

This is a repository copy of *Catalytic activation of unstrained, non-activated ketones mediated by platinum(II) – multiple C–C bond cleavage and CO extrusion*.

White Rose Research Online URL for this paper:
<https://eprints.whiterose.ac.uk/153631/>

Version: Published Version

Article:

Sarju, Julia Paula, Dey, Debashish, Torroba, Javier et al. (3 more authors) (2019) Catalytic activation of unstrained, non-activated ketones mediated by platinum(II) – multiple C–C bond cleavage and CO extrusion. *Organometallics*. ISSN 0276-7333

<https://doi.org/10.1021/acs.organomet.9b00650>

Reuse

Items deposited in White Rose Research Online are protected by copyright, with all rights reserved unless indicated otherwise. They may be downloaded and/or printed for private study, or other acts as permitted by national copyright laws. The publisher or other rights holders may allow further reproduction and re-use of the full text version. This is indicated by the licence information on the White Rose Research Online record for the item.

Takedown

If you consider content in White Rose Research Online to be in breach of UK law, please notify us by emailing eprints@whiterose.ac.uk including the URL of the record and the reason for the withdrawal request.

Catalytic Activation of Unstrained, Nonactivated Ketones Mediated by Platinum(II): Multiple C–C Bond Cleavage and CO Extrusion

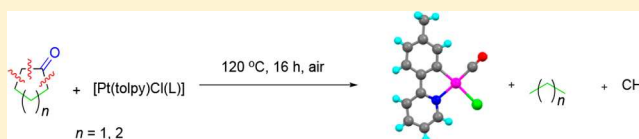
Julia P. Sarju,[†] Debashish Dey,[†] Javier Torroba,[†] Adrian C. Whitwood,[†] Kelly Redeker,[‡] and Duncan W. Bruce^{*,†}

[†]Department of Chemistry, University of York, Heslington, York YO10 5DD, U.K.

[‡]Department of Biology, University of York, Wentworth Way, York YO10 5DD, U.K.

Supporting Information

ABSTRACT: The complexes $[\text{Pt}(\text{tolpy})\text{Cl}(\text{L})]$ (tolpy = 2-(4-tolyl)pyridyl; L = dms, dms, py, PPh_3 , CO) are precursors for the catalytic cleavage of C–C bonds and extrusion of CO from a series of unactivated ketones such as cyclohexanone; deuterium labeling experiments demonstrate the involvement of a transfer hydrogen step in the mechanism.

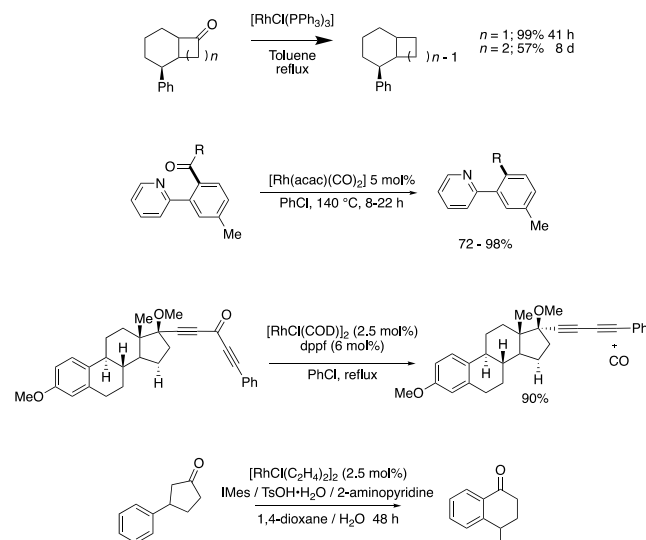


Catalytic decarbonylation reactions have the potential to be synthetically useful, atom-economical transformations for a commonly encountered functional group, potentially affording compounds that might otherwise be difficult to access.^{1–6} Such reactions are well-known and trivial with aldehydes, but ketones present a significantly greater challenge.¹ For example, Gozin et al. and Ameen et al. highlighted the importance of transition-metal-catalyzed C–C bond cleavage in petroleum refinement and the processing of oxygen-rich bioderived fuels.^{7,8}

Stoichiometric extrusion of a carbonyl fragment was first reported in 1965 by Rusina and Vlcek when cyclohexanone was heated with RhCl_3 and PPh_3 , affording $[\text{RhCl}(\text{CO})(\text{PPh}_3)_2]$ and unknown hydrocarbon products.⁹ Since then, most examples of ketone decarbonylation have employed strained substrates^{10–13} or those that allow tethering of the substrate to the metal via a directing group (e.g., Scheme 1—arylpiperidine example).^{14–19} These reactions, which are normally stoichiometric, are often mediated by coordinatively unsaturated rhodium complexes,^{20,21} with forcing conditions, high temperatures, and long reaction times being required.^{22–24} However, in 2016 Lee et al. achieved ketone $\text{C}_\alpha\text{--C}_{\text{CO}}$ bond activation of a number of systems, including cyclohexanone, at room temperature using a rhodium(II) porphyrin system generating Rh(II)-acyl complexes. While this approach does not lead to decarbonylation, the mild reaction conditions reflect a significant improvement on the earlier results.²⁵ More recently, Dong and co-workers have developed an elegant catalytic strategy for $\text{C}_\alpha\text{--C}_{\text{CO}}$ bond activation in which the carbonyl is activated by catalytic amounts of amine or carbene and the thermodynamic driving force is provided by concomitant formation of new C–C bonds.²⁶

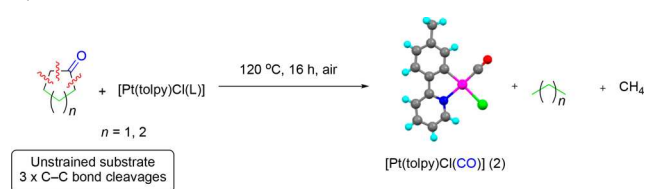
As part of earlier studies on ortho-platinated 2,5-bis(4-alkoxyphenyl)pyridines,²⁷ Pt^{III} dimers were formed unexpectedly via oxidation of the Pt^{II} complexes by free or bound dms in the presence of acid, consistent with related oxidations reported previously by Kukushkin et al.^{28,29} and Alexandrova et al.^{30,31} In further studies of this reaction, the surprising observation was

Scheme 1. Examples of Metal-Mediated C–C Activation of Ketonic Substrates with Strained¹⁰ or Tethered^{4,16,26} Substrates



made that heating $[\text{Pt}(\text{tolpy})(\text{Cl})(\text{S-dms})]$ (**1**; tolpy = 2-(4-tolyl)pyridyl) in air with cyclohexanone afforded the known complex $[\text{Pt}(\text{tolpy})(\text{Cl})(\text{CO})]$ (**2**; Scheme 2), characterized by ν_{CO} 2098 cm^{-1} , $\delta(^{195}\text{Pt})$ –3947 ppm and by single-crystal X-ray methods (see the Supporting Information for details). With **1** and cyclohexanone as the only reagents, the carbonyl ligand evidently came from decarbonylation of cyclohexanone with accompanying C–C bond cleavage. To the best of our knowledge, this transformation has remained undeveloped since the report of cyclohexanone decarbonylation by Rusina and Vlcek.⁹ More than 50 years on from their report, our

Received: October 1, 2019

Scheme 2. Platinum-Catalyzed Activation of Cyclohexanone^a

^aThe transformation involves the cleavage of the three C–C bonds indicated. The X-ray single crystal structure of **2** is illustrated.

observation provides an opportunity to study this transformation in greater detail.

Thus, GC and GC-MS analysis of the headspace gas after reaction of cyclohexanone with **1** confirmed the formation of butane and methane, with trace amounts of other small hydrocarbons (see Scheme 2), as detailed in the Supporting Information. In fact, the reaction of cyclopentanone with **1** under the same conditions showed the formation of methane and propane, thereby suggesting that both substrates are activated via the same mechanism. Rusina and Vlcek⁹ did not report an analysis of any organic products, and so their reaction was repeated, revealing the formation of butane, cyclohexane, cyclohexene, and benzene in the approximate ratio of 1:0.8:1:3, implying a different mechanistic route in their case.

Given the known photochemical instability of cyclohexanone and cyclopentanone in the gas phase,³³ and reports of photochemical C–C bond activations,³⁴ control experiments established that activation of cyclohexanone mediated by **1** proceeded in the absence of natural light to give the same products. In addition, irradiation of a room-temperature solution of **1** in cyclohexanone (λ_{\max} 254 nm) at room temperature led to no observable reaction, confirming that the decarbonylation is thermal in nature.

To investigate the reaction further, it was carried out in the presence of the related complexes **2–6** (Figure 1) which, like **1**, have a neutral fourth ligand. Complex **6** was found to be inactive, while **2–5** led to reactions, and important in these observations is that **2** is active, showing that the process is catalytic. The related dimer **7** was also active. The Pt complexes **8–10**, each

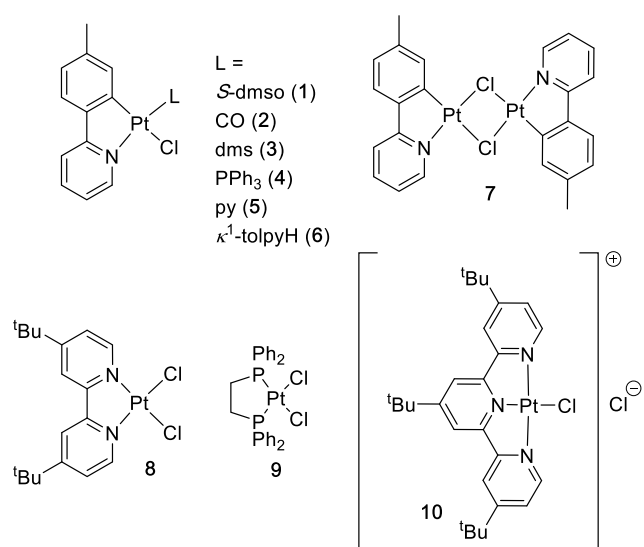
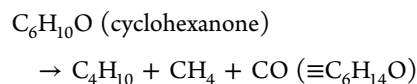


Figure 1. Complexes tested for the thermal decarbonylation of ketones.

with a neutral chelating ligand, were also evaluated and neither **9** nor **10** showed any evidence of decarbonylation. Complex **8** did, however, show the formation of butane and the starting complex was the only one that could be identified at the end of the reaction. Palladium analogues of **1** and **7** were not active, suffering extensive decomposition even at low reaction temperatures.

Returning to the organic products, the reaction stoichiometry shows a significant imbalance in hydrogen content to the extent of four hydrogen atoms:



With no other reagents present, this hydrogen must arise from the cyclohexanone substrate, suggesting the possibility of a transfer hydrogenation process. While cyclohexanone is not generally known for its utility in such chemistry, Izawa et al. did show some precedent for such a reaction, reporting a palladium-mediated oxidation/aromatization of cyclohexanone to phenol.³⁵

Therefore, to demonstrate a transfer hydrogenation step, the reaction of cyclohexanone with complex **1** was repeated in the presence of 1,3-cyclohexadiene, which is well-known as a transfer hydrogenation donor.³⁶ At the end of the reaction, benzene (formed when cyclohexadiene acts as a transfer hydrogenation substrate) was observed as a product by electronic spectroscopy, strongly supporting the involvement of transfer hydrogenation.

Further compelling evidence for the mediation of transfer hydrogenation comes from the observation that, while acetone does not react thermally with complex **1**, when the reaction is carried out in the presence of 1,3-cyclohexadiene, formation of **2** along with methane and CO is observed. Likewise it is found that acetophenone will only react in the presence of the transfer hydrogenation substrate. Furthermore, carrying out the reaction with acetone-*d*₆ led to the formation of CD₃H, confirming that 1,3-cyclohexadiene is the source of the hydrogen atoms incorporated in the product. This observation is significant, as there is only a single previous report of the decarbonylation of acetone.³⁷

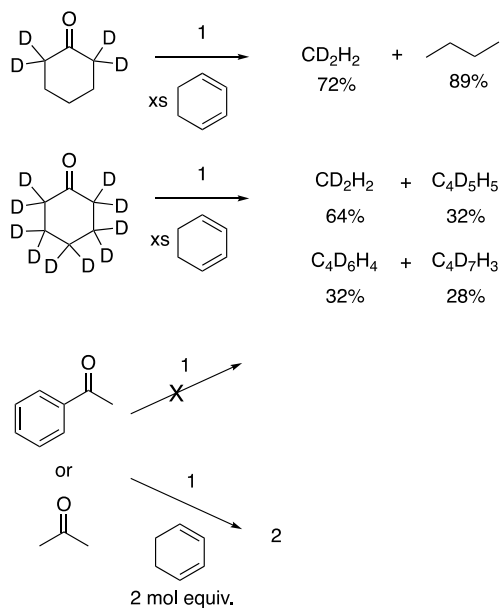
An important observation, however, is that the activation of these ketones by complex **1** is accompanied by the formation of particulate Pt with average hydrodynamic radius 10–50 nm, as determined by dynamic light scattering. Addition of mercury to the reaction mixture³⁸ led to a significant reduction in the formation of butane, suggesting intervention by these platinum nanoparticles. However, when the reaction is tracked by in situ infrared spectroscopy, immediate formation of complex **2** is observed, which would suggest that an early decarbonylation step is homogeneous (a heterogeneous process would typically require an induction period as the nanoparticles form). In addition, it is observed that, when cyclohexanone is heated with either **6** or **10**, nanoparticles are formed but there is no decarbonylation. This would also support the proposal of an early, homogeneous decarbonylation step. Transfer hydrogenation, however, may be mediated by the platinum nanoparticles.

Previous examples of C–C bond scission with coupled decarbonylation (e.g., Scheme 1) have typically led to simple extrusion of CO, and while no mechanistic detail was given, the fact that the present reaction with cyclohexanone give a different range of products would imply a different mechanism. Thus, it is

assumed that the ketone coordinates to Pt (either η^1 through oxygen or η^2 through C=O) following dissociation of the neutral, monodentate ligand (L in Scheme 2), after which the C–C bond α to the carbonyl is cleaved (analogy with the formation of metal-acyl complexes in the Rh^{II}-porphyrin systems).²⁵ A second C–C cleavage β to C=O would then extrude an oxygenated C₂ unit (which would readily fragment to CO and methane) leaving a C₄ moiety.

Support for these suggestions comes from deuterium cross-labeling studies conducted using cyclohexanone-*d*₁₀ with 1,3-cyclohexadiene as the transfer hydrogen donor. Under these conditions, the major C₁ product was CD₂H₂ (64%), which suggests a fairly selective reaction (consistent with a homogeneous process), while butane was found as a mixture of isotopomers, mainly C₄D₅H₅ (32%), C₄D₆H₄ (32%), and C₄D₇H₃ (28%), more consistent with a relatively unselective heterogeneous process. Similarly, use of 2,2,6,6-tetradeuterio-cyclohexanone and 1,3-cyclohexadiene gave 72% CD₂H₂ (again quite selective) and 89% C₄H₁₀. Some of the key mechanistic observations are collected in Scheme 3.

Scheme 3. Complexes Tested for the Thermal Decarbonylation of Ketones^a



^aThe percent refers to the proportion of that isotopomer as a proportion of all isotopomers of that compound.

In summary, we have achieved the cleavage of C–C bonds in unstrained and nonactivated ketones such as cyclopentanone and cyclohexanone through the action of [Pt(tolpy)(Cl)(L)] (1–5) in a thermal process. Decarbonylation occurs alongside a transfer hydrogenation step, where evidence suggests mediation by platinum nanoparticles. Suppression of nanoparticle activity or formation does not prevent decarbonylation, leading to the conclusion that this process is homogeneous, a proposal supported by cross-labeling studies.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-
met.9b00650.

Details of complex synthesis and of the different reactions (PDF)

Accession Codes

CCDC 1956985 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for D.W.B.: duncan.bruce@york.ac.uk.

ORCID

Julia P. Sarju: 0000-0002-7087-4382

Adrian C. Whitwood: 0000-0002-5132-5468

Duncan W. Bruce: 0000-0002-1365-2222

Author Contributions

The manuscript was written through contributions of all authors.

Funding

We thank the University of York (J.P.S.) and Comunidad Autonoma de La Rioja (Spain) (J.T.) for funding.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Iman Khazal is thanked for the preparation of platinum complexes 8–10 used in this study, and Dr. Jason Lynam (York) is thanked for very helpful discussions.

■ REFERENCES

- (1) Jun, C.-H. Transition metal-catalyzed carbon-carbon bond activation. *Chem. Soc. Rev.* **2004**, *33*, 610–618.
- (2) Rybtchinski, B.; Milstein, D. Metal insertion into C–C Bonds in solution. *Angew. Chem., Int. Ed.* **1999**, *38*, 870–883.
- (3) Dermenci, A.; Dong, G. Decarbonylative C–C bond forming reactions mediated by transition metals. *Sci. China: Chem.* **2013**, *56*, 685–701.
- (4) Dermenci, A.; Whittaker, R. E.; Dong, G. Rh(I)-catalyzed decarbonylations of diynone via C–C activation: orthogonal synthesis of conjugated diynes. *Org. Lett.* **2013**, *15*, 2242–2245.
- (5) Chen, F.; Wang, T.; Jiao, N. Recent advances in transition-metal-catalyzed functionalization of unstrained carbon–carbon bonds. *Chem. Rev.* **2014**, *114*, 8613–8661.
- (6) Souillart, L.; Cramer, N. Catalytic C–C bond activations via oxidative addition to transition metals. *Chem. Rev.* **2015**, *115*, 9410–9464.
- (7) Gozin, M.; Weisman, A.; Ben-David, Y.; Milstein, D. Activation of a carbon–carbon bond in solution by transition-metal insertion. *Nature* **1993**, *364*, 699–701.
- (8) Ameen, M.; Azizan, M. T.; Yusup, S.; Ramli, A.; Yasir, M. Catalytic hydrodeoxygenation of triglycerides: An approach to clean diesel fuel production. *Renewable Sustainable Energy Rev.* **2017**, *80*, 1072–1088.
- (9) Rusina, A.; Vlcek, A. A. Formation of Rh(I)-carbonyl complex by the reaction with some non-alcoholic, oxygen-containing solvents. *Nature* **1965**, *206*, 295–296.
- (10) Murakami, M.; Amii, H.; Ito, Y. Selective activation of carbon-carbon bonds next to a carbonyl group. *Nature* **1994**, *370*, 540–541.
- (11) Murakami, M.; Amii, H.; Shigeto, K.; Ito, Y. Breaking of the C–C Bond of cyclobutanones by rhodium(I) and its extension to catalytic synthetic reactions. *J. Am. Chem. Soc.* **1996**, *118*, 8285–8290.

- (12) Xu, T.; Dong, G. Rhodium-catalyzed regioselective carboacylation of olefins: A C-C Bond activation approach for accessing fused-ring systems. *Angew. Chem., Int. Ed.* **2012**, *51*, 7567–7571.
- (13) Chen, P.; Xu, T.; Dong, G. Divergent syntheses of fused β -naphthol and indene scaffolds by rhodium-catalyzed direct and decarbonylative alkyne–benzocyclobutenone couplings. *Angew. Chem., Int. Ed.* **2014**, *53*, 1674–1678.
- (14) Müller, E.; Segnitz, A. Decarbonylierung durch Komplexbildung von α,α' -diäthynylketonen mit tris(triphenylphosphin)rhodium(I)-chlorid: Eine neue Methode zur Herstellung von konjugierten Diinen. *Justus Liebigs Ann. Chem.* **1973**, *1973*, 1583–1591.
- (15) Chatani, N.; Ie, Y.; Kakiuchi, F.; Murai, S. $\text{Ru}_3(\text{CO})_{12}$ -catalyzed decarbonylative cleavage of a C–C Bond of alkyl phenyl ketones. *J. Am. Chem. Soc.* **1999**, *121*, 8645–8646.
- (16) Lei, Z. Q.; Li, H.; Li, Y.; Zhang, X. S.; Chen, K.; Wang, X.; Sun, J.; Shi, Z. J. Extrusion of CO from aryl ketones: rhodium(I)-catalyzed C–C Bond cleavage directed by a pyridine Group. *Angew. Chem., Int. Ed.* **2012**, *51*, 2690–2694.
- (17) Whittaker, R. E.; Dong, G. Controlled Rh-catalyzed mono- and double-decarbonylation of alkynyl α -diones to form conjugated ynones and disubstituted alkynes. *Org. Lett.* **2015**, *17*, 5504–5507.
- (18) Zeng, R.; Dong, G. Rh-catalyzed decarbonylative coupling with alkynes via C–C activation of isatins. *J. Am. Chem. Soc.* **2015**, *137*, 1408–1411.
- (19) Zeng, R.; Chen, P.-h.; Dong, G. Efficient benzimidazolidinone synthesis via rhodium-catalyzed double-decarbonylative C–C activation/cycloaddition between isatins and isocyanates. *ACS Catal.* **2016**, *6*, 969–973.
- (20) Daugulis, O.; Brookhart, M. Decarbonylation of aryl ketones mediated by bulky cyclopentadienylrhodium bis(ethylene) complexes. *Organometallics* **2004**, *23*, 527–534.
- (21) Kaneda, K.; Azuma, H.; Wayaku, M.; Tehanishi, S. Decarbonylation of α - and β -diketones catalyzed by rhodium compounds. *Chem. Lett.* **1974**, *3*, 215–216.
- (22) Ruhland, K. Transition-metal-mediated cleavage and activation of C–C single bonds. *Eur. J. Org. Chem.* **2012**, *2012*, 2683–2706.
- (23) Somerville, R. J.; Martin, R. Forging C–C Bonds through decarbonylation of aryl ketones. *Angew. Chem., Int. Ed.* **2017**, *56*, 6708–6710.
- (24) Morioka, T.; Nishizawa, A.; Furukawa, T.; Tobisu, M.; Chatani, N. Nickel-mediated decarbonylation of simple unstrained ketones through the cleavage of carbon–carbon bonds. *J. Am. Chem. Soc.* **2017**, *139*, 1416–1419.
- (25) Lee, S. Y.; Feng, S.; Chan, K. S. Room temperature carbon(CO)–carbon(α) bond activation of ketones by rhodium(II) porphyrins with water. *Dalton Trans.* **2016**, *45*, 3522–3527.
- (26) (a) Xia, Y.; Lu, G.; Liu, P.; Dong, G. Catalytic activation of carbon–carbon bonds in cyclopentanones. *Nature* **2016**, *539*, 546–550. (b) Xia, Y.; Wang, J.; Dong, G. Distal-Bond-Selective C@C Activation of Ring-Fused Cyclopentanones: An Efficient Access to Spiroindanones. *Angew. Chem., Int. Ed.* **2017**, *56*, 2376–2380.
- (27) Santoro, A.; Wegrzyn, M.; Whitwood, A. C.; Donnio, B.; Bruce, D. W. Oxidation of organoplatinum(II) by coordinated dimethylsulfoxide: metal–metal bonded, dinuclear, liquid-crystalline complexes of platinum(III). *J. Am. Chem. Soc.* **2010**, *132*, 10689–10691.
- (28) Kukushkin, Y. N.; Vyazmenskii, Y. E.; Zorina, I. L.; Pazukhina, Y. I. Complexes of palladium and platinum with dimethyl sulfoxide. *Zh. Neorg. Khim.* **1968**, *13*, 1595–1599.
- (29) Kukushkin, V. Y. Metal-ion mediated deoxygenation of sulfoxides. *Coord. Chem. Rev.* **1995**, *139*, 375–407.
- (30) Alexandrova, L.; D'Yachenko, O. G.; Kazankov, G. M.; Polyakov, V. A.; Samuleev, P. V.; Sansores, E.; Ryabov, A. D. Mechanism of biologically relevant deoxygenation of dimethyl sulfoxide coupled with Pt(II) to Pt(IV) oxidation of orthoplatinated oximes. Synthetic, kinetic, electrochemical, X-ray structural, and density functional study. *J. Am. Chem. Soc.* **2000**, *122*, 5189–5200.
- (31) Ryabov, A. D.; Otto, S.; Samuleev, P. V.; Polyakov, V. A.; Alexandrova, L.; Kazankov, G. M.; Shova, S.; Revenco, M.; Lipkowski, J.; Johansson, M. H. Structural and mechanistic look at the orthoplatination of aryl oximes by dichlorobis(sulfoxide or sulfide)-platinum(II) complexes. *Inorg. Chem.* **2002**, *41*, 4286–4294.
- (32) Mdleleni, M. M.; Bridgewater, J. S.; Watts, R. J.; Ford, P. C. Synthesis, structure, and spectroscopic properties of ortho-metalated platinum(II) complexes. *Inorg. Chem.* **1995**, *34*, 2334–2342.
- (33) Blacet, F. E.; Miller, A. The photochemical decomposition of cyclohexanone, cyclopentanone and cyclobutanone. *J. Am. Chem. Soc.* **1957**, *79*, 4327–4329.
- (34) Lee, S. Y.; Fung, H. S.; Feng, S.; Chan, K. S. Visible light photocatalysis of carbon–carbon σ -Bond anaerobic oxidation of ketones with water by cobalt(II) porphyrins. *Organometallics* **2016**, *35*, 2480–2487.
- (35) Izawa, Y.; Pun, D.; Stahl, S. S. Palladium-catalyzed aerobic dehydrogenation of substituted cyclohexanones to phenols. *Science* **2011**, *333*, 209–213.
- (36) Brieger, G.; Nestruck, T. J. Catalytic transfer hydrogenation. *Chem. Rev.* **1974**, *74*, 567–580.
- (37) Çelenligil-Çetin, R.; Watson, L. A.; Guo, C.; Foxman, B. M.; Ozerov, O. V. Decarbonylation of acetone and carbonate at a pincer-ligated Ru center. *Organometallics* **2005**, *24*, 186–189.
- (38) Widegren, J. A.; Finke, R. G. A review of the problem of distinguishing true homogeneous catalysis from soluble or other metal-particle heterogeneous catalysis under reducing conditions. *J. Mol. Catal. A: Chem.* **2003**, *198*, 317–341.