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Short communication

Unexpected formation of $Cp^*IrCl_2PPh_3$ from the reaction of $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ with PPh_3 in dichloroethane involving C–Cl bond activation

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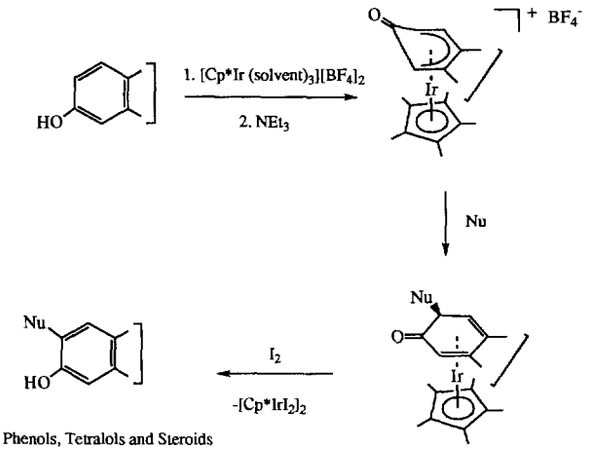
Abstract

The reaction of $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ (**1**) with PPh_3 in refluxing $C_2H_4Cl_2$ afforded unexpectedly but reproducibly the known compound $Cp^*IrCl_2PPh_3$ (**2**) which was identified by ^{1}H-NMR spectroscopy and single crystal X-ray diffraction. This unexpected chemical transformation to give **2** involves 'C–Cl' abstraction from dichloroethane mediated by the 'Cp^*Ir' fragment. A rationale for this surprising transformation is advanced. © 1997 Elsevier Science S.A.

Keywords: C–Cl bond; Ligand formation; *Ortho*-position of the phenol ring

1. Introduction

We recently reported a novel system for regioselective *ortho*-functionalization of phenols, tetralols and steroids promoted by the 'Cp^*Ir' fragment and using NaOMe as the attacking nucleophile [1,2] (Scheme 1). The procedure consists of three steps: (a) placement of the 'Cp^*Ir' moiety at the aromatic ring, followed by treatment with NEt_3 affords the (oxo-cyclohexadienyl)iridium complexes. (b) The latter react with NaOMe in methanol to give the η^4-dienone compounds. (c) Subsequent oxidative decomplexation by iodine provides the *ortho*-substituted phenols along with the starting organometallic material recycled in the form $[Cp^*IrI_2]_2$.



Scheme 1.

As a continuation of this project, we extended our investigations to other nucleophiles such as phosphines. Our goal was to introduce a phosphine unit at the *ortho*-position of the phenol ring in order to obtain the 2-phosphino-phenol ligands. Such ligands PR_2-(C_6H_5OH) containing both a hard and soft donor groups are difficult to prepare by direct methods and are of great importance in homogeneous catalysis [3–6]. In this communication we report an attempt to prepare such a molecule by addition of PPh_3 to the (oxo-cyclohexadienyl)iridium complex $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ (**1**) in refluxing $C_2H_4Cl_2$ and which afforded unexpect-

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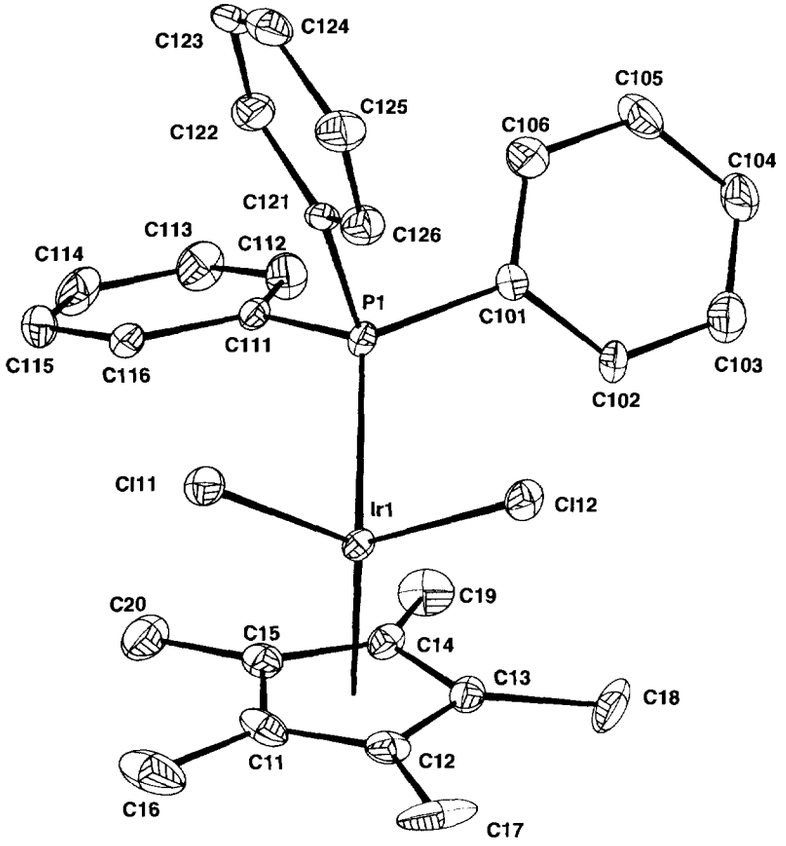


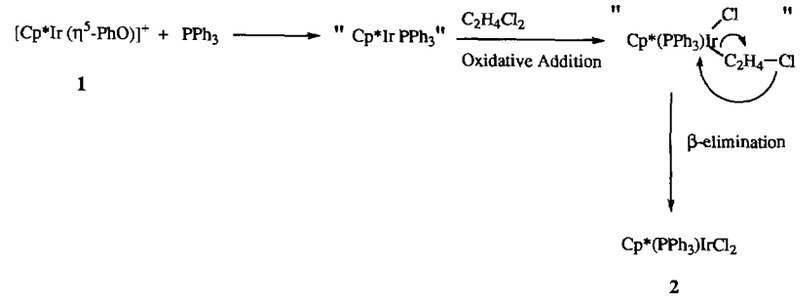
Fig. 1. Cameron view of the structure of $Cp^*IrCl_2PPh_3$ (**2**) showing the atom numbering system. Selected bond distances (Å) and angles (deg): Ir(1)–Cl(11) = 2.406(3), Ir(1)–Cl(12) = 2.408(3), Ir(1)–P(1) = 2.324(3), Ir(1)–C(11) = 2.22(1), Ir(1)–C(12) = 2.20(1), Ir(1)–C(13) = 2.18(1), Ir(1)–C(14) = 2.18(1), Ir(1)–C(15) = 2.19(1), Cl(11)–Ir(1)–Cl(12) = 90.6(1), Cl(11)–Ir(1)–P(1) = 88.3(1), Cl(12)–Ir(1)–P(1) = 89.8(1).

edly the iridium complex $Cp^*IrCl_2PPh_3$ (**2**) identified spectroscopically and by X-ray diffraction analysis [7]. [1]

2. Results and discussion

Treatment of $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ (**1**) with PPh_3 at room temperature for 24 h and analysis of the solution mixture showed the presence of only the starting materials. The previous reaction was then repeated but under reflux in dichloroethane. The initial yellow color solution changed to orange. Reaction work-up afforded an orange microcrystalline compound in 82% yield. The ^{1}H-NMR spectrum recorded in $CDCl_3$ showed the absence of the phenoxo-protons, suggesting decoordination of the η^5-PhO unit. However we note by proton integration the presence of one phosphine ligand PPh_3 relative to the η^5-Cp^* unit which appears as a doublet at 1.36 ppm [7]. The IR-spectrum showed the absence of the large band at 1050 cm^{-1} attributed to the BF_4^- counter ion. In order to identify this orange complex without ambiguity, crystals of **2** were grown up from $CHCl_3$–pentane mixture by slow diffusion method. The compound crystallizes in the monoclinic unit cell with space group $P2_1/n$. [1] The unit cell contains two independent molecules of **2**. Fig. 1 shows the molecular structure of **2** (form a). The structure reveals the usual three-legged piano stool coordination displayed by this kind of complexes. Consistent with the NMR data we note that the PPh_3 ligand and the η^5-Cp^* are indeed attached to the iridium center. The distance from the metal to the centroid of the η^5-C_5Me_5 ligand is 1.80 (3) Å and typical to those of analogous Ir(III) compounds $[Cp^*IrX_2]_2$ (X = Cl, Br, I) where this distance lies in

[1] Crystal data for $Cp^*IrCl_2PPh_3$ (**2**): $C_{23}H_{30}Cl_2PIr$, F_w = 660.6, monoclinic, space group $P2_1/n$, a = 8.686(4) Å, b = 32.169(3) Å, c = 18.172(2) Å, V = 5077(2) Å^3, Z = 8, D_{calc} = 1.73 g cm^{-3}, μ = 55.3 cm^{-1}, θ = 1°–26°, 578 variables refined with 9957 independent reflections to R = 0.0516, R_w = 0.0594 and GOF = 1.09. The data were corrected for Lorentz and polarization effects. Computations were performed by using the PC version of CRYSTALS [8]. Scattering factors and corrections for anomalous dispersion were taken from Ref. [9]. The structure was solved by standard Patterson and Fourier technics and refined by full-matrix least-squares with anisotropic thermal parameters for all nonhydrogen atoms. Hydrogen atoms were introduced in calculated positions in the last refinements and were allocated an overall refinable isotropic thermal parameter.



Scheme 2. A proposed mechanism for the formation of **2**.

the range of 1.77–1.81 Å [10] but shorter than those values reported for *ortho*-metallated triphenyl phosphine Ir(III) complexes with $d \approx 1.89$–1.92 Å [11]. Interestingly and surprisingly we note the presence of two chloride ligands coordinated to the iridium center which overall allows the metal center to attain the 18 e^- count rule.

It should be mentioned that the synthesis of **2** was reported by Kang et al. and Booth et al. by treating the dimeric compound $[Cp^*IrCl_2]_2$ with PPh_3 [12,13]. Surprisingly we have found that when $CHCl_3$ was used as the chloride source instead of $C_2H_4Cl_2$, the iridium complex $Cp^*IrCl_2PPh_3$ (**2**) was not formed. We feel that in our case, a plausible explanation (Scheme 2) to this chemical transformation would be that (1) the addition of the phosphine unit to $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ (**1**) would occur at the metal center and displace the η^5-PhO unit yielding the 16e^- fragment 'Cp^*IrPPh_3'. (ii) The latter reacts with $C_2H_4Cl_2$ presumably through oxidative addition process subsequent β-elimination of the second chloride unit affords the known complex $Cp^*IrCl_2PPh_3$ (**2**).

The formation of $Cp^*IrCl_2PPh_3$ (**2**) from $[Cp^*Ir(\eta^5\text{-}C_6H_5O)][BF_4]$ (**1**) and PPh_3 in refluxing $C_2H_4Cl_2$ was found to be reproducible. Although this is an unexpected reaction, we note that, such complexes are very reactive and in particular the analogous dihydride complex $Cp^*IrPPh_3H_2$ is a well known reagent for C–H activation of saturated hydrocarbons and its reactivity was extensively investigated [14].

In this communication we reported a constraint to our system for phenol functionalization mediated by the Cp^*Ir and using PPh_3 as the attacking nucleophile. However we have found that the trialkyl phosphines (PMe_3, PEt_3, PMe_2Ph) behaved differently and afforded the phosphino-phenol salts $[PR_3(C_6H_5OH)][BF_4]$ in reasonable to good yields. These phosphino-phenol salts represent stable starting materials to prepare the corresponding bidendate ligands. The results of these investigations and a detailed study on the mechanism of formation of **2** will be published in future reports.

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