Available online at www.sciencedirect.com
SCIENCE DIRECT®
Journal of Organometallic Chemistry 690 (2005) 925–931
Journal of Organometallic Chemistry
www.elsevier.com/locate/jorganchem

Structure and reactivity of derivatives of dihalogenomethyl indium(III) halides, X_2InCHX_2 (X = Cl, Br, I)

Clovis Peppe [a,*], Dennis G. Tuck [b,1], Fabiano M. de Andrade [a], José A. Nóbrega [c], Martin A. Brown [b], Robert A. Burrow [a]

[a] Departamento de Química, Laboratório de Materiais Inorgânicos, Universidade Federal de Santa Maria, Campus UFSM, 97105-900 Santa Maria-RS, Brazil
[b] Department of Chemistry and Biochemistry, University of Windsor, Windsor, Ont., Canada N9B3P4
[c] Departamento de Química, CCT, Universidade Estadual da Paraiba-UEPb, R. Juvêncio Arruda s/n, 58109-790 Campina Grande-PB, Brazil

Received 2 October 2004; accepted 19 October 2004
Available online 19 November 2004

Abstract

The reactions of indium monohalides, InX with haloforms, CHX_3, in 1,4-dioxane (diox), produce the dioxane adducts of dihalogeno–dihalogenomethyl–indium(III), $X_2In(diox)_nCHX_2$ (X = Cl, Br, $n = 1$; X = I, $n = 2$) compounds. The ionic derivative $[(C_2H_5)_4N]$ $[Cl_3InCHCl_2]$ was prepared and its crystal structure determined by X-ray means. The reactions of the $X_2In(diox)_nCHX_2$ compounds are significantly different from those of the related X_2InCH_2X compounds. The dihalogenomethyl derivatives react with strong electrophiles suggesting dihalogenomethyl substituents of mild nucleophilic character, while the carbon atoms in the halogenomethyl derivatives are electrophilic.

Keywords: Indium; Organoindium; Carbenoid; Crystal structure; Carbon–carbon bond formation

1. Introduction

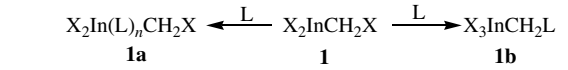
Metal carbenoids such as the Simmons–Smith reagent, iodomethylzinc iodide, $IZnCH_2I$ have found extensive applications in olefin cyclopropanation [1]. More recently, it was determined that they are able to homologate copper(I) reagents, RCu by adding methylene units to produce new organocopper–zinc reagents of the type $R(CH_2)_nCu \cdot ZnI_2$ able to react with electrophiles [2]. The synthesis and structural investigation of related new metal carbenoids is therefore of great interest.

Previous papers have investigated the preparation, crystal structure and reactivity of X_2InCH_2X (X = Br, I) compounds, **1** and their derivatives with anionic and neutral donors, L. Adduct formation may occur at either the metallic center, **1a** favored by hard ligands, or at the halogenomethyl carbon atom, in which case ylid complexes of InX_3, **1b** were identified (Scheme 1) [3].

Related work has shown that the analogous dihalogenomethyl compounds X_2InCHX_2 (X = Cl, Br, I) could also be prepared by the reaction of InX with CHX_3 in acetonitrile, although the only stable derivatives then obtained were the salts of the $[X_3InCHX_2]^-$ anions. All efforts to obtain adducts with neutral donors such as dimethylsulfoxide (dmso), triphenyl phosphine and 1,1,3,3-tetramethyl-2-thiourea (tmtu) resulted in the formation of adducts of the corresponding indium(III) halide, InX_3L_n(X = Cl, L = tmtu, $n = 2$; X = Cl, I, L = Ph_3P, $n = 2$; X = Cl, Br, L = dmso, $n = 3$; X = I, L = tmtu, $n = 1$) [4]. We now report the isolation of

* Corresponding author. Tel.: +55552208868; fax: +55552208031.
E-mail address: peppe@quimica.ufsm.br (C. Peppe).
[1] In memmorian.

0022-328X/$ - see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.jorganchem.2004.10.036



X= Br, L = diox, n= 2;
X= Br, L = thf, n= 2;
X= Br, L= Br^-, n= 1;
X= I, L= I^-, n= 1;
X= Br, L= $(C_6H_5)_3PO$, n= 2.

X= Br, L = tmen, $(C_2H_5)_3N$, $(C_6H_5)_3E$ (E= P, As, Sb), $(C_6H_5CH_2)_2S$, $(C_6H_5)_3PS$, $[(CH_3)_2N]_2CS$; X= I, L = tmen, $(C_6H_5)_3P$.

Scheme 1. The coordination chemistry of X_2InCH_2X compounds, **1**.

the 1,4-dioxane (diox) adducts, $X_2In(diox)_nCHX_2$. The salts $[(C_2H_5)_4N]$ $[Cl_3InCHCl_2]$ and $[(C_6H_5)_4P]$ $[Br_3InCHBr_2]$ were also prepared from $X_2In(diox)$-CHX_2, and the structure of the chlorine derivative determined by X-ray methods. Further, we have demonstrated that the dihalogenomethyl substituents on the $X_2In(diox)_nCHX_2$ compounds is of a mild nucleophilic character, reacting only with strong electrophiles, such as allyl bromide derivatives, carboxylic and mineral acids.

2. Experimental

2.1. General

The preparation of InX (X = Cl, Br, I) source and treatment of starting materials, methods of elemental analysis, and spectroscopic techniques were those described earlier [4]. Allyl bromide and 3-bromo-2-methyl-prop-1-ene were commercial reagents (Aldrich) and distilled before used. 1,4-Dioxane was dried over sodium/benzophenone and distilled before used. Other reagents and solvents (ACS grade) were used as supplied.

2.2. Preparation of $X_2In(diox)_nCHX_2$ ($X = Cl$, Br, $n = 1$; $X = I$, $n = 2$)

InX (X = Cl, 0.40 g, 2.66 mmol; X = Br, 0.40 g, 2.05 mmol; X = I, 0.50 g, 2.07 mmol) was suspended in 20 mL of freshly distilled dry 1,4-dioxane (diox). Excess CHX_3 (X = Cl, 1.00 mL, 12.50 mmol; X = Br, 0.55 mL, 6.30 mmol; X = I, 1.63 g, 4.14 mmol) was added to the suspension and the mixture stirred to complete dissolution of InX (X = Cl, 6 h; X = Br, 4 h; X = I, 16 h). At this point, any small quantity of solid impurity was removed by filtration, the volatiles removed from the filtrate under high vacuum, and the solution held at low pressure for ca. 3 h. This procedure yields the chloro and bromo derivatives as white solids (X = Cl, 0.71 g, 2.00 mmol, 75%; X = Br, 0.90 g, 1.68 mmol, 82%). The iodine compound was isolated by adding toluene (10 mL) to the yellow solid obtained; this removes excess CHI_3, leaving $I_2In(diox)_2CHI_2$ as a yellow powder (0.95 g, 1.32 mmol, 64%). All the $X_2In(diox)_nCHX_2$ compounds are air sensitive. Spectroscopic studies and handling for elemental analysis were conducted under dry nitrogen. Anal. Calc. for $Cl_2In(diox)CHCl_2$, $C_5H_9O_2InCl_4$: In 32.1%. Found: 31.1%. ^1H NMR (CD_3CN): $\delta = 5.60$ (s, 1H), 3.60 (s, 8H); ^{13}C NMR (CD_3CN): $\delta = 67.58, 46.65$. Calc. for $Br_2In(diox)CHBr_2$, $C_5H_9O_2InBr_4$, In 21.5%. Found: 21.2%. ^1H NMR (CD_3CN): $\delta = 5.36$ (s, 1H), 3.60 (s, 8H); ^{13}C NMR (CD_3CN): $\delta = 67.77, 37.31$. Calc. for $I_2In(diox)_2CHI_2$, $C_9H_{17}O_4InI_4$, In 14.1%, I 62.5. Found: 13.9%, 62.4%. ^1H NMR (CD_3CN): $\delta = 4.30$ (s, 1H), 3.59 (s, 16H); ^{13}C NMR (CD_3CN): $\delta = 67.50, -47.75$.

2.3. Preparation of [Q] [X_3InCHX_2] [$Q = (C_2H_5)_4N$, $X = Cl$; $Q = (C_6H_5)_4P$, $X = Br$]

The salts $[Q][X_3InCHX_2]$ were prepared from the corresponding $X_2In(diox)CHX_2$ compounds. Thus, to a solution of $X_2In(diox)CHX_2$ (X = Cl, 2.66 mmol; X = Br, 2.05 mmol) in 20 mL of dry acetonitrile was added an equimolar amount of QX [X = Cl, $Q = (C_2H_5)_4N$, 2.66 mmol; X = Br, $Q = (C_6H_5)_4P$, 2.05 mmol]. The mixture was stirred for ca. 2 h. At this point, any solid impurity was removed by filtration. The salts [Q] [X_3InCHX_2]were isolated as described below:

$[(C_2H_5)_4N]$ $[Cl_3InCHCl_2]$: Removal of all the volatiles from the filtrate solution, gave an oil, which was redissolved in 20 mL of a mixture (1:1, v/v) of acetonitrile:ethanol (95%). Slow evaporation of the solvent in air deposited colorless crystals of $[(C_2H_5)_4N]$ $[Cl_3InCHCl_2]$ (0.70 g, 1.6 mmol, 60%). Anal. Calc. for $C_9H_{21}NInCl_5$: In 26.4%. Found: 25.9%. ^1H NMR [$(CD_3)_2$ CO]: $\delta = 5.63$ (s, 1H), 3.47 (q, $J = 7.5$ Hz, 8H); 1.37 (tt, $J = 7.5$ Hz, $J = 2.4$ Hz, 12H); ^{13}C NMR [$(CD_3)_2$ CO]: $\delta = 53.01, 46.65, 7.67$.

$[(C_6H_5)_4P]$ $[Br_3InCHBr_2]$: Addition of 20 mL of ethanol (95%) to the acetonitrile filtrate solution and slow concentration in air deposited colorless crystals of $[(C_6H_5)_4P]$ $[Br_3InCHBr_2]$ (1.45 g, 1.67 mmol, 82%). Anal. Calc. for $C_{25}H_{21}PInBr_5$: In 13.2%. Found: 13.2%. ^1H NMR [$(CD_3)_2CO$]: $\delta = 7.87–7.82$ (m, 20H), 5.34 (s, 1H); ^{13}C NMR [$(CD_3)_2CO$]: $\delta = 136.39, 135.60$