# Direct Observation of Reductive Elimination of Methyl Iodide from a Rhodium(III) Pincer Complex: The Importance of Sterics

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Oxidative addition and reductive elimination are fundamental transformations of great importance in many catalytic and stoichiometric processes.[1] For instance, they are involved in palladium-catalyzed cross-coupling reactions of organic halides.[1–3] While stoichiometric oxidative addition reactions of organic halides to low-valent late transition metal centers are common, the reverse reaction, reductive elimination of these compounds, is generally thermodynamically uphill and has rarely been observed. The few examples of reductive elimination of *aryl* halides from late transition metal centers involve Pt(IV)[4,5] and Pd(II).[6,7] Reductive elimination of an *alkyl* halide was reported for methyl halide complexes of Pt(IV) upon thermolysis.[8] The anionic acetyl complex [(CH$_3$CO)Rh-(CO)I$_3$]$^-$ decomposes by loss of methyl iodide.[9a] In the presence of CO, the generated dicarbonyl complex [(CH$_3$CO)Rh(CO)$_2$I$_3$]$^-$ reductively eliminates acetyl iodide.[9] These reactions are thought to be key steps in the mechanism of the industrial Rh-catalyzed methanol carbonylation to acetic acid,[9,10] in which the unstable [CH$_3$Rh(CO)$_2$I$_3$]$^-$ was detected spectrally as a minor component of the reaction mixture and kinetically studied, providing mechanistic insight into this process.[9b] However, despite their importance, we are unaware of studies of reductive elimination of alkyl halides from isolable Rh(III) alkyl complexes.[7,11]

We report here reductive elimination of methyl iodide from a methyl Rh(III) pincer complex at room temperature. Upon treatment with CO, a stable Rh(I) complex is cleanly obtained. We show that steric effects can have a major impact on the overall reductive elimination process, and may override electronic effects. A plausible mechanism is proposed.

When the naphthyl-based PCP-type complexes [(C$_{10}$H$_5$(CH$_2$-PR$_2$)$_2$)Rh($\eta^1$-N$_2$)] (R = $^i$Pr **1a**,[12] R = $^t$Bu **1b**[13]) were treated in benzene with an equimolar amount of methyl iodide at room temperature, the corresponding dark-red, oxidative addition products [(C$_{10}$H$_5$(CH$_2$PR$_2$)$_2$)Rh(CH$_3$)(I)] (R = $^i$Pr **2a**, R = $^t$Bu **2b**) were instantly and quantitatively formed (Scheme 1). The $^{31}$P{$^1$H} NMR spectra of these complexes exhibited the two inequivalent trans phosphine signals as ddd (AB) patterns. The signals due to **2a** appeared at $\delta$ = 48.53 and at $\delta$ = 45.79 ppm ($^1J_{RhP}$ = 116.5 Hz, $^2J_{PP}$ = 54.6 Hz), and the ones due to **2b** appeared at $\delta$ = 58.54 and at $\delta$ = 55.94 ppm ($^1J_{RhP}$ = 117.9 Hz, $^2J_{PP}$ = 13.4 Hz). The Rh–Me group appeared in the $^1$H NMR spectrum of **2a** as an unresolved doublet of triplets signal at $\delta$ = 1.68 ppm and in the case of **2b**, as a dt signal at $\delta$ = 1.79 ppm ($J_{RhH}$ = 8.2 and $J_{PH}$ = 4.1 Hz). The $^{13}$C{$^1$H} NMR spectrum of **2a** clearly showed a well-defined doublet resonance at $\delta$ = 171.43 ppm ($^2J_{PC}$ = 35.5 Hz) assigned to the C$_{ipso}$ atom of the cyclometalated aryl core, as well as a dt signal at $\delta$ = −1.12 ppm ($^2J_{RhC}$ = 29.3 and $^2J_{PC}$ = 6.7 Hz), assigned to the methyl ligand coordinated in the apical position, as found in related systems.[14] The corresponding signals in the $^{13}$C-

**Scheme 1**
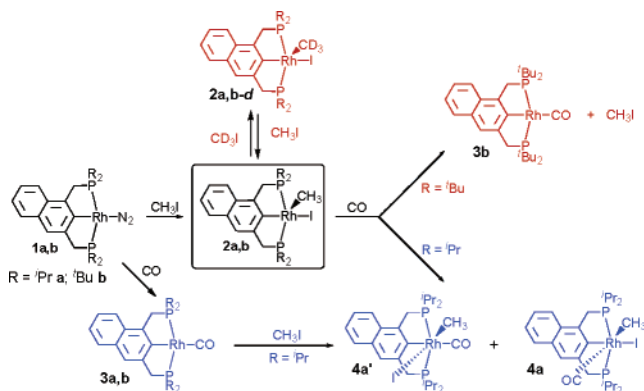


{$^1$H} NMR spectrum of **2b** appeared at $\delta$ = 174.73 ppm as a doublet ($^1J_{RhC}$ = 35.4 Hz) as well as a signal with a dt pattern at $\delta$ = 3.92 ppm ($^1J_{RhC}$ = 29.6; $^2J_{PC}$ = 6.0 Hz).

Significantly, when benzene solutions of the P$^t$Bu$_2$ complex **2b** were treated with an excess (~100 equiv) of CO overnight, slow but almost quantitative reductive elimination to form the carbonyl complex [(C$_{10}$H$_5$(CH$_2$P$^t$Bu$_2$)$_2$)Rh(CO)] (**3b**) took place.[15] **3b** was independently prepared by treatment of **1b** with CO.[13] Formation of methyl iodide was confirmed by NMR spectroscopy and by GC/MS. The reverse reaction between **3b** and methyl iodide did not take place, even when a large excess (~100 equiv) of methyl iodide was used for 48 h.

In striking difference, treatment of the analogous P$^i$Pr$_2$ complex **2a** with CO in benzene did not result in reductive elimination of methyl iodide to yield **3a**. Rather, the CO adducts **4a** (17%) and **4a′** (83%) were formed (Scheme 1).[16] The $^{31}$P{$^1$H} NMR spectrum of the reaction mixture of **4a** and **4a′** exhibited two sets of signals with ddd (AB) patterns. The signals assigned to **4a** are centered at $\delta$ = 56.45 and at $\delta$ = 51.45 ppm ($^2J_{PP}$ = 380.7 and $^1J_{RhP}$ = 101.3 Hz). Those of **4a′** are centered at $\delta$ = 62.96 and at $\delta$ = 59.16 ppm ($^2J_{PP}$ = 356.3 and $^1J_{RhP}$ = 101.2 Hz). The Rh–Me groups gave rise in the $^{13}$C{$^1$H} NMR spectra to two sharp dt resonances at $\delta$ = −8.93 ppm ($^1J_{RhC}$ = 25.3; $^2J_{PC}$ = 5.7 Hz) and at $\delta$ = −2.92 ppm ($^1J_{RhC}$ = 22.3, $^2J_{PC}$ = 4.9 Hz). The substantial difference in the chemical shifts indicates different ligands trans to Rh–Me.

Formation of the CO adducts **4a** and **4a′**, with no reductive elimination being observed, underlines the importance of steric factors in this process. As opposed to the reaction of **2a** with CO, reductive elimination of methyl iodide upon treatment of **2b** with CO is thermodynamically favored over formation of the corresponding Rh(III) carbonyl adducts due to steric reasons, even though electronic effects are expected to lead to the opposite mode of reactivity, the P$^t$Bu$_2$ group being a better donor than P$^i$Pr$_2$.

Reductive elimination of CH$_3$I from the P$^i$Pr$_2$ complexes **4a** and **4a′** is not only kinetically but also thermodynamically unfavorable;

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**Scheme 2**
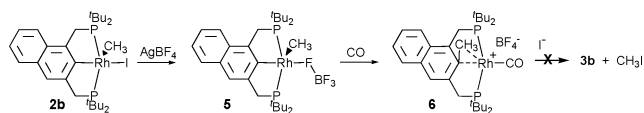


treatment of benzene or $CH_2Cl_2$ solutions of the Rh(I)CO complex **3a** with a slight excess ($\sim$1.5 equiv) of $CH_3I$ resulted in oxidative addition to form the complexes **4a** (17%) and **4a′** (83%), in contrast to the lack of reactivity of **3b** with $CH_3I$, showing the dominant effect of sterics over electronics in oxidative addition. The CO stretch is indicative of the higher electron density at the metal center of **3b** (1930 cm$^{-1}$) as compared with **3a** (1938 cm$^{-1}$).

Further experiments were carried out in order to gain more insight into this rare reductive elimination process. Significantly, upon treatment of benzene solutions of **2a** or **2b** with $CD_3I$ overnight, the labeled methyl iodide complexes **2a**-*d* and **2b**-*d* were obtained (confirmed by $^1$H and $^2$H NMR spectroscopy), indicating that a reversible reductive elimination process was operative *in both* systems, although no overall reductive elimination was observed upon treatment of the less bulky **2a** with CO. No change in the rate of the $CH_3/CD_3$ exchange with **2b** was noticed in the presence of 50 equiv of iodide ($^n$Bu$_4$NI), suggesting that iodide dissociation is probably not involved in this process.

No intermediates were detected when the reaction of **2b** with CO to yield **3b** was monitored by NMR spectroscopy, and no changes in the reaction rate were noticed in the presence of an excess ($\sim$50 equiv) of methyl iodide or $^n$Bu$_4$NI. The lack of retardation in the presence of excess methyl iodide may indicate that **2b** undergoes reversible reduction to produce a Rh(I) methyl iodide complex, followed by associative substitution of the methyl iodide ligand by CO to form **3b**. This is unlike the P$^t$Bu$_3$-promoted reductive elimination of 2-bromotoluene from [Pd(*o*-tol)(P($^t$Bu)$_3$)-(Br)], which was retarded by added aryl bromide.[6b] The observation that added iodide anion had no effect on the rate suggests that a mechanism involving initial iodide dissociation followed by iodide attack on the coordinated methyl group is unlikely.[17] In addition, iodide dissociation upon CO coordination and subsequent external nucleophilic attack of the iodide anion on the methyl ligand is also unlikely. A cationic Rh(III)Me intermediate is expected to undergo methyl migration to the *ipso* carbon upon CO coordination to yield the $\eta^2$ C−C agostic complex (analogous to **6**, Scheme 2, but with iodide counter anion, as described below), in competition with methyl iodide elimination from the neutral **2b**.

Indeed, when **2b** was treated with CO in the more polar (compared to benzene) $CH_2Cl_2$ solvent overnight, a significant amount of $\eta^2$ C−C agostic complex ($\sim$38%), in addition to **3b** ($\sim$54%) was detected by NMR spectroscopy. Formation of the agostic complex was suppressed when 10 equiv of iodide ($^n$Bu$_4$-NI) were added. Furthermore, abstraction of the iodide ligand of **2b** with AgBF$_4$ yielded the BF$_4$ coordinated complex **5**,[13] which upon treatment with CO underwent methyl migration to the *ipso* carbon, forming the $\eta^2$ C−C agostic complex **6**,[13] as observed with other Rh pincer systems[14,18] (Scheme 2). Treatment of $CH_2Cl_2$ or benzene solutions of **6** with an equimolar amount (or excess) of $^n$Bu$_4$NI at room temperature did not result in formation of $CH_3I$ and **3b**, confirming that $\eta^2$ C−C agostic intermediates such as **6** are not involved in the mechanism.

Unlike the mechanism proposed here for methyl iodide reductive elimination from the Rh(I) complex **2b**, halide dissociation followed by nucleophilic attack on carbon was described for the reductive

elimination of methyl iodide from the Pt(IV) complex [(Ph$_2$PCH$_2$-CH$_2$PPh$_2$)Pt(CH$_3$)$_3$(I)][8b,c] and for the reductive elimination of aryl bromide upon treatment of [{(CH$_2$)$_n$(PR$_2$)$_2$}Pt(C$_6$H$_4$F)$_2$] with bromine.[5]

In conclusion, facile, quantitative reductive elimination of methyl iodide was observed upon treatment of the Rh(III) methyl iodide complex **2b** with CO under mild conditions, yielding the Rh(I) carbonyl complex **3b**. In contrast, the less bulky ($^i$Pr vs $^t$Bu) **2a** formed CO adducts and did not eliminate methyl iodide, although the lower electron density at the metal in **2a** was expected to render reductive elimination more favorable in this case, underlining the major importance of steric effects on this process. Moreover, the Rh(I) carbonyl **3a** oxidatively added methyl iodide, while **3b** did not. $CD_3I/CH_3I$ exchange studies with **2a,b** in absence of CO indicate that reversible formation of methyl iodide (which probably stays coordinated) takes place in both systems. When CO is present, it displaces methyl iodide in the bulkier $^t$Bu system, while with the $^i$Pr system formation of the Rh(III) adducts **4a** and **4a′** is favored. Iodide dissociation followed by its attack on the rhodium-methyl group is unlikely.

**Supporting Information Available:** Preparation procedures and characterization for **1b**, **2a**, **2b**, **3a**, **3b**, **4a**, **4a′**, **5** and **6**. This material is available free of charge via the Internet at http://www.pubs.acs.org.

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(15) Although no intermediates were observed by NMR spectroscopy, rapidly reversible interaction of **2b** with CO cannot be excluded.
(16) Reaction of **2a** with CO at −50 °C resulted in **4a** exclusively, indicating that it is the kinetic product. Upon warming up to room temperature, an equilibrium mixture of 17% **4a**, 83% **4b** was obtained, which did not change upon cooling to −50 °C.
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