Selective Deprotonation and Decarbonylation from Hydridocarbonyl-iridium(III) Compounds with Trimethylamine N-oxide

Chong Shik Chin,* Moonhyun Oh, Gyongshik Won, Haeyeon Cho, and Dongchan Shin

Department of Chemistry, Sogang University, Mapoku, Seoul 121-742, Korea

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Me₃NO selectively abstracts the proton from [IrH(CO)(PPh₃)₂L(A)]⁺,⁻,²⁺ (1) (A: -CCPh, Cl⁻, CH₃CN and L: CH₃CN, Cl⁻, ClO₄⁻) to give the trans-elimination products, Ir(CO)(PPh₃)₂(A) (2). The reductive elimination of H⁺ and Cl⁻ from Ir(H)Cl₂(CO)(PPh₃)₂ (1b) to give IrCl(CO)(PPh₃)₂ (2b) is first order in both 1b and Me₃NO. The rate law d[2b]/dt=kobs[1b]=k2[Me₃NO] suggests the formation of (PPh₃)₂(Cl)₂(CO)Ir-H-ON⁺Me₃ in the rate determining step (k₂) followed by the fast dissociation of both H-ON⁺Me₃ and the trans ligand Cl⁻. The rate significantly varies with the cis ligand A and the trans ligand L and is slower with both A and L being Cl⁻ than other ligands. Me₃NO selectively eliminates CO from [Ir(H)₂(CO)(PPh₃)₂]⁺ (3) (L=CH₃CN, ClO₄⁻) to produce [Ir(H)₂(PPh₃)₂(L)²⁺]⁺ (4) (L'=CH₃CN, PPh₃) in the presence of L. Me₃NO does not readily remove either H⁺ or CO from  cis-, trans- and trans-,trans-Ir(H)(-CCPh)₂(CO)(PPh₃)₂ and cis-,trans-Ir(H)₂Cl(CO)(PPh₃)₂.

The choice whether hydridocarbonyls, 1 and 3 undergo the deprotonation or decarbonylation may be understood mostly in terms of thermodynamic stability of the products and partly by kinetic preference of Me₃NO on proton and CO.

Introduction

Both deprotonation and decarbonylation of metal hydridocarbonyls are of interests since they produce coordinatively unsaturated metal species that may play important roles in metal catalyzed reactions. Although transition metal-hydrogen bonds are commonly referred to as metal-hydrides (H⁻), some of them are abstracted in the form of protons (H⁺). Various strong and weak bases have been used to abstract protons from transition metal hydrides when their conjugate bases are stable. Trimethylamine N-oxide (Me₃NO) has been widely used as an effective reagent for the decarbonylation of metal carbonyls (including hydridocarbonyls), while photochemical decarbonylation of metal carbonyls has been reported mainly with non-preparative aspects.

We, in attempts to obtain decarbonylation products, found that the reaction of equimoles of Me₃NO with a hydridocarbonyl complex, [IrH(-CCPh)(CH₃CN)(CO)(PPh₃)₂]ClO₄ selectively eliminates the proton to produce Ir(-CCPh)(CO)(PPh₃)₂ leaving the coordinated CO intact in high yield. This observation prompted us to look into the reactions of related iridium(III) hydridocarbonyls with Me₃NO. We now wish to report that Me₃NO selectively abstracts the proton from monohydridocarbonyl iridium(III) compounds while it selectively eliminates CO of dihydridocarbonyl iridium(III) compounds.

Results and Discussion

Selective Deprotonation from Monohydridocarbonyl Iridium(III) Compounds. When equimoles of Me₃NO are used, [IrH(-CCPh)(CH₃CN)(CO)(PPh₃)₂]⁺ (1a) is converted into Ir(-CCPh)(CO)(PPh₃)₂ (2a) in almost quantitative yield (eq. 1). In the presence of excess Me₃NO, however, complex 2a reacts further with Me₃NO to give the unidentified product(s) which does not contain a coordinated CO. Other hydridocarbonyls, 1b-f and the carbonyl metal complexes, 2b, c behave likewise in their reactions with Me₃NO.

Abstraction of the proton from 1 by Me₃NO would give the intermediate of the five-coordinated 18-electron Ir(I) species which would readily dissociate another ligand to produce more stable complex 2 (eq. 1). The trans ligand L to the proton abstracted by Me₃NO would be the one that is most readily eliminated from the intermediate, which is, in fact, confirmed by the reactions of 1a, d, e (see eq. 1). It may also be likely that the trans Cl⁻ and CH₃CN (not the Cl⁻ and CH₃CN cis to the hydride) are eliminated in the reactions of 1b and 1f, respectively.
due to the less labile trans ligand Cl⁻. This prompted us to look into the effects of the trans ligand L on this reducive trans-elimination of H⁺ and L by Me₃N⁺. Detailed kinetic measurements have been carried out for the reaction of 1b with Me₃NO by measuring the formation of 2b (Fig. 1).

The reaction, 1b + Me₃NO → 2b + Me₃N⁺·OHCl⁻ is first order both in 1b and Me₃NO. The pseudo first order rate constants (kobs) show no dependency on the concentration of the trans ligand Cl⁻. The simple second order rate law d[2b]/dt = kobs[1b] = k₂[1b][Me₃NO] (see Table 1) suggests the formation of "(PPh₃)₂(Cl)₂Ir-H-ON⁺Me₃" in the rate determining step (k₂) followed by the fast dissociation of both H⁺-ON⁺Me₃ and the trans ligand Cl⁻. The formation of "(PPh₃)₂(Cl)₂Ir-H-ON⁺Me₃" in the first step is supported by the negative entropy of activation (ΔS° = -29.5 ± 1.5 cal/degmol) obtained from k₂ in the temperature range of 17-40 °C. It may now be said that the lability of the trans ligand does not significantly affect the rate of the deprotonation from complex 1.

Kinetic electrophilicity of M-H in related compounds may also be discussed with respects to the ancillary ligands. The electrophilicity of M-H in 1b-d may be predicted by the trans ligand L (Cl⁻, ClO₄⁻ and CH₃CN). The slower reaction of 1b (than those of 1c, d) may be understood by the electrophilic effects of trans ligand L. The hydride trans to more basic Cl⁻ in 1b would be less electrophilic than those trans to less basic CH₃CN and ClO₄⁻ in 1c, d (pK₆ for Cl⁻, RCN and ClO₄⁻ are 7, ~10 and 10, respectively). The ¹H NMR data (δ) for the hydrides, however, do not simply agree with the relative electrophilicity of the hydrides of 1b-d. The hydride of 1b appears at δ -15.34 whereas 1c and 1d show the hydrides at δ -17.42 and -22.41, respectively (see also Experimental).

**Selective Decarbonylation from Dihydridocarbonyl iridium (III) Compounds.** Deprotonation is not observed in the reactions of related dihydridocarbonyls, cis, trans-Ir(H)₂(CO)(PPh₃)₂ (1b) and cis, trans-Ir(H)₂(OC)(PPh₃)₂(ClO₄) (3b) with Me₃NO. Compounds, 3 undergo CO elimination reaction to give [Ir(H)₂(PPh₃)₂L'(CH₃CN)]⁺ (L' = CH₃CN, PPh₃) (4) in their reactions with Me₃NO in the presence of L' (eq. 2). Kinetic measurements have not been carried for the reactions of 3 with Me₃NO since no appropriate experimental method has been found yet. It is noteworthy that the product 2' expected from the deprotonation of 3 have not been isolated previously whereas product 4 are stable even in solution in air.

**Neither Deprotonation Nor Decarbonylation from cis, trans-Ir(H)₂Cl(CO)(PPh₃)₂ (5), cis, trans-Ir(H)(-CCPh)₂(CO)(PPh₃)₂ (6) and trans, trans-Ir(H)(-CCPh)₂(CO)(PPh₃)₂ (7).** Some iridium(III) hydridocarbonyls, on the other hand, do not readily lose the proton or CO in their reactions with Me₃NO. cis, trans-Ir(H)₂Cl(CO)(PPh₃)₂ (5), cis, trans-Ir(H)(-CCPh)₂(CO)(PPh₃)₂ (6) and trans, trans-Ir(H)(-CCPh)₂(CO)(PPh₃)₂ (7) do not undergo either deprotonation or decarbonylation even in the presence of excess Me₃NO and CH₃CN (eq. 3). The reaction mixture of 5 (or 6, 7) and excess Me₃NO yields unidentifiable compound(s) when it is stirred for more than 5 hours at room temperature.

Table 1. Rate Constants (kobs and k₂) and Activation Parameters for the Reaction, IrCl(CO)(PPh₃)₂ (1b)+Me₃NO→IrCl(CO)(PPh₃)₂ (2b)+Me₃NOH+Cl⁻ in CHCl₃ at 17 °C, [Ir] = 5.0×10⁻⁵ M

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<th>[Me₃NO], 10⁻³ M</th>
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<td>25.00</td>
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ΔH° = -9.50±0.44 kcal/mol, ΔS° = -29.5±1.5 cal/degmol, ΔE° = ±9.99±0.43 kcal/mol at 17–40 °C.
Deprotonation vs. Decarbonylation. The fact that Me$_3$NO selectively abstracts the proton from monohydridocarbonyls, 1 while it selectively eliminates the CO from dihydridocarbonyls, 3 could be discussed in several aspects. There has been no report to our knowledge, on the relative electrophilicity between M-H and M-CO for a given compound. It does not seem feasible to discuss the relative electrophilicity of M-H and M-CO of 1 and 3 until much more works have been done in this field. The spectral data, for example, (see Experimental section for $\nu_{\text{ex-CO}}$ and $\delta$ of Ir-H of 1 and 3) do not provide a good explanation for the selective attack of Me$_3$NO on the hydrides of 1 in preference to the carbonyl groups in 3.

It seems certain, however that the products 2 and 4 are so stable that they can be isolated without much precaution whereas most of 4' and 2' have never been isolated except that IrH(Cl)$_2$(PPh$_3$)$_3$ has been known to be very stable. While the deprotonation is a reduction of six coordinated iridium(III) species to four coordinated iridium(I) species, the decarbonylation is a simple dissociation of a ligand. Another ligand L', therefore, should be present in the reaction mixture to produce stable six coordinated complexes such as 4 when the CO abstraction occurs in preference to the deprotonation as seen in eq. 2. Of the four coordinated 16 electron compound 2', the hydridocarbonyl, trans-Ir(H)(CO)(PPh$_3$)$_2$ has been only suggested (never isolated) as an intermediate in reactions of related complexes. Carbon monoxide seems to be the best ligand to stabilize the related four coordinated non-hydrido iridium(I) compounds containing two PPh$_3$ such as Vaska's complex. On the other hand, dihydridoiridum(III) compounds such as 4 seem to be stabilized without coordinated CO while many monohydrido complexes with no coordinated CO such as 4' are not stable enough to be isolated.

In general, products 2 and 4 seem to be the thermodynamic products since the proton abstraction products, 2 and decarbonylation products, 4 seem more stable than 4' and 2', respectively. However, the deprotonation from Ir(H)(Cl)$_2$(CO) (PPh$_3$)$_2$ (1b) in preference to the decarbonylation may not be unambiguously understood either by a kinetic or thermodynamic phenomenon since both of IrCl(CO)(PPh$_3$)$_2$ (2b) and Ir(H)(Cl)$_2$(PPh$_3$) (expected from decarbonylation of 1b) are known to be very stable under the experimental conditions (25 $^\circ$C, N$_2$, CHCl$_3$ or C$_6$H$_6$).

That neither the proton abstraction products nor the decarbonylation products are obtained from the reactions of 5, 6 and 7 (eq. 3) may also be explained by kinetic phenomenon (high activation energy process) for both deprotonation and decarbonylation reactions since Ir-CCPh(CO)(PPh$_3$)$_2$ (2a)$^{9}$ and Ir(H$_2$Cl)(PPh$_3$)$_2$$^{12}$ are also known to be stable under the experimental conditions.

Experimental Section

Caution! Extensive precautions must be taken, since perchlorate salts and perchlorato-transition metals are potentially explosive.$^{13}$

General Considerations and Instruments. Reactions were carried out in an atmosphere of dry nitrogen. Solvents were dried and distilled before use. $^1$H and $^{13}$CNMR and IR spectra were recorded on a Varian Gemini 200 or 300 MHz spectrometer and Shimadzu IR-450 spectrophotometer.

Preparation of Reactants. Complex 1a, 1b, 1d, 4a$^{11}$ and 3b$^{18}$ were prepared by the literature methods. Relevant spectral data, $\nu_{\text{CO}}$ (cm$^{-1}$, Nujol) and Ir-$H$ (CDCl$_3$, ppm) (see discussion) are as follows: 1a (2010, -17.42); 1b (2024, -15.34); 1d (2054, -22.41); 3a (2035, -8.47 (trans to CO), -18.21 (trans to CH$_3$CN)); 3b (2004, -6.29 (trans to CO), -25.34 (trans to ClO$_4$)). $[\text{Ir(H)}(\text{Cl})(\text{CH}_3\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (1e): Yellow CHCl$_3$ (15 mL) solution of $[\text{Ir(H)}(\text{CN})(\text{CO})(\text{PPh}_3)_2]\text{ClO}_4$ (2c) (0.10 g, 0.11 mmol) was slowly bubbled with HCl for a minute until the reaction mixture turned pale yellow. Hexane (25 mL) was immediately added and the pale yellow micro-crystals were collected over a filter, washed and dried in vacuum. The yield was 0.095 g (10 mmol, 91%). $^1$H NMR (CDCl$_3$): $\delta$ 1.89 (s, 3H, CH$_3$CN), -16.50 (t, 1H, J$_{\text{Ir-H}}$=10.2 Hz, Ir-$H$). 

Njol, cm$^{-1}$: 2080 (s, $\nu_{\text{CO}}$). Anal. Calcd for IrP$_3$C$_5$H$_{44}$O$_7$: C, 50.88; H, 3.72; N, 1.21. Found: C, 51.09; H, 3.85; N, 1.25.

Reactions with Me$_3$NO. All the reactions of 1 with Me$_3$NO were carried out under nitrogen in the same manner.
as described above for the preparation 4b. Byproducts, Me₃N+OHClO₄⁻ and Me₃N+OHCl⁻ have been isolated and identified by ¹H NMR (two singlets at δ 3.32 and 3.23 in CDCl₃ at 200 MHz and 25 °C) and IR (KBr, ca. 2750 cm⁻¹ (m, νC-H) and ca. 1100 cm⁻¹ (s, ClO₄⁻)).

Kinetic Measurements. A Hewlett Packard 8452A diode array spectrophotometer was used to follow the spectral changes during the reaction at intervals of 1-20 seconds. All the kinetic measurements were carried out in the similar manner as described below for the reaction of 1b with Me₃NO. Appropriate amounts of the stock solutions of 1b (3.5×10⁻³ M in CHCl₃) and Me₃NO (3.5×10⁻² M in CHCl₃) were quickly added to CHCl₃ in a 3.5 mL cell to make the reaction mixture. The reaction mixture was shaken for a few seconds before the spectral changes (increases in absorbance) were measured at 388 nm.

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References


7. CH₃CN of 1e is readily replaced with various unsaturated organic compounds. Reactivities of 1e will be reported elsewhere.


9. trans, trans-IrH(-CCPh)₂(CO)(PPh₃)₂ will be reported in detail elsewhere.


