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Competitive Activation of a Methyl C−H Bond of Dimethylformamide at an Iridium Center

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Summary: During the synthesis of [AsPh$_4$][Ir(CO)$_2$I$_3$Me] by refluxing IrCl$_3$·3H$_2$O in DMF (DMF = dimethylformamide) in the presence of aqueous HCl, followed by sequential treatment with [AsPh$_4$]Cl, NaI, and methyl iodide and finally recrystallization from methylene chloride/pentane, three crystalline byproducts were obtained: [AsPh$_4$]$_2$[Ir(CO)I$_5$], [AsPh$_4$]$_2$[trans-Ir(CO)I$_4$Cl], and [AsPh$_4$][Ir(CO)(κ^2O, C-CH$_2$NMeCHO)Cl$_2$I]. The last of these, whose structure (along with the others) was determined by X-ray diffraction, results from activation of a methyl C−H bond of dimethylformamide, rather than the normally much more reactive aldehydic C−H bond.

Dimethylformamide (DMF) is a common and convenient carbonylation reagent in organometallic chemistry.[1−5] The mechanism of these carbonylation reactions has not often been studied in detail, but activation of the aldehydic C−H bond to give a carbamoyl intermediate, followed by C−N bond cleavage (the reverse of either migratory insertion or nucleophilic addition), seems a likely route. Structures resulting from DMF activation at the aldehydic C−H bond have previously been reported. Hidai and co-workers found that *cis*-[WH(η^2-CONMe$_2$)(dpe)$_2$] (dpe = (diphenylphosphino)ethane) can be obtained from DMF and *trans*-[W(N$_2$)$_2$(dpe)$_2$] after 20 min; on longer reaction it converts to [W(CO)(DMF)(dpe)$_2$].[6] Another decarbonylation intermediate, Ru(H)$_2$(Cl)(η^2-CONMe$_2$)(P^{i}Pr$_3$)$_2$, was generated by reaction of Ru(H)(H$_2$)Cl(P^{i}Pr$_3$)$_2$ with DMF.[7]

The activation of aldehydic C−H bonds at transition metal centers is well-known, most prominently in the catalytic decarbonylation of aldehydes.[8] Because this process appears to be relatively facile, reaction at other C−H sites in aldehydes would rarely be expected to be competitive. Indeed, we have found only one example: reaction of Rh(ttp)Cl (ttp = tetrakis(4-tolyl)porphyrinato) with *p*-methylbenzaldehyde or *p*-*tert*-butylbenzaldehyde gives (initially) a few percent of (ttp)Rh(CH$_2$C$_6$H$_5$CHO) or (ttp)Rh(CH$_2$-CMe$_2$C$_6$H$_5$CHO), respectively, along with the major product, (ttp)Rh(COAr).[10] To our knowledge there have been no reports of C−H activation of a methyl group of DMF or any closely related species. We report here the structure of an unusual iridium complex resulting from such a reaction.

Studies in our laboratories required the synthesis of the iridium carbonyl complexes [AsPh$_4$][Ir(CO)$_2$I$_2$] (**1**) and [AsPh$_4$][Ir(CO)$_2$I$_3$Me] (**2**). Kalck and co-workers reported that decarbonylation of DMF by IrCl$_3$ initially formed [Ir(CO)(DMF)Cl$_2$]$^-$ (**3**), which underwent further transformation to [Ir(CO)$_2$Cl$_2$]$^-$, which was isolated as the [AsPh$_4$]$^+$ salt (**4**).[1] Halide exchange of the latter with NaI or KI in methanol gave **1** in quantitative yields, as monitored by infrared spectroscopy (Scheme 1). In a separate paper, **1** (synthesized by a different route: refluxing IrCl$_3$ and NaI in a mixture of 2-methoxyethanol and water while bubbling CO through the solution) was found to react with methyl iodide to give **2**.[9]

In our hands, the reaction of **1** (synthesized via decarbonylation of DMF as in Scheme 1) with MeI gave mainly the expected product **2**, according to infrared spectroscopy. However, on attempted recrystallization of the crude product from a mixture of CH$_2$Cl$_2$ and pentane two different species were obtained: red needles and a smaller amount of yellow crystals. Both were examined by X-ray crystallography.

A red needle from one such reaction was determined to be a known complex, [AsPh$_4$]$_2$[Ir(CO)I$_5$] (**5a**), whose structure has been reported.[11,12] Another needle from a duplicate reaction, surprisingly, turned out to have a different (but closely related) structure: [AsPh$_4$]$_2$[*trans*-Ir(CO)I$_4$Cl] (**5b**). More interesting is the minor yellow product, which was crystallographically determined to be [AsPh$_4$][Ir(CO)(κ^2*O*, *C*-CH$_2$NMeCHO)Cl$_2$I] (**6**), the product of C−H activation of a methyl group from DMF (Figure 1). As noted

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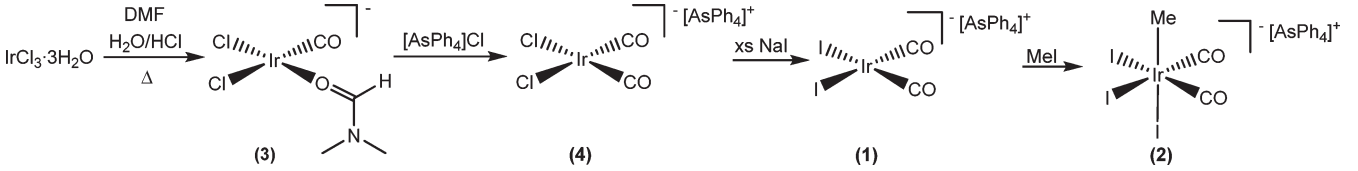
Scheme 1



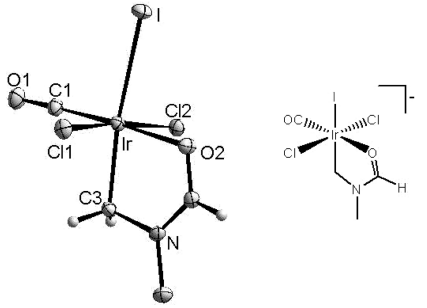


Figure 1. Anisotropically refined thermal ellipsoid representation of $[Ir(CO)(\kappa^2\text{-}CH_2N(CH_3)CHO)Cl_2I]^-$, the anion of **6**. The $[AsPh_4]^+$ cation is not shown, and phenyl and methyl hydrogen atoms have been removed for clarity. Selected bond distances (Å) and angles (deg): Ir−C1 = 1.8221(12), Ir−C3 = 2.0651 (11), Ir−I = 2.76746(12); C1−Ir−C3 = 95.23(5), C3−Ir−I = 171.68(3).

above, this appears to be an unprecedented transformation for DMF; the structure demonstrates that the aldehydic C−H bond has remained intact during the methyl C−H activation.

The metalated methyl group in **6** is located trans to the iodide ligand, with an Ir−C3 bond length of 2.0651(11) Å. The aldehydic oxygen is also coordinated to Ir, forming a five-membered ring; the Ir−O2 bond distance is 2.0875(9) Å, while the O2−C2 distance is 1.2704(15) Å, somewhat longer than that of unbound, liquid-phase DMF (1.24 Å).[13] Otherwise, the complex displays fairly typical octahedral geometry, with normal carbonyl Ir−C1 (1.8221(12) Å) and C1−O1 (1.1455(15) Å) bond lengths and very small deviations from 90° angles, except for those constrained by the five-membered ring (C1−Ir−C3 = 95.23(5)°; C3−Ir−I = 171.68(3)°).

The origin of **6** is not clear: although there was no evidence of either free or bound DMF in the sample of precursor **1** by IR spectroscopy, trace amounts must have been present. (Formation of **6** was quite reproducible with different batches of the starting material **1**.) One obvious candidate is intermediate **3**, which contains DMF; reaction with MeI could conceivably initiate the observed C−H activation. However, authentic samples of **3** do not react with MeI at all. While the exact mechanism for formation of **6**, specifically the timing of the methyl C−H activation step, remains uncertain, the fact that the latter can compete at all with activation of the much more reactive aldehydic C−H bond is unexpected and intriguing.

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Experimental Section

General Considerations. All chemicals and solvents were used as received, without further purification. $IrCl_3 \cdot 3H_2O$ was purchased from Alfa Aesar; $[AsPh_4]Cl$, MeI, CH_2Cl_2, hexanes, and DMF were all purchased from Sigma-Aldrich. Infrared spectra were recorded on a Nicolet 6700 by ThermoFisher Scientific using OMNIC software. X-ray diffraction experiments were carried out in the Beckman Institute Crystallographic Facility on a Bruker KAPPA APEXII X-ray diffractometer.

$[AsPh_4][Ir(CO)_2I_2]$ (1). $[AsPh_4][Ir(CO)_2Cl_2]$ (372.0 mg, 0.5296 mmol) was dissolved in methanol and stirred with 5 equiv of NaI (952.6 mg, 6.355 mmol) for 30 min. Volatiles were removed in vacuo. The product was extracted with CH_2Cl_2, and volatiles were removed again in vacuo to give the desired product in virtually quantitative yield.

$[AsPh_4][Ir(CO)(\kappa^2O,C\text{-}CH_2NMeCHO)Cl_2I]$ (6) and $[AsPh_4]_2[Ir(CO)I_4X]$ (5; X = Cl, I). **1** (200 mg, mmol), prepared using the method of decarbonylation of DMF,[1] was reacted with neat MeI (2 mL) for 1 h. Volatiles were removed in vacuo to give a red-orange solid, whose infrared spectrum matched the literature spectrum for $[AsPh_4][Ir(CO)_2I_3Me]$ ($\nu_{CO}(CH_2Cl_2)$ 2098, 2046 cm^{-1}).[9] The solid was dissolved in approximately 7 mL of CH_2Cl_2. This solution was layered with hexanes and stored at −36 °C overnight to give red needles (**5**) and trace yellow crystals (**6**) suitable for X-ray diffraction (80 mg total). The infrared spectrum of these crystals displayed only one CO stretch at 2046 cm^{-1}, corresponding to **5a**.[11] Crystallographic data have been deposited at the CCDC; the deposition number for **6** is 679443, and that for **5b** is 725088.

Structural Data for 6. Details are as follows: crystals from CH_2Cl_2/hexanes; $[C_{24}H_{20}As]^+[C_4H_5NO_2Cl_2IIr]^-$, M_r = 872.41; triclinic, space group $P\bar{1}$; a = 10.0906(3) Å, b = 10.4936(3) Å, c = 14.0657(4) Å; α = 90.0840(10)°, β = 107.5460 (10)°, γ = 94.2860(10)°; U = 1415.63(7) Å^3; d_{calcd} = 2.047 g/cm^3; T = 100(2) K; maximum 2θ x°; Mo Kα radiation (λ = 0.710 73 Å); 24 422 unique reflections were obtained and 19 699 with $I > 2.5\sigma(I)$ were used in the refinement; data were collected on a Bruker KAPPA APEXII X-ray diffractometer; for significant reflections merging R value 0.0277; residuals R_f = 0.0448, R_w = 0.0408 (significant reflections); GOF 1.404.

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Supporting Information Available: A CIF file giving crystallographic data for **6**. This material is available free of charge via the Internet at http://pubs.acs.org.