# *Communications*

## Decarbonylation of Acetone and Carbonate at a Pincer-Ligated Ru Center

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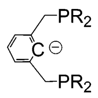
*Summary: A Ru center ligated by a pincer bis(o-phosphinoaryl)amine (PNP) ligand in (PNP)RuH($H_2$) is sufficiently electron rich to break C−O and C−C bonds, resulting in the ultimate decarbonylation of hydrocarbonate and acetone, respectively, to give (PNP)RuH(CO). The decarbonylation of acetone is accompanied by hydrogenolysis of the C−C bonds to produce methane.*

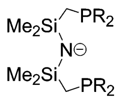
Carbon−carbon bond activation is one of the key challenges of contemporary organometallic chemistry.[1] Cleavage of a C−C bond can be encouraged by a directing effect or by using a substrate with inherently weaker or labile C−C bonds but is generally both thermodynamically and kinetically more difficult than C−H cleavage.[1,2] In particular, C−H activation of the RC(O)−H bond in aldehydes is rather common,[3] while examples of RC(O)−R activation in ketones are few. Hartwig, Andersen, and Bergman reported cleavage of a C−C bond in acetone (not leading to decarbonylation) at 45 °C,[4d] but most examples of C−C cleavage in ketones involve drastic conditions (110−180 °C).[4] These reactions can ultimately lead to the decarbonylation of aldehydes and ketones, forming R−H and/or R−R as the organic products.

In this work we describe decarbonylation of acetone that proceeds under conditions milder than those for other reported ketone decarbonylation reactions.[4] In our system, decarbonylation is accompanied by formal C−C bond hydrogenolysis and formation of methane from acetone. The related extraction of CO from carbonate is also reported here.

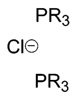
We have recently begun to explore the transition-metal chemistry of the new pincer PNP ligand **1** and reported some aspects of its chemistry with Zr, Rh, Ir, Ni, Pd, and Pt.[5a−e] A similar ligand was reported by others.[5f,g] **1** can be viewed as a chelate analogue of the ubiquitous *mer*-Cl($R_3P$)$_2$ motif **C**. It is also analogous to the known pincer ligands **A** and **B**. However, **1** is more rigid than either **A** or **B** and is hydrolytically robust, in contrast to **B**.[6,7] We envisioned that (PNP)$RuH_3$ (**4**), by analogy to the known (**B**)$RuH_3$ [8] and (**C**)$RuH_3$,[9] would serve as a convenient starting material for the organometallic chemistry of Ru.



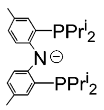
**A**



**B**



**C**



**1** or **PNP**

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[1] (a) Rybtchinski, B.; Milstein, D. *Angew. Chem., Int. Ed.* **1999**, *38*, 870. (b) Murakami, M.; Ito, Y. *Top. Organomet. Chem.* **1999**, *3*, 97. (c) Mitsudo, T.; Kondo, T. *Synlett* **2001**, 309. (d) Jun, C.-H.; Moon, C. W.; Lee, H.; Lee, D.-Y. *J. Mol. Catal. A* **2002**, *189*, 145. (e) Perthuisot, C.; Edelbach, B. L.; Zubris, D. L.; Simhai, N.; Iverson, C. N.; Muller, C.; Satoh, T.; Jones, W. D. *J. Mol. Catal. A* **2002**, *189*, 157. (f) Jun, C.-H.; Moon, C. W.; Lee, D.-Y. *Chem.-Eur. J.* **2002**, *8*, 2422.

[2] (a) Tipper, C. F. H. *J. Chem. Soc.* **1955**, 2045. (b) Periana, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1986**, *108*, 7346. (c) Wick, D. D.; Northcutt, T. O.; Lachicotte, R. J.; Jones, W. D. *Organometallics* **1998**, *17*, 4484. (d) Jun, C.-H.; Lee, H. *J. Am. Chem. Soc.* **1999**, *121*, 880. (e) Jun, C.-H.; Lee, H.; Lim, S.-G. *J. Am. Chem. Soc.* **2001**, *123*, 751. (f) Bart, S. C.; Chirik, P. J. *J. Am. Chem. Soc.* **2003**, *125*, 886.

[3] (a) Bennet, M. A.; Bruce, M. I.; Matheson, T. W. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. 4, pp 721−723. (b) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 768−775, and references therein.

[4] (a) Murakami, M.; Amii, H.; Ito, Y. *Nature* **1994**, *370*, 540. (b) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. *J. Am. Chem. Soc.* **1996**, *118*, 8285. (c) Rusina, A.; Vlček, A. *Nature* **1965**, *206*, 295. (d) Hartwig, J. F.; Andersen, R. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 2717. (e) Daugulis, O.; Brookhart, M. *Organometallics* **2004**, *23*, 527. (f) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. *J. Am. Chem. Soc.* **1999**, *121*, 8645.

[5] (a) Weng, W.; Yang, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4700. (b) Ozerov, O. V.; Guo, C.; Fan, L.; Foxman, B. M. *Organometallics* **2004**, *23*, 5573. (c) Fan, L.; Yang, L.; Guo, C.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 4778. (d) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792. (e) Fan, L.; Foxman, B. M.; Ozerov, O. V. *Organometallics* **2004**, *23*, 326. (f) Liang, L.-C.; Lin, J.-M.; Hung, C.-H. *Organometallics* **2003**, *22*, 3007−3009. (g) Winter, A. M.; Eichele, K.; Mack, H.-G.; Potuznik, S.; Mayer, H. A.; Kaska, W. C. *J. Organomet. Chem.* **2003**, *682*, 149.

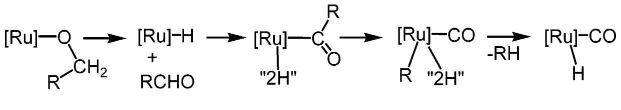
[6] van der Boom, M. E.; Milstein, D. *Chem. Rev.* **2003**, *103*, 1759.

[7] (a) Fryzuk, M. D. *Can. J. Chem.* **1992**, *70*, 2839−2845. (b) Fryzuk, M. D.; Berg, D. J.; Haddad, T. S. *Coord. Chem. Rev.* **1990**, *99*, 137. (c) Ozerov, O. V.; Gerard, H. F.; Watson, L. A.; Huffman, J. C.; Caulton, K. G. *Inorg. Chem.* **2002**, *41*, 5615.

[8] Watson, L. A.; Coalter, J. N.; Ozerov, O.; Pink, M.; Huffman, J. C.; Caulton, K. G. *New J. Chem.* **2003**, 263.

10.1021/om049061m CCC: $30.25

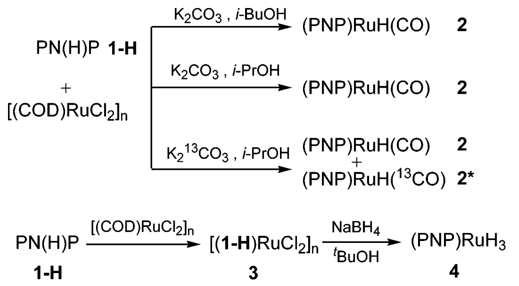
**Scheme 1**



Compounds (**C**)$RuH_3$ are often prepared by a thermal reaction between a $Ru^{II}$ precursor, bulky phosphine, and base in a secondary alcohol that serves as a hydrogen donor.[9] Utilization of a primary alcohol typically leads to the abstraction of CO and formation of (**C**)RuH(CO).[10] Dehydrogenation of a primary alcohol leads to an aldehyde that can be decarbonylated (Scheme 1).[3,10] Decarbonylation of a ketone (from a secondary alcohol) is less likely because it requires a C−C (vs C−H for aldehyde) oxidative addition step.

In contrast, our attempts to synthesize **4** by using $K_2CO_3$ as base led to the exclusive formation of (PNP)-RuH(CO) (**2**) *in secondary as well as primary alcohols* (Scheme 2). When $K_2{}^{13}CO_3$ was used, a ca. 1:3 mixture of **2** and **2*** was produced. Furthermore, 30−70% of **2** was produced when $Et_3N$ and NaOH were used as bases in ${}^{i}$PrOH. Evidently, *both* the carbonate base and the secondary alcohol solvent are decarbonylated under the reaction conditions. Gratifyingly, utilization of $NaBH_4$ and of a *tertiary* alcohol led to the high-yield isolation of **4** (Scheme 1). The initially formed **3** is an insoluble yellow solid; its proposed empirical formula is supported by the elemental analysis.

**Scheme 2**



Solution IR and NMR data ($\nu_{CO}$ 1907 $cm^{-1}$; ${}^{13}C$ NMR $\delta$ 208.4 (t, Ru(*C*O), ${}^{2}J_{CP} = 10$ Hz); ${}^{1}H$ NMR $\delta$ −24.68 (t, Ru−*H*, $J_{HP}$ = 18 Hz)) support the X-ray structural determination (Figure 1) in the solid state of an approximately square-pyramidal geometry for **2**. This structure is analogous to compounds (**A**)RuH(CO)[11] and (**C**)RuH(CO),[10] where the hydride is also located in the apical position. The strongly upfield ${}^{1}H$ NMR Ru−*H* resonance in **2** is diagnostic of a hydride trans to an empty site.[10,11] Structural preferences of five-coordinate $d^6$ complexes have been thoroughly analyzed.[12] The two isotopomers give rise to two different hydride resonances in the ${}^{1}H$ NMR spectrum (Figure 2, $J_{HC}$ = 8 Hz). **2*** displays an expected isotopic shift for the carbonyl stretch in the IR spectrum ($\nu_{CO}$ 1860 $cm^{-1}$, Figure 3).

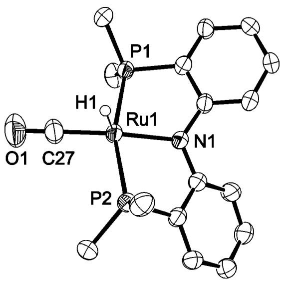


**Figure 1.** ORTEP drawing (50% thermal ellipsoids) of **2** showing selected atom labeling.[13] Omitted for clarity: hydrogens except Ru−H, those of methyl groups of the ${}^{i}$Pr groups, and those on the aryl rings. Selected distances (Å) and angles (deg): Ru1−C27, 1.816(5); Ru1−N1, 2.070(3); Ru1−P1, 2.3069(11); Ru1−P2, 2.3306(11); Ru1−H1, 1.46(5); N1−Ru1−C27, 169.7(2); P1−Ru1−P2, 161.52(4).

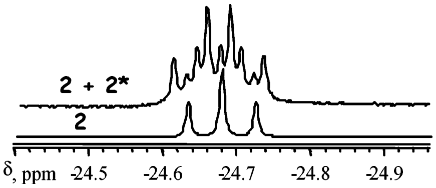


**Figure 2.** Ru−H resonances in the ${}^{1}H$ NMR spectra of **2** and a mixture of **2** and **2***.

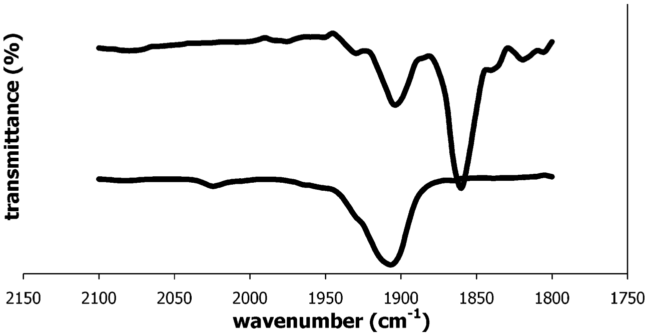


**Figure 3.** CO region of the IR spectra of **2** and a mixture of **2** and **2***.

The solution NMR data for **4** support the proposed formulation. The overall observed symmetry is $C_{2v}$, with the Ru$H_3$ resonance being a broad singlet at −15.9 ppm of intensity 3H in the ${}^{1}H$ NMR spectrum, similarly to (**C**)$RuH_3$.[9] To investigate whether **4** possesses a $RuH(H_2)$ or a $Ru(H)_3$ structure, we used DFT to optimize the geometry of the model compound **4a**. We also computed the DFT-optimized geometries of model compounds **2a** and **6a** (see the Supporting Information for details). The model PNP ligand used for the DFT calculations has Me groups instead of ${}^{i}$Pr on P, and H instead of Me on the aryl backbone. The DFT-optimized structure of **2a** closely matches the geometry of **2** determined by X-ray diffraction. The DFT optimization of **4a** results in a RuH($\eta^2$-$H_2$) structure with an approximately square-pyramidal geometry about Ru. This

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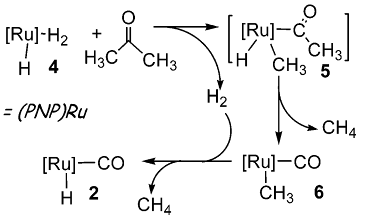
(9) (a) Christ, M. L.; Sabo-Etienne, S.; Chaudret, B. *Organometallics* **1994**, *13*, 3800. (b) Wilhelm, T. E.; Belderrain, T. R.; Brown, S. N.; Grubbs, R. H. *Organometallics* **1997**, *16*, 3867.

(10) (a) Gill, D. F.; Shaw, B. L. *Inorg. Chim. Acta* **1979**, *32*, 19. (b) Marchenko, A. V.; Huffman, J. C.; Valerga, P.; Tenorio, M. J.; Puerta, M. C.; Caulton, K. G. *Inorg. Chem.* **2001**, *40*, 6444. (c) Esteruelas, M. A.; Werner, H. *J. Organomet. Chem.* **1986**, *303*, 221. (d) Chen, Y.; Chan, W. C.; Lau, C. P.; Chu, H. S.; Lee, H. L.; Jia, G. *Organometallics* **1997**, *16*, 1241 and references therein.

(11) Gusev, D. G.; Dolgushin, F. M.; Antipin, M. Y. *Organometallics* **2000**, *19*, 3429.

(12) (a) Lam, W. H.; Shimada, S.; Batsanov, A. S.; Lin, Z.; Marder, T. B.; Cowan, J. A.; Howard, J. A. K.; Mason, S. A.; McIntyre, G. J. *Organometallics* **2003**, *22*, 4557 and references therein.

**Scheme 3**

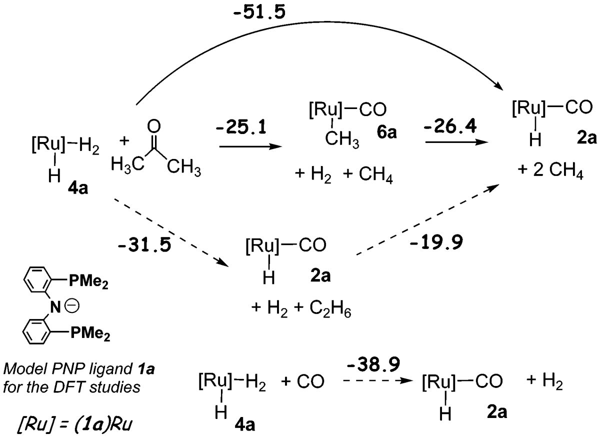


is very similar to the closely analogous (**B**)$RuH_3$ [8] and (**C**)$RuH_3$.[9] The DFT-optimized structure of **6a** has a square-pyramidal geometry similar to **2**/**2a** with a Me group trans to the empty site.

We surmised that if **4** or a species derived therefrom is an intermediate in the observed formation of **2**, an authentic sample of **4** should decarbonylate acetone (formed in situ by dehydrogenation of ${}^{i}$PrOH under our reaction conditions) and $CO_3^{2-}$ (or $HCO_3^-$ or $CO_2$ formed in situ). Thermolysis of **4** in the presence of 4 equiv of acetone in PhF (75 °C, 18 h) resulted in 95% conversion to **2**. Production of $CH_4$ (but not $H_3C-CH_3$) was detected by ${}^1$H NMR. The net hydrogenolysis of the C−C bonds in acetone instead of the C−C coupling likely stems from the hydrogen-rich nature of **4**. Formation of 1 equiv of methane from acetone has been reported.[4d] We propose the mechanism outlined in Scheme 3 to account for our observations. It is supported by the observation of a mixture of **2** and **6** when **4** is thermolyzed (40−70 °C) in neat acetone. A sample of **6**[14] was fully converted to **2** in the time of mixing when exposed to an $H_2$ atmosphere. Addition of ${}^{i}$PrOH to **6** also resulted in the conversion to **2**, albeit much more slowly.

The DFT studies on the model compounds confirm the exoergic nature of the decarbonylation, with the overall free energy of the reaction being rather surprisingly large at −51.5 kcal/mol (Scheme 4). Both the formation of **6**/**6a** and the subsequent hydrogenolysis of the Ru−Me bond are strongly favorable, consistent with the experimental observations. While we have not undertaken studies of the mechanism, DFT studies allow us to pinpoint the components of the thermodynamic "driving force" of this reaction. Formation of the Ru−CO linkage is clearly important: CO binds to the (PNP)-RuH fragment 38.9 kcal/mol ($\Delta G°_{298}$) more strongly than $H_2$ (Scheme 4). The formation of the strong C−H bonds is important as well: the hypothetical decarbonylation with production of $C_2H_6$ is calculated to be 19.9 kcal/mol less favorable. Last, entropy favors the observed reaction ($T\Delta S$ at 298 K = 9.8 kcal/mol), consistent with the increase in the number of molecules.[15]

**Scheme 4. DFT Thermodynamic Analysis of Acetone Decarbonylation**[a]



[a] Free energies of reactions in kcal/mol are given above the arrows. Dashed arrows represent hypothetical reactions.

Thermolysis of **4** in *tert*-amyl alcohol in the presence of $NaHCO_3$ also produced **2** (60 °C, $t_{1/2} \approx 18$ h). The decarbonylation of carbonates and hydrocarbonates probably proceeds via the intermediacy of formates or a Ru($\eta^1$-$CO_2H$) species.[16]

Investigations of $Ru^{II}$ and $Os^{II}$ metal complexes devoid of significant $\pi$-acid ligands have shown that these are strongly $\pi$-basic and tend to exploit the offered organic substrate as a $\pi$-acid ligand.[17] A PNP-ligated Ru center such as in **4** falls into this category as well and is sufficiently reactive to abstract the $\pi$-acidic CO ligand from ${}^{i}$PrOH, acetone, and carbonate. Our observations have a bearing on the Ru-catalyzed transfer hydrogenation, where secondary alcohols are frequently used as sources of $H_2$, and on the Ru-catalyzed hydrogenation of $CO_2$ to formic acid.[18] CO abstraction by Ru would be a catalyst deactivation event for both processes.

The C−C activation and decarbonylation of acetone reported here proceed under conditions milder than those in other related ketone decarbonylation reports.[4] The acetone molecule is converted to a coordinated CO ligand and two molecules of $CH_4$ with the help of a hydrogen-rich Ru center. Ketone decarbonylation is a potentially useful synthetic transformation, and further activity will be aimed at investigating the scope and the applicability of this reaction.

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(13) ORTEP plots were created using Ortep-3 for Windows: Farugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565.

(14) (a) **6** was independently synthesized by reacting **2** with MeLi followed by MeI. The upfield (−14.1 ppm) resonance of Ru−$CH_3$ in the ${}^{13}$C NMR spectrum is reminiscent of that in $({}^{i}Pr_3P)_2$RuMe(CO)Cl (−13.4 ppm).[13b] This is consistent with the Me group, as the strong trans influence ligand, being trans to the empty site. The Ph group in the structurally characterized $({}^{t}Bu_2PMe)_2$RuPh(CO)Cl is trans to the empty site. See the Supporting Information for experimental details on **6** and computational details for **6a**. (b) Katayama, H.; Ozawa, F. *Organometallics* **1998**, *17*, 5190. (c) Huang, D.; Streib, W. E.; Bollinger, J. C.; Caulton, K. G.; Winter, R. F.; Scheiring, T. *J. Am. Chem. Soc.* **1999**, *121*, 8087.

(15) Watson, L.; Eisenstein, O. *J. Chem. Educ.* **2002**, *79*, 1269.

(16) Crabtree, R. H. *The Organometallic Chemistry of the Transition Metals*, 3rd ed.; Wiley-Interscience: New York, 2001; pp 339 and 345−349, and references therein.

(17) (a) Coalter, J. N., III; Huffman, J. C.; Caulton, K. G. *Organometallics* **2000**, *19*, 3569. (b) Ferrando-Miguel, G.; Coalter, J. N., III; Gérard, H.; Huffman, J. C.; Eisenstein, O.; Caulton, K. G. *New J. Chem.* **2002**, *26*, 687. (c) Coalter, J. N., III; Bollinger, J. C.; Huffman, J. C.; Werner-Zwanziger, U.; Caulton, K. G.; Davidson, E. R.; Gérard, H.; Clot, E.; Eisenstein, O. *New J. Chem.* **2000**, *24*, 9. (d) Brooks, B. C.; Gunnoe, T. B.; Harman, W. D. *Coord. Chem. Rev.* **2000**, *206−207*, 3.

(18) (a) Ng, S. M.; Yin, C.; Yeung, C. H.; Chan, T. C.; Lau, C. P. *Eur. J. Inorg. Chem.* **2004**, 1788. (b) Noyori, R.; Hashiguchi, S. *Acc. Chem. Res.* **1997**, *30*, 97. (c) Zassinovich, G.; Mestroni, G.; Gladiali, S. *Chem. Rev.* **1992**, *92*, 1051.

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**Supporting Information Available:** Text, figures, and tables giving experimental details, characterization data, crystallographic information, and the DFT computational details; crystallographic data are also given as a CIF file. This material is available via the Internet free of charge at http://pubs.acs.org.

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