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A mechanistic study of thermal C–H reductive elimination from a six-coordinate d^6 iridium complex [1]

Glen P. Rosini, Kun Wang, Bhushan Patel, Alan S. Goldman *

Department of Chemistry, Rutgers — The State University of New Jersey, Piscataway, NJ 08855-0939, USA

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Abstract

The thermolysis of *trans*-$IrL_2(CO)Cl(H)(C_6H_5)$ (**1a**; L = P(i-Pr)$_3$; H *trans* to CO) produces benzene and the Vaska-type complex $IrL_2(CO)Cl$. A mechanistic study of the reaction has shown that **1a** reversibly loses CO at 120 °C (as evidenced by the incorporation of ^{13}CO) and isomerizes to the previously unreported **1b** (H *trans* to Cl). It was found that **1b** is the complex primarily responsible for the formation of benzene upon thermolysis under CO atmosphere; direct loss of benzene from **1a** was determined to be, at most, a minor pathway. Benzaldehyde was also formed as a product of thermolysis of **1a** under CO atmosphere. The first-order rate constant for benzene elimination in the absence of CO was found to be 8.5×10^{-5} s^{-1}. The presence of only 5 Torr CO results in a decrease to 2.0×10^{-5} s^{-1}, but little further inhibition is observed above 5 Torr CO. Added dihydrogen (100 Torr) was found to effect a novel *catalysis* of benzene elimination from **1a** in the absence of CO atmosphere; it is suggested that trace amounts of dihydrogen, present in solutions of **1a**, are responsible for the enhanced rate of elimination in the absence of CO. The thermolysis of **1-d$_6$** in toluene was found to proceed without any toluene incorporation, implying that arene loss is irreversible. © 1998 Elsevier Science S.A.

Keywords: Thermolysis; Reductive elimination; Iridium complexes; Aryl complexes; Hydride complexes; Six-coordinate complexes

1. Introduction

In 1968 Jack Halpern noted that "the development of successful approaches to the activation of C–H bonds ... constitutes one of the most important and challenging problems in [homogeneous catalysis]" [1]. It was not until 1982 that the first examples of intermolecular alkane C–H bond addition were observed [2,3]. However, in the intervening years, and through to the present date, kinetics of the reverse reaction, C–H bond elimination, have been carefully studied by Halpern and others. Though one goal of such studies is to elucidate an understanding of C–H bond addition, it should not be overlooked that C–H bond elimination itself is a step in many important currently practiced catalytic processes.

Halpern's work led to the conclusions that C–H elimination was typically a kinetically facile process and thus the relative scarcity of examples of C–H addition was the result of thermodynamic rather than kinetic barriers [4]. Subsequent kinetic studies of C–H addition reactions have supported this conclusion. Many such studies revealed a rate-determining step (either thermo- or photochemical) in which a coordination site is opened, followed by C–H addition which was inferred to be rapid. In other work the addition process has been monitored directly and is found to be extremely facile, occurring at temperatures as low as 12 K [5–8].

Notwithstanding the above, many examples are known in which C–H bond elimination is not kinetically facile. Elimination of C–H bonds, as well as other non-polar addenda such as C–C bonds or even H_2, often appears to require prior ligand loss [9]. In particular, a significant kinetic barrier to direct addition/elimination where the adduct has a six-coordinate d^6 configuration is well known [9] and has been well explained theoretically [10]. The kinetic barrier to addition/elimination involving the corresponding five-coordinate d^6 complexes, by contrast, has been shown to be very small [11]. Accordingly, ligand loss from the six-coordinate complexes is generally presumed to be directly followed by facile elimination from the five-coordinate intermediate.

The phenyl hydride complex $IrL_2(CO)ClPhH$ (L = P(i-Pr)$_3$) was reported several years ago by Werner et al. [12]. We observed that this complex slowly decomposes to give the very stable Vaska-type complex $IrL_2(CO)Cl$. In this

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* Corresponding author. Tel.: + 1 908 445 5232; fax: + 1 908 445 5312; e-mail: goldman@rutchem.rutgers.edu

[1] Dedicated to Professor Jack Halpern, mentor and continual source of inspiration.

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paper, we report on kinetic studies of this decomposition reaction which yield several unanticipated results.

2. Experimental

2.1. General procedures

All solvents were either freshly distilled under vacuum from NaK alloy, or purchased anhydrous from Aldrich and stored under nitrogen. All samples were stored and prepared under nitrogen in a Vacuum Atmospheres Dry-Lab glove box. UV–Vis spectra were obtained using a Varian DMS 100S spectrophotometer. ^1H, ^{31}P and ^{13}C NMR spectra were obtained using a Varian XL-400 NMR spectrometer. IR spectra were obtained with a Mattson Genesis Series FT-IR spectrophotometer. Irradiations were conducted using a 200 W Hg-arc Oriel lamp, and the proper wavelengths were achieved using filters obtained from FJ Gray. $IrL_2(CO)Cl(H)(C_6H_5)$, **1a** [12], and $IrL_2(N_2)Cl$ [13] were prepared as previously reported.

2.2. The preparation of $IrL_2Cl(H)(C_6H_5)$ (2)

A 30 ml sample of 10 mM $IrL_2(N_2)Cl$ [13] in benzene was placed in a 75 ml ampoule under nitrogen. The sample was then irradiated ($\lambda > 330$ nm) for periods of 10–15 min, followed by thermolysis at 50 °C for 15–30 min until the reaction was complete by ^{31}P NMR spectroscopy (the solution turns from yellow to orange–red). The yield by ^{31}P NMR was above 95%. Recrystallization from hexanes gave the product as a dark orange–red product. Samples of **2-d₆** were prepared as above using C_6D_6 as the solvent.

2.3. The thermolysis of $IrL_2(CO)Cl(H)(C_6H_5)$ (1a)

A 2.5 ml sample of 0.5 mM **1a** in toluene was placed in a 1 cm cuvette cell fitted with an air-tight Teflon seal and with an adaptor allowing connection to a high vacuum line to permit the addition of gases. The samples were then placed under the desired atmosphere and the reaction was conducted in a GC oven maintained at 120 °C, followed by analysis at room temperature. The reaction was monitored by UV–Vis spectroscopy, by following the growth of the bands due to $IrL_2(CO)Cl$ at 379.1 and 431.8 nm. The data were then fitted exponentially using SigmaPlot (Jandel Scientific) to obtain rate constants for the formation of $IrL_2(CO)Cl$. The reaction was also monitored by ^1H and ^{31}P NMR spectroscopy by preparing a 0.6 ml sample of 20 mM **1a** in d_8-toluene in a J. Young resealable NMR tube. The sample was then heated at 120 °C in a GC oven and ^1H and ^{31}P NMR spectra were obtained at room temperature. Under these conditions, a new organometallic species was observed to grow. This species was assigned as **1b** on the basis of its ^1H, ^{31}P and ^{13}C NMR spectra (see below). Benzaldehyde formation was also observed by ^1H NMR spectroscopy.

2.4. Spectroscopic characterization of 1b

Thermolysis of a 0.6 ml sample of 20 mM **1a** in d_8-toluene for 10 h under CO results in the steady state formation of 10% **1b** (conducting the reaction under ^{13}CO results in formation of **1b-¹³C**). ^1H, ^{31}P and ^{13}C NMR spectroscopy allows for an unequivocal assignment of the structure of **1b** based on its full spectroscopic characterization.

^1H NMR: 8.87 (d, $J_{H-H} = 7.2$ Hz, 1 H), 7.70 (d, $J_{H-H} = 7.5$ Hz, 1 H), 6.7–6.8 (m, 3 H), 2.13 (m, 6 H, $P(CHMe_2)_3$), 1.0–1.2 (36 H, $P(CHMe_2)_3$, overlaps with **1a**), −17.95 (t, $J_{H-P} = 12.6$ Hz, $J_{H-C} = 4.3$ Hz; cf. 49.4 Hz for **1a**). ^{31}P NMR: 7.94 (s). ^{13}C NMR: 177.7 (m, CO). IR (toluene): $\nu_{CO} = 1999$ cm^{-1}.

2.5. Measurement of the rate of CO loss from 1a

A 2 ml sample of 20 mM **2** in toluene was placed under 100 Torr of ^{13}CO in a 75 ml ampoule to generate **1a-¹³C**. The excess ^{13}CO was then removed in vacuo, followed by the addition of 800 Torr of CO. The sample was then placed in a GC oven at 120 °C, and the exchange followed by IR spectroscopy by monitoring the growth of **1a** ($\nu_{CO} = 1978$ cm^{-1}) and **1b** ($\nu_{CO} = 1999$ cm^{-1}). The rate of CO exchange was obtained with an exponential data fit, yielding a rate constant of 4.78×10^{-4} s^{-1}.

2.6. The thermolysis of $IrL_2(CO)Cl(D)(C_6D_5)$ (1a-d₆)

A 0.7 ml sample of 20 mM **1a-d₆** in toluene was placed in a resealable J. Young NMR tube, along with a capillary of d_6-acetone containing 2.4 mM of $P(OPh)_3$ as an internal phosphorus standard. The NMR tube was then placed in a GC oven at 90 °C for 12 h and then at 120 °C for 12 h, and the reaction monitored by ^{31}P NMR and ^1H NMR spectroscopy. No incorporation of the toluene to form $IrL_2(CO)Cl(H)(C_8H_7)$ was observed.

2.7. The thermolysis of $IrL_2Cl(D)(C_6D_5)$ (2-d₆)

A 0.7 ml sample of 20 mM **2-d₆** in toluene was placed in a resealable J. Young NMR tube, along with a capillary of d_6-acetone containing 2.4 mM of $P(OPh)_3$ as an internal phosphorus standard. The NMR tube was then placed in a GC oven at 90 °C for 2 h at which time no toluene incorporation was observed. The sample was then heated at 120 °C for 2 h, and the reaction monitored by ^{31}P and ^1H NMR spectroscopy. Small peaks attributable to the incorporation of the toluene to form $IrL_2Cl(H)(C_8H_7)$ were observed; however, the decomposition of **2-d₆** was the major reaction observed.

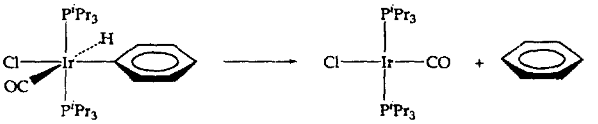
3. Results and discussion

3.1. Preparation of $IrL_2Cl(H)(C_6H_5)$ (2)

The reaction of $[Ir(COE)_2Cl]_2$ and L in refluxing benzene, as reported by Werner et al. [12], yields a 2:1 mixture of **2** and $IrL_2Cl(H)_2$, which must then be separated by repeated recrystallizations. In an attempt to obtain a better yield of **2** (without the concurrent formation of the dihydride complex), we have investigated the photochemistry of $IrL_2Cl(N_2)$ in benzene. Photochemical dinitrogen loss followed by the C–H activation of benzene might be expected to give **2** in high yield. This was found to be the case, with yields of **2** greater than 95% (with less than 2% dihydride formation). We are also currently examining the synthetic utility of $IrL_2Cl(N_2)$ for the generation of hydrocarbyl hydrides that have not been previously synthesized.

3.2. The thermolysis of $IrL_2(CO)Cl(H)(C_6H_5)$ (1a)

Thermolysis of **1a** under argon atmosphere results in clean elimination of benzene, forming $IrL_2Cl(CO)$ as the sole iridium-containing product, as evidenced by ^1H and ^{31}P NMR spectroscopy (Eq. (1)):



(1)

In preliminary kinetic runs, UV–Vis spectroscopy was used to monitor the growth of the product peaks at 431.8 and 379.1 nm (**1a** is a colorless species, and does not significantly absorb at these wavelengths; see Fig. 1 for a typical reaction profile). The presence of added $P(i\text{-}Pr)_3$ (5 mM) and Cl^- (10 mM KCl/0.1 M 18-crown-6) did not inhibit the rate of reaction (1). By contrast, CO atmosphere exerted a strong inhibitory effect (see Fig. 2), implying a pathway for benzene loss which proceeds via reversible loss of CO. However, the plot of rate versus P_{CO} in Fig. 2 shows a non-zero asymptotic rate (about $1.7\times10^{-5}\ s^{-1}$) suggesting the concomitant existence of a slower, direct, benzene loss pathway. These conclusions are most simply accommodated as outlined in Scheme 1. We will separately discuss the two pathways below.

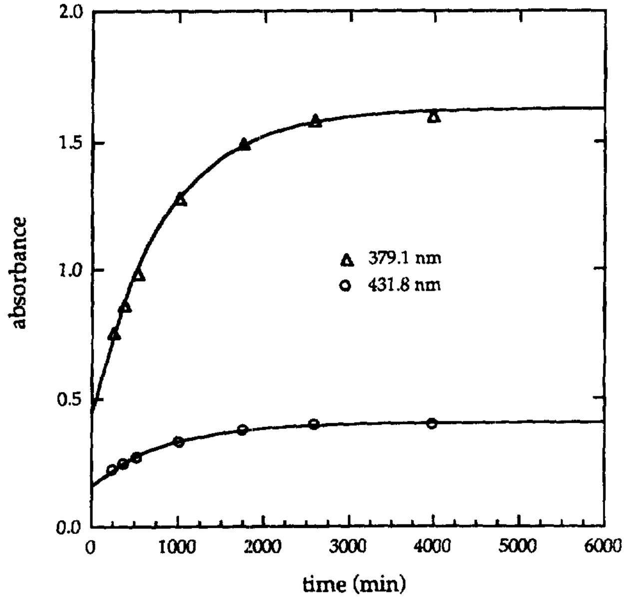


Fig. 1. Thermolysis of **1a** (0.5 mM in toluene) at 120 °C, 5 Torr CO. Lines represent best fit to a first-order exponential equation ($k=2.0\times10^{-5}\ s^{-1}$).

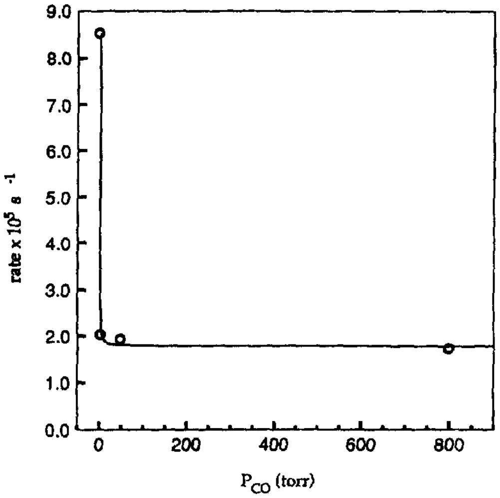


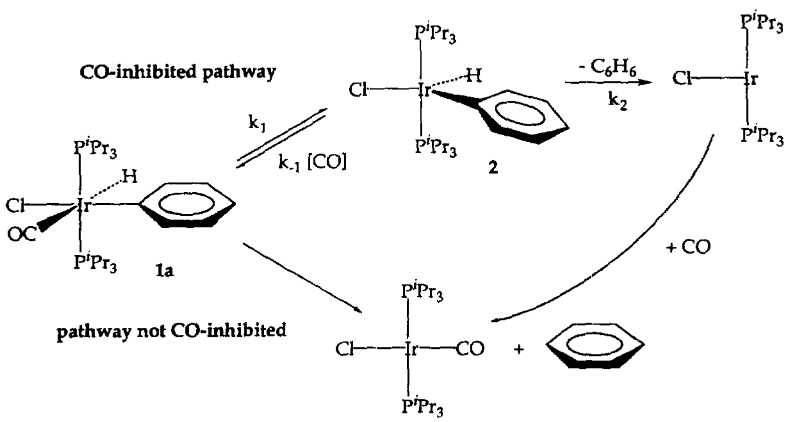
Fig. 2. Rate of reaction (1) (formation of $IrL_2(CO)Cl$) vs. P_{CO} (0.5 mM **1a** in toluene, at 120 °C).

3.2.1. The pathway inhibited by added CO

The indirect pathway depicted in Scheme 1 involves reversible loss of CO followed by loss of benzene. As noted above, reductive eliminations (or oxidative additions) proceeding via ligand loss are very well precedented [9]. In this case, somewhat unusually, the putative intermediate resulting from ligand loss, namely, IrL_2ClPhH (**2**), is an isolable complex [12]; this permits more rigorous testing of the proposed mechanism.

Heating a solution of **2** in toluene-d_6 only results in very slow disappearance of **2** ($5\times10^{-5}\ s^{-1}$) with IrL_2ClH_2 being the only major product observed. No significant benzene/toluene-d^6 exchange is detected by either ^{31}P or ^1H NMR. Qualitatively, the failure of **2** to undergo arene exchange argues against the mechanism of Scheme 1; it might be counter-argued, however, that the benzene-loss product, IrL_2Cl, undergoes decomposition to IrL_2ClH_2 rather than arene exchange. In that context, we can at least consider the decomposition rate, $5\times10^{-5}\ s^{-1}$, as a conservative upper limit for the rate of benzene loss from **2** at 120 °C.

The equilibrium (or steady-state) concentration of **2** in solutions of **1a** is very small; **2** is not detectable by either ^{31}P or ^1H NMR in a solution of **1** at 120 °C (or lower). Indeed, solutions of **1** under argon do not appear any different from solutions under 1 atm CO which would strongly diminish any



Scheme 1. Mechanism for benzene loss from **1** consistent with *preliminary* data.

small equilibrium concentration of **2**. In combination with this low concentration of **2**, the very low rate constant for benzene loss from **2** (below $5 \times 10^{-5}\ s^{-1}$) is inconsistent with the mechanism indicated in Scheme 1; i.e., the value of $k_2(\mathbf{2})$ is much too small to permit the pathway in Scheme 1 to account for the observed rate ($8.5 \times 10^{-5}\ s^{-1}$ (**1**)) observed for reaction (1) in the absence of added CO.

Although the pathway of Scheme 1 thus appeared inconsistent with the observed kinetics, the fact of CO inhibition still strongly argued for a CO-loss pathway. In order to test the proposal of reversible loss of CO from **1a**, **1a-^{13}C** was synthesized by the addition of ^{13}CO to a solution of **2**. The sample of **1a-^{13}C** was then placed under 800 Torr of ^{12}CO. No exchange was observed at room temperature as monitored by IR spectroscopy. At 120 °C, however, CO exchange was facile and the exchange rate was determined to be $4.8 \times 10^{-4}\ s^{-1}$ (see Fig. 3).

The following three observations appeared incongruent: (i) the reaction was inhibited by CO, (ii) CO loss was sufficiently fast to be an initial reaction step, but (iii) the presumed product of CO loss, **2**, was apparently not a kinetically competent intermediate. We considered that the conditions involved in the decomposition of **1** were subtly different from those used to determine the rate of benzene loss from **2**. We noted that solutions of **1** inevitably contain some of the dihydride $IrL_2(CO)ClH_2$. At high temperature this dihydride would lose H_2 (Eq. (5)). H_2 is known to react with **2** to give IrL_2ClH_2 and benzene (Eq. (3)). IrL_2ClH_2 would then react with CO to regenerate $IrL_2(CO)ClH_2$ (Eq. (4)), followed by Eq. (5), thereby completing a cycle in which H_2 catalyzed reaction (1).

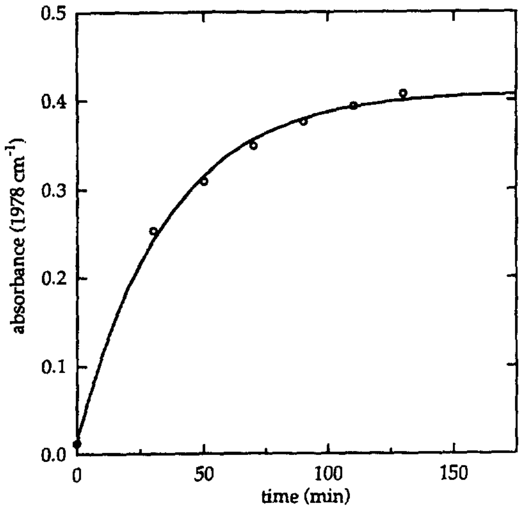


Fig. 3. Growth of **1a-^{12}CO** from thermolysis of **1a-^{13}CO** under 800 Torr ^{12}CO.

$$
\begin{array}{lr}
IrL_2(CO)ClPhH \rightarrow IrL_2ClPhH + CO & (2) \\
H_2 + IrL_2ClPhH \rightarrow IrL_2ClH_2 + PhH & (3) \\
IrL_2ClH_2 + CO \rightarrow IrL_2(CO)ClH_2 & (4) \\
IrL_2(CO)ClH_2 \rightarrow IrL_2(CO)Cl + H_2 & (5) \\
\hline
IrL_2(CO)ClPhH \rightarrow IrL_2(CO)Cl + PhH & (1)
\end{array}
$$

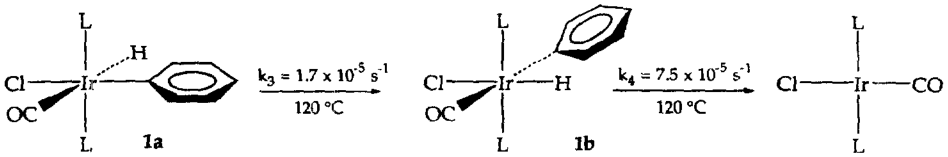
Indeed, added H_2 was found to catalyze Eq. (1); data are shown in Table 1. Presumably H_2 reacts with **2** and not directly with the 18-electron complex **1**, in accord with Eqs. (2)–(5).

We may interpret the occurrence of a H_2-catalyzed elimination pathway as follows. The intrinsic kinetic barrier to elimination from **1** is very high. Elimination of benzene from **2**, by contrast, probably has a very low intrinsic kinetic barrier but a high thermodynamic barrier. The key to this pathway is the facile substitution of PhH by H_2 (a known reaction)

Table 1
Rate of reaction (1) under varying pressures of H_2 and CO [a]

P_{CO} (Torr)	P_{H_2} (Torr)	Rate ($10^{-4}\ s^{-1}$)
0	0	0.85
0	100	3.4
5	0	0.20
5	100	2.1
5	400	2.0
5	800	1.9

[a] Conditions: 0.5 mM **1a** in toluene, at 120 °C (monitored by UV–Vis spectrosopy).



Scheme 2. Primary mechanism of benzene loss operative under CO atmosphere.

[12]. In other words, benzene elimination from the 'H_2 adduct' of **2** is much more kinetically facile than elimination from the CO adduct of **2**, $IrL_2(CO)ClPhH$ (indeed, we do not know if the 'H_2 adduct' even has a finite lifetime). Essentially, a H_2-for-CO substitution gives a species (possibly, but not necessarily Ir(V)) which does not possess the kinetic stability of the d^6 octahedral carbonyl, **1**. Following benzene loss, the re-addition of CO gives a different d^6 octahedral complex, the dihydride $IrL_2(CO)ClH_2$; however, the H_2 elimination is kinetically much more facile than benzene elimination, even though the former is thermodynamically much less favorable.

3.2.2. The pathway not inhibited by added CO

Samples of **1a** heated at 120 °C under 1 atm CO, monitored by ^1H and ^{31}P NMR spectroscopy, clearly show the growth of a new species, **1b**, that reaches a maximum steady state concentration of 15% of total complex concentration after 8 h, and then decreases in concentration upon further heating, yielding only $IrL_2Cl(CO)$ at the completion of the reaction. Additionally, close monitoring of the growth of $IrL_2Cl(CO)$ shows an initial lag period (Fig. 4), and the greatest rate of growth coincides with the time of maximum concentration of **1b**. This behavior is consistent with and strongly supportive of the intermediacy of **1b** in the reaction of **1a** to give $IrL_2Cl(CO)$. Full spectroscopic analysis of **1b** (^1H, ^{31}P, ^{13}C NMR, IR; see Section2) has enabled its definitive assignment as the isomer of **1a** (H *trans* to CO) in which the hydride is *trans* to the chloride (Scheme 2). Most notable is the change in the chemical shift of the hydride from **1a** (δ −7.4) to **1b** (δ −18.0). Such an upfield shift is indicative of the change in position from *trans* to CO in **1a** to *trans* to Cl in **1b**. The ^{13}C–H (hydride) coupling constants of the ^{13}CO enriched species also strongly support these assignments (**1a**, 49.4 Hz; **1b**, 4.3 Hz).

The data graphed in Fig. 4 were fit (using least-squares analysis) to the simple mechanism shown in Scheme 2. A best fit was obtained using $k_3 = 1.74 \times 10^{-5}$ s^{-1} and $k_4 = 7.47 \times 10^{-5}$ s^{-1} as the rate constants for isomerization and reductive elimination, respectively. Note that Scheme 2 does not include direct elimination of benzene from **1a**. Qualitatively this is consistent with the induction period observed before there is growth of benzene or $IrL_2(CO)Cl$. Quantitatively, when an additional variable is added, namely, a rate constant for direct benzene elimination from **1a** (k_5), no statistically significant improvement in the fit is obtained. The best fit is found for a value of $k_5 = 1.5 \times 10^{-6}$ s^{-1} which is statistically insignificant and obviously much smaller than the rate of elimination from **1b**.

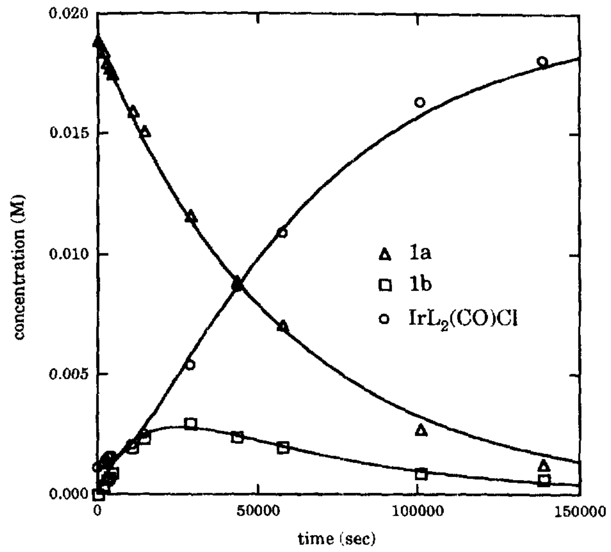


Fig. 4. Reaction profile of the thermolysis of **1a** monitored by ^{31}P NMR. Lines represent best fit to the data, yielding the rate constants shown in Scheme 2.

Presumably, the isomerization proceeds via loss of CO from **1a**, followed by re-addition at the site *trans* to phenyl. Since **1a** is prepared by addition of CO to **2** at ambient temperature, and CO exchange does not occur at ambient temperature, **1a** is clearly the kinetically preferred CO-addition product. The relative rates of CO loss (4.8×10^{-4} s^{-1}; see above) and isomerization (1.74×10^{-5} s^{-1}) indicate a kinetic preference of about 30:1 for formation of **1a** versus **1b** upon addition of CO to **2** at 120 °C. The source of this selectivity is not obvious; this issue is currently being studied by ab initio computational methods. Note that the observed isomerization indicates that the thermodynamic difference between **1a** and **1b** is much smaller than the kinetic preference.

The ^1H NMR spectra of the samples of **1** thermolyzed under CO revealed not only the formation of benzene as the elimination product, but also benzaldehyde. The benzene:benzaldehyde ratio was 2.0:1 under 800 Torr CO and 11:1 under 100 Torr. Growth of benzaldehyde, like growth of benzene, also had an initial lag period and a maximum rate of growth coincident with the maximum concentration of **1b**; this implies that formation of benzaldehyde, like formation of benzene, also proceeds via isomer **1b** (Fig. 5).

It is not obvious why benzene elimination proceeds predominantly via isomer **1b**, but neither is there any obvious reason a priori why this should not be the case. However, the observation that benzaldehyde also is apparently formed via **1b** is considerably more surprising. The stereochemistry of

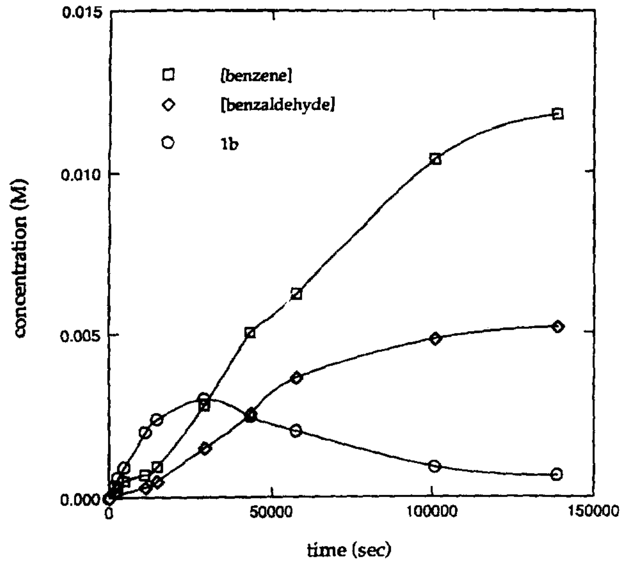


Fig. 5. Growth of benzene, benzaldehyde and **1b** upon thermolysis of **1a**.

1b does not allow CO insertion to occur (due to the *trans* disposition of the CO and Ph groups). An alternative mechanism might involve reversible HCl loss from **1b** yielding $IrL_2(Ph)(CO)$, which under CO atmosphere would rapidly insert CO [14] and eliminate benzaldehyde after re-addition of HCl. This hypothesis is currently under study as part of a mechanistic study of this carbonylation reaction.

4. Conclusions

We have elucidated two pathways for the elimination of benzene from a prototypical d^6 octahedral complex. We see no evidence for a direct elimination pathway. Our estimated upper limit for direct elimination, $1.5 \times 10^{-6}\ s^{-1}$ at 120 °C, corresponds to a rather high kinetic barrier, $\Delta G^{\neq} \geq 34$ kcal/mol.

One pathway elucidated involves a novel catalysis by H_2. We note here two implications. Firstly, it may be possible to use H_2 to catalyze oxidative additions of C–H bonds or other substrates when such additions are thermodynamically favorable. Secondly, one can envision pathways in which addenda other than H_2 might act to induce elimination. In some cases these pathways might be easily overlooked, for example, if the C–H bonds of either ligand or solvent were to catalyze an elimination reaction.

The second elimination pathway involves isomerization which presumably proceeds via reversible loss of CO. Thus, both pathways involve ligand loss, as is considered to be common for elimination from d^6 six-coordinate complexes. Neither pathway, however, involves direct elimination from the resulting five-coordinate intermediate. Thus we suggest that the many mechanistic observations which indicate that ligand loss is required for elimination/addition must be interpreted cautiously.

Acknowledgements

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References

[1] J. Halpern, Discuss. Faraday Soc., 46 (1968) 7.
[2] A.H. Janowicz and R.G. Bergman, J. Am. Chem. Soc., 104 (1982) 352.
[3] B.A. Arndtsen, R.G. Bergman, T.A. Mobley and T.H. Peterson, Acc. Chem. Res., 28 (1995) 154.
[4] J. Halpern, Inorg. Chim. Acta, 100 (1985) 41.
[5] A.J. Rest, I. Whitwell, W.A.G. Graham, J.K. Hoyano and A.D. McMaster, J. Chem. Soc., Chem. Commun., (1984) 624.
[6] A.J. Rest, I. Whitwell, W.A.G. Graham, J.K. Hoyano and A.D. McMaster, J. Chem. Soc., Dalton Trans., (1987) 1181.
[7] R.H. Schultz, A.A. Bengali, M.J. Tauber, B.H. Weiler, E.P. Wasserman, K.R. Kyle, C.B. Moore and R.G. Bergman, J. Am. Chem. Soc., 116 (1994) 7369.
[8] A.A. Bengali, R.H. Schultz, C.B. Moore and R.G. Bergman, J. Am. Chem. Soc., 116 (1994) 9585.
[9] J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, Principles and Applications of Organotransition Metal Chemistry, University Science Books, Mill Valley, CA, 1987, pp. 324–333 and Refs. therein.
[10] (a) H. Rabaa, J.-Y. Saillard and R. Hoffmann, J. Am. Chem. Soc., 108 (1986) 4327; (b) N. Koga and K.J. Morokuma, J. Phys. Chem., 94 (1990) 5454; (c) P.J. Hay, in A. Dedieu (ed.), Transition Metal Hydrides, VCH, New York, 1991, p. 136; (d) A. Sargent, M. Hall and M. Guest, J. Am. Chem. Soc., 114 (1992) 517; (e) T.R. Cundari, J. Am. Chem. Soc., 114 (1992) 10 557; (f) T. Ziegler, F.E. Folga and A. Berces, J. Am. Chem. Soc., 115 (1993) 636; (g) F. Abu-Hasanayn, A.S. Goldman and K. Krogh-Jespersen, J. Phys. Chem., 97 (1993) 5890–5896.
[11] C. Daniel, N. Koga, J. Han, X.Y. Fu and K.J. Morokuma, J. Am. Chem. Soc., 110 (1988) 3773–3787; (b) N. Koga and K.J. Morokuma, J. Phys. Chem., 94 (1990) 5454; (c) N. Koga and K.J. Morokuma, J. Am. Chem. Soc., 115 (1993) 6883–6892; (d) T.R. Cundari, J. Am. Chem. Soc., 116 (1994) 340–347 and Refs. therein.
[12] H. Werner, A. Höhn and M. Dziallas, Angew. Chem., Int. Ed. Engl., 25 (1986) 1090.
[13] H. Werner and A. Höhn, Z. Naturforsch., Teil B, 39 (1984) 1505.
[14] G. Yagupsky, C.K. Brown and G. Wilkinson, J. Chem. Soc. A, (1970) 1392.