

Preliminary communication

The reaction of benzene with diethylamine in the presence of an iridium(I) /mercury(II) based system: a model route for the direct amination of aromatic hydrocarbons

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Abstract

N,N-Diethylaniline is formed under mild conditions either by the direct amination of benzene with diethylamine in the presence of $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ **1** and HgSO_4 , or by reacting $(\text{C}_6\text{H}_5)_2\text{Hg}$ or $\text{C}_6\text{H}_5\text{HgCl}/\text{Ag}_2\text{SO}_4$ with diethylamine in the presence of **1**. A preliminary investigation about the chemistry underlying these reactions is also reported.

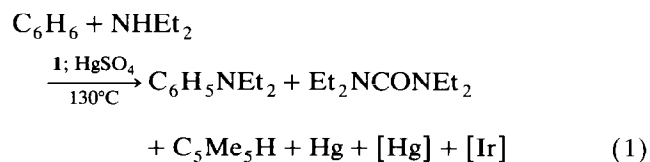
Keywords: Iridium; Amination; C–H activation; N–H activation; Mercury; Catalysis

1. Introduction

There is an increasing need of novel synthetic strategies for the selective functionalization of hydrocarbons under mild conditions using C–H bond activation reactions [1]. In this connection, the direct amination of arenes and alkanes is a fascinating challenge. Since the seventies there have been literature reports [2] of an interesting approach to the synthesis of aniline by reaction of benzene with ammonia at high temperature and pressure in the presence of NiO/ZrO₂-based catalytic systems. More recently, Crabtree and coworkers have succeeded in the very elegant mercury-photosensitized direct amination of methane and ethane with ammonia [3].

In a search for transition metal-based systems to facilitate or catalyse the amination of arenes by ammonia or amines under moderate conditions, we devoted our attention to metal centres that can activate aromatic C–H bonds [1a,b] and amine N–H bonds [4]. We discovered eventually that, benzene reacts with dieth-

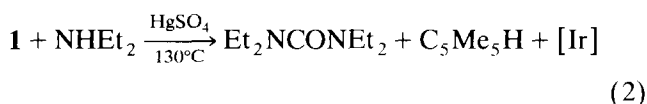
ylamine at 130°C in the presence of $[\text{Ir}(\eta^5\text{-C}_5\text{Me}_5)(\text{CO})_2]$ **1** and HgSO_4 , under dinitrogen for 24 h to give *N,N*-diethylaniline as the major organic product (0.4 mol per mole of **1**), *N,N,N',N'*-tetraethylurea (0.04 mol per mole of **1**), pentamethyl-cyclopentadiene (0.01 mol per mole of **1**), metallic mercury (ca. 1 mol per mole of **1**), and an unidentified iridium compound, [Eq. (1)] [5]. After this reaction time, unreacted **1** (ca. 7% of the starting amount) and HgSO_4 (ca. 40% of the starting amount) are still present in the reaction mixture [6].



The addition of carbon monoxide (1 atm), or dioxygen (1 atm) or the radical inhibitor, 2,6-di-*tert*-butyl-4-methylphenol, all prevent the formation of *N,N*-diethylaniline but have no effect on the formation of the other products. Blank reactions in the absence of **1**, or in the absence of HgSO_4 [7] showed that none of the above products is formed at 130°C, even with reaction times of 180 h. Rather the reaction of diethylamine with **1** and HgSO_4 gives *N,N,N',N'*-tetraethylurea and $\text{C}_5\text{Me}_5\text{H}$ in the same amounts as above, in addition to

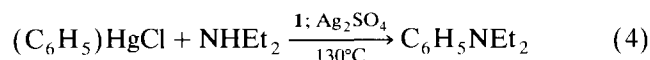
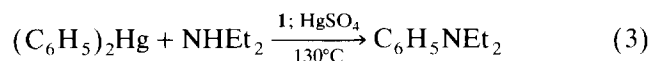
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metallic mercury and an unidentified iridium compound [Eq. (2)].



The treatment of a pentane or benzene (2 ml) solution of **1** (typically 0.05 mmol) with microcrystalline HgSO_4 (average size of grains, 0.005 mm) produces a solid adduct of **1** and HgSO_4 (molar ratio, 1/4) within 2–3 min. at room temperature without formation of CO [8]. Whatever the interaction between **1** and HgSO_4 (a molecular adduct between the metal–base **1** [9] and HgCl_2 implying an iridium–mercury bond is known [10]), it causes a marked shift of the CO stretching frequencies (KBr) from 1929 and 1998 cm^{-1} in (**1**) [11] to 2030 and 2080 cm^{-1} (**1**/ HgSO_4 adduct) [12]. The implied increased C–O bond force constant suggests that such carbonyl ligands should be susceptible of nucleophilic attack by primary or secondary amines, this being the prerequisite for the formation of *N,N,N',N'*-tetraethylurea and diethylammonium salts [13] [14]. The formation of $\text{C}_5\text{Me}_5\text{H}$ [Eq. (1) and (2)] is then easily understood in terms of a partial protolysis of the Cp^*-Ir bond. Accordingly, we find that the treatment of **1** with $\text{NH}_4(\text{HSO}_4)$ or NH_4Cl in a benzene/diethylamine mixture (molar ratio, 1/2) at 130°C gives $\text{C}_5\text{Me}_5\text{H}$, in amounts increasing with reaction time.

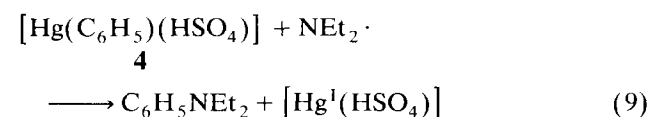
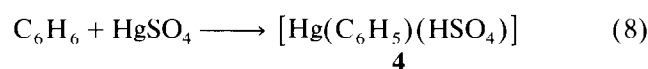
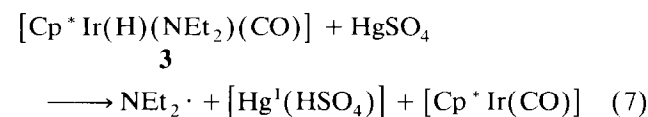
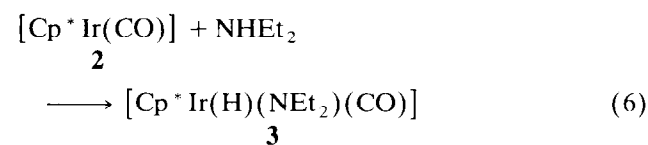
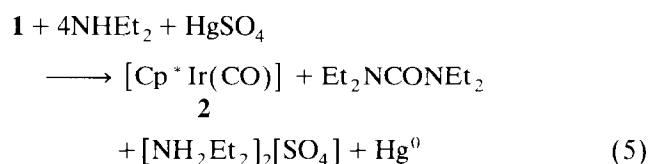
N,N-Diethylaniline is also formed (0.2 mol per mole of **1**) when $(\text{C}_6\text{H}_5)_2\text{Hg}$ or $(\text{C}_6\text{H}_5)\text{HgCl}$, rather than benzene are employed as sources of phenyl groups, but only if **1** is present too [Eq. (3) and (4)] and that no radical inhibitor is added.



We believe that these findings suggest the following conclusions: (i) **1** plays a key-role in the amination reaction. (ii) A phenylmercury(II) species, which could arise from the electrophilic activation of benzene by HgSO_4 [15], may be involved in a key-step of the reaction of benzene with diethylamine [16]. (iii) Some radical species could be involved in the phenylmercury(II) \rightarrow *N,N*-diethylaniline transformation.

In order to try to understand why both 2,6-di-*tert*-butyl-4-methylphenol and dioxygen inhibit the formation of *N,N*-diethylaniline, we studied the above reactions by ESR spectroscopy and trapped the $\text{NET}_2\cdot$ radical as its nitroxide derivative, $\text{Et}_2\text{NO}\cdot$ [17], when a mixture of **1**, NHET_2 , C_6H_6 , and HgSO_4 was kept at 80°C in air in the cavity of an ESR spectrometer [18]. Under the same conditions, no radical species was detected in blanks carried out in the absence of **1** of

HgSO_4 . Similarly, when the experiments were run under pure argon, the $\text{NET}_2\cdot$ radical was not detected, probably because of its very short lifetime [17]. These findings, do not imply that the $\text{NET}_2\cdot$ radical is actually part of the amination reactions, but suggest a very complex and intriguing reaction mechanism which we are currently trying to clarify. Even if some proposals are speculative, most of the facts can be accounted for by the scheme of reactions shown below. **1** is proposed to react with NHET_2 and HgSO_4 to give rise to the coordinatively unsaturated iridium(I) species **2** [Eq. (5)], which undergoes an oxidative addition reaction with NHET_2 [4] [Eq. (6)] to yield the diethylamidohydride derivative **3** [19]. The mercury(II) oxidatively-induced degradation [20] of **3** then results in the formation of the $\text{NET}_2\cdot$ radical [Eq. (7)], which, in turn, is responsible for the formation of *N,N*-diethylaniline by reacting with a phenylmercury(II) species such as **4** [Eq. (9)] [21].



2. Experimental section

In a typical run, a Pyrex Carius tube (25 ml capacity) fitted with a Bibby Quickfit Rotaflo PTFE tap (DISA, Milan) was charged under dinitrogen with C_6H_6 (11.3 mmol), NHET_2 (22.6 mmol), **1** (0.11 mmol), microcrystalline HgSO_4 (0.22 mmol), and then kept at 130°C for 24 h.

Reaction mixtures were analyzed by a Perkin-Elmer AUTOSYSTEM gas-chromatograph equipped with a 25 m capillary column BP-20 (SGE), and by a GC-MS Perkin-Elmer Q-910 instrument. Products were identified by comparison of their GC retention times and MS fragmentation patterns with those of authentic sam-

ples. Yields were evaluated by using tetradecane as internal standard.

ESR spectral measurements were made as described elsewhere [22].

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- [5] Although very sensitive to temperature and 1/HgSO₄/NH₂Et₂/C₆H₆ starting molar ratios), the reaction gives highly reproducible results. In particular, no benzene amination occurs below 110°C even with reaction times of 180 h. However, above 130°C the *N,N*-diethylaniline yields drop (1%, at 150°C).
- [6] Owing to its high volatility, 1 was qualitatively and quantitatively analyzed by GLC; unreacted HgSO₄ was extracted from the solid residue arising from reaction mixtures using a saturated aqueous NaCl solution.
- [7] A negligible effect is exercised by other mercury(II) derivatives such as HgF₂, HgCl₂, HgBr₂, HgI₂, Hg(NO₃)₂, Hg(OCOCH₃)₃, Hg(OCOCF₃)₂, Hg(ClO₄)₂, HgS, Hg(SCN)₂, Hg[Co(SCN)₄]₂, and HgO.
- [8] No reaction takes place when 1 reacts for 96 h with a single crystal [crystal size (mm), 0.58×0.30×0.13] of HgSO₄ prepared as reported by K. Aurivillius, C. Stalhandske (*Z. Kristallogr.*, 153 (1980) 121) and tested by X-ray diffraction measurements before use.
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- [18] The first-derivative X-band ESR spectrum (*g*_{iso} = 2.0055; Δ*H*_{pp} = 1.7 G) of this radical has been computer-simulated implying an interaction of the electron spin with a nitrogen nucleus (*A*_N = 16.87 G) and with four methylene hydrogen nuclei (*A*_H = 11.65 G) [14].
- [19] We do not rule out the possibility that 2 also undergoes an oxidative addition with benzene, giving a hydridophenyliridium(III) compound, but we reject the suggestion that phenyliridium(III) species are responsible for the formation of *N,N*-diethylaniline since neither [Ir(η⁵-C₅Me₅)(C₆H₅)(Cl)(CO)] [J.W. Kang, P.M. Maitlis, *Organomet. Chem.*, 26 (1971) 393] nor [Ir(η⁵-C₅Me₅)(C₆H₅)₂(PPh₃)] [P. Diversi, S. Iacoponi, G. Ingrosso, F. Laschi, A. Lucherini, P. Zanello, *J. Chem. Soc., Dalton Trans.* (1992) 351] give rise to *N,N*-diethylaniline upon reaction with diethylamine at 130°C for 24 h, either in the presence or in the absence of HgSO₄.
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