HCl	-H	92	73—75 (760)
CH_2=$CHCH_2Br$	-CH_2CH=CH_2	90	58—59 (50)
MeI	-Me	59	59—61 (100)
PhI	-Ph	52	69—70 (10)
MeCOCl	-COMe	74	73—74 (50)
PhCOCl	-COPh	89	62—63 (0.1)
Me_2NCOCl	-$CONMe_2$	52	75—76 (1.5)

[a] DMF was used as solvent. [b] All products characterised by their ^{19}F, ^1H n.m.r., i.r., and mass spectra. [c] Isolated yield.

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† This reagent is prepared *via* the direct reaction of zinc powder with 1-chloro-2-iodohexafluorocyclopentene at room temperature in dimethylformamide (DMF). After a short induction period, a mildly exothermic reaction resulted and 2-chlorohexafluorocyclopentenylzinc was formed in 96% yield as determined by ^{19}F n.m.r. spectroscopy using $PhCF_3$ as the internal standard. 1-Chloro-2-iodohexafluorocyclopentene was synthesised by the method of A. W. Wu, S. K. Choi, J. D. Park, and R. L. Soulen, *J. Fluorine Chem.*, 1979, **13**, 379.

‡ ^{19}F N.m.r. −98.8, −110.7, −127.3 p.p.m; chemical shifts were measured relative to external trifluoroacetic acid and referenced to fluorotrichloromethane utilizing the conversion factor of 77 p.p.m.

with acid halides at 0 °C afforded the corresponding 1-acyl-2-chlorohexafluorocyclopentenes in a good yield. The treatment of a solution of (**1**) at room temperature with allyl bromide gave the 1-allyl-2-chlorohexafluorocyclopentene in a quantitative yield.

When methyl iodide and iodobenzene were mixed with the solution of (**1**) at room temperature, the corresponding 1-substituted-2-chlorohexafluorocyclopentene is produced in a moderate yield. These results represent much higher yields than those obtainable by the method previously reported in the literature.[2]

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References

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