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Diiridium Bimetallic Complexes Function as a Redox Switch to Directly Split Carbonate into Carbon Monoxide and Oxygen

Tsun-Ren Chen*, Fang-Siou Wu, Hsiu-Pen Lee, and Kelvin H.-C. Chen

Department of Applied Chemistry, National Pingtung University, Pingtung, Taiwan,90003

Supporting Information Placeholder

ABSTRACT: A pair of diiridium bimetallic complexes exhibited a special type of oxidation-reduction reaction, which could directly split carbonate into carbon monoxide and oxygen via a low energy pathway not needing any sacrificial reagent. One of the bimetallic complexes, $Ir^{III}(\mu\text{-}Cl)_2Ir^{III}$, can catch carbonato group from carbonate and reduce it to carbon monoxide. The second one of complexes, a rare bimetallic complex $Ir^{IV}(\mu\text{-}oxo)_2Ir^{IV}$, can react with chlorine to release oxygen by the oxidation of oxygen ions with synergistic oxidative effect of iridium ions and chlorine atoms. The activation energy needed for the key reaction is quite low (~20 kJ mol^{-1}), which is far less than the dissociation energy of the $C{=}O$ bond in CO_2 (~750 kJ mol^{-1}). These diiridium bimetallic complexes could be applied as redox switch to split carbonate or combined with well-known processes in chemical industry to build up a catalytic system to directly split carbon dioxide into carbon monoxide and oxygen.

Carbon dioxide, the end product of cellular respiration in organisms and the final matter produced by combustion of organism or fossil fuels, could have the characteristic of greenhouse effect due to it can absorb and emit infrared radiation at its two infrared-active vibrational frequencies.[1] This effect causes carbon dioxide to warm the surface and lower atmosphere and cool the upper atmosphere, which was deemed the main reason for the rise in average global temperature.[2] By the time before pre-industrial stage, the concentration of carbon dioxide in Earth's atmosphere was regulated by photosynthetic organisms and other process in ecosystem. Since the beginning of the age of industrialization, human activities, such as the consuming of fossil fuels, deforestation, and industrial development, have caused the atmospheric concentration of carbon dioxide to increase by about 43%, which ruptured the balance of carbon dioxide in Earth's atmosphere, and gave rise to some problems on our ecosystem. Furthermore, the increment of global temperature also brought about the increasing of the concentration of carbon dioxide in the atmosphere, it is a bad feedback! So, some people have been devoting to confront these challenges, and many scientists have suggested some ideas or techniques to treat this issue. Most of those reports were focused on three kinds of concepts, the reduction of carbon dioxide by electrocatalyzing, [3-18] photocatalyzing, [19-22] or chemical reducing. [23-26]

By the methods of electrocatalytic reduction, there are some good reports in this field, but there still remain some challenges for these methods, such as how to improve the power efficiency for the reduction of carbon dioxide, and to develop the inexpensive and nontoxic electrodes for mass production. By the techniques of photocatalytic reduction, the recombination of photo-generated electrons and holes are pretty fast, which result in a poor light-harvesting capacity and low quantum efficiency. Moreover, the adsorption ability of carbon dioxide is low on catalyst surfaces, which leads to the low activity of surface for the catalysts toward the activation of carbon dioxide. The advantage by using chemical reaction to reduce carbon dioxide is that it can be applied to mass production; however, to compensate the energy needed for breaking $C{=}O$ bond in carbon dioxide, some high-energy reactants such as hydrogen or unsaturated compound should be used. And, some stoichiometric amounts of sacrificial materials should be supplied to the systems, which may lead to some environmental problems.

In this report, we discovered an approach to directly split carbonate into carbon monoxide and oxygen by adopting a pair of diiridium bimetallic complexes as a set of redox switch which could provide a low energy pathway to trap carbonato and release carbon monoxide and oxygen. Besides, some simple but skillful processes in chemical industry could be combined to it to build up a self-contained system. This system can be used to absorb carbon dioxide and produce carbon monoxide and oxygen by using sun power or electric power; moreover, the restrictive factors for the processes by using the methods of electrocatalytic or photocatalytic reduction are not the problem for the approach reported here.

The experimental details for the preparation and identification of diiridium bimetallic complexes and the other compounds were described in Supporting Information. The molecular structures were showed in Figure 1. When a chloro-bridged bimetallic complex $[(dfpbo)_2Ir^{III}(\mu\text{-}Cl)_2Ir^{III}(dfpbo)_2]$ (**1**) (dfpbo =2-(3.5-difluorophenyl)benzoxazolato-N,C^2)[27,28] was treated with silver carbonate or potassium carbonate, a carbonato bridged bimetallic complex, $[(dfpbo)_2Ir^{III}]_2(\mu\text{-}CO_3)$ (**2**), was an expected product. However, since the structure of **2** is too unstable to be isolated, it directly releases a carbon monoxide and form a stable product, an oxo-bridged diiridium bimetallic complex $[(dfpbo)_2Ir^{IV}(\mu\text{-}O)_2Ir^{IV}(dfpbo)_2]$ (**3**).

A single-crystal X-ray structure determination confirmed the bimetallic nature of complex **3** (Figure 2a). Complex **3** possesses a structure of square planner connecting two iridium cores with distorted-octahedral coordination geometry around iridium. For the square planner coordination geometry, O(2)-Ir-O(2A) angle is 76.0(2)° deviating from 90° by 14°, which implies that there is an angle strain in this structure. The Ir-O bond length of the core structure for complex **3** is 2.163(3) Å, which is longer than that of typical singly oxo-bridged iridium bimetallic complex.[29]

Counting the number of valence electrons at iridium atoms of complexes **1**-**3** by the 18-electon rule for organometallic complexes,[30] we realized that the oxidation state of iridium atoms for complex **3** is +4, whereas those for complexes **1** and **2** are +3. Furthermore, when complex **2** was transformed into **3**, the carbon atom of μ-CO_3 in complex **2** was reduced from +4 to +2 to become the carbon atom of carbon monoxide, which implies that in this reaction, the iridium atoms lost electrons and the carbon atom of μ-CO_3 got electrons.

By comparing the normalized X-Ray absorption near edge structure (XANES) spectra at the Ir L3-edge of complex **1** (Figure 3a) with complex **3** (Figure 3b), we can see that the iridium atoms of complex **3** have a higher positive charge than that of complex **1**,[31] which reveals that iridium atoms were oxidized when complex **1** react with carbonate. It is an unusual phenomenon that the carbonato group act as an oxidizer at a low reaction temperature (~25℃). It is also worth noting that when complex **1** was transformed into complex **3**, the central metal is subject to a reaction like an oxidation addition, but the bond number of the iridium did not changed, which is a special oxidation reaction with a long distance electron transfer from iridium atom to the β-atom, the carbon atom of μ-CO_3.

By counting the d^n configuration of complex **3**, we can deduce that complex **3** has a 17e configuration which, in general, possesses reactivity and tend to react with several kinds of reagent to form the stable structures with an 18e configuration. For example, complex **3** is apt to react with aldehydes and halogen. When benzadehyde was added to the solution of complex **3** in o-dichlorobenzene, the color of complex **3**, was immediately disappeared. In this reaction, the benzaldehyde caught the oxygen atom of complex **3**, the benzaldehyde was oxidized to become a benzoyl, and the benzoyl was directly bonding to iridium to from an iridium complex, $[(dfpbo)_2Ir\ (benzoyl)]$ (**4**) (Figure 1). By comparing the normalized XANES spectra at the Ir L3-edge of complex **3** (Figure 3b) and complex **4** (Figure 3c), we can see that the iridium atoms of complex **4** have a lower positive charge than that of complex **3**, which shows that iridium atoms were reduced when complex **3** react with benzaldehyde.

When chlorine gas was introduced into the solution of complex **3** in o-dichlorobenzene, the color of complex **3**, was also immediately disappeared. The product of this reaction has been identified by NMR (Figure S1, lower), IR (Figure S2, lower), and MS spectra (Figure S3, lower), which are identical to those of the initial material, complex **1** (Figure S1-S3, upper). Therefore, we can know that when complex **3** reacted with chlorine, the initial material, $[(dfpbo)_2Ir^{IV}(\mu\text{-}Cl)_2Ir^{IV}(dfpbo)_2]$, was formed and the bridged oxygen were excluded from complex **3**. Furthermore, we can also see that both of the iridium atoms of complex **3** and chlorine atoms were reduced and the oxygen ions of μ-O were oxidized, which implied that when the iridium atoms got electrons from oxygen ions, chlorine atoms were also acquiring electrons from oxygen ions, that is, there is a synergistic oxidative effect of iridium ions and chlorine atoms on the oxidation of oxygen ions.

Since the above-discovered diiridium bimetallic complexes exhibited remarkable characteristics, we can build up a catalytic system as Figure 4 to treat carbon dioxide to give carbon monoxide and oxygen. The system has a core cycle constructed from the above-mentioned reactions of diiridium bimetallic complexes, which functions as a set of redox switch to catch carbonato group from carbonate and release carbon monoxide and oxygen. Besides, two materials, carbonate and chlorine, should be supplied for the core cycle; therefore, two sub-cycles were added to the system. One of the sub-cycles was called carbon dioxide cycle, where the carbon dioxide is absorbed by hydroxide to form a carbonate. The chloride formed in the carbon dioxide cycle can be transformed into hydroxide and chlorine. The hydroxide was used to absorb carbon dioxide, and the chlorine was applied to the second sub-cycle, the chlorine cycle. In the chlorine cycle, the chlorine was reacted with complex **3** to from **1** and release oxygen, in which, the chlorine atoms become the components of iridium complex. When complex **1** reacted with carbonato group, the chlorine atoms were released out of the core cycle. The two sub-cycles can be pushed forward by some well-known techniques in chemical industry with high efficiency, for example, the photolysis or electrolysis of chloride; therefore, we will focus on the study for core cycle.

To investigate the energy needed for the catalytic system, computational studies were performed on the materials used for the system. The calculation results including electronic and zero-point energies, thermal energies, enthalpies and free energies for all the materials were summarized on Table S3. The thermal properties (ΔE, ΔH, ΔG, and ΔS) for the reaction of complex **1** with silver carbonate or potassium carbonate were summarized on Table S4. The other calculation data were also summarized in Supporting Information (Table S5, and S8-S13). According to these data, we can see that the standard free energy of complex **3** (ΔG_f° = -115.6 kcal mol^{-1}) is higher than that of complex **1** (ΔG_f° = -118.7 kcal mol^{-1}) by ~3 kcal mol^{-1}, which implies that a free energy higher than 3 kcal mol^{-1} should be supplied for the transformation of complex **1** into complex **3**.

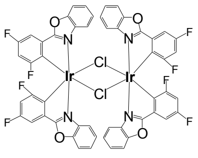
In detail, we can see that when complex **1** reacted with silver carbonate (ΔG_f° = -43.5 kcal mol^{-1}), two mole of silver chloride (ΔG_f° = -30.5 kcal mol^{-1}), one mole of carbon monoxide (ΔG_f° = -24.1 kcal mol^{-1}), and one mole of complex **3** were formed. Therefore, the standard free energy change for the reaction of complex **1** with silver carbonate is -38.5 kcal mol^{-1}, which showed that the free energy released from the reaction of complex **1** with silver carbonate can cover the energy needed for the transformation of complex **1** into complex **3**, and the reaction is exergonic and spontaneous at room temperature. When reactant potassium carbonate (ΔG_f° = -41.5 kcal mol^{-1}) was used instead of silver carbonate, the standard free energy change for the reaction is -38.3 kcal mol^{-1}. And, if calcium carbonate (ΔG_f° = -36.3 kcal mol^{-1}) was used instead of potassium carbonate, the standard free energy change for the reaction is -18.7 kcal/mol. That is, no matter what kind of carbonate is used, the transformation of complex **1** into complex **3** is an exergonic and spontaneous reaction under room temperature.

To realize the minimum energy needed for disrupting carbonato group, we investigated the kinetics characteristic of the reaction of complex **1** with carbonate. When complex **1** reacted with silver carbonate in an inert solvent, complex **3** is the only product in solution, in which complex **3** is very stable and has typical absorption peaks at 415, 437, and 486 nm distinct from that of complex **1**. Therefore, uv-visible spectrometer was used to monitor the progress of the reaction. The experimental details were described in Supporting Information and the experimental data were also summarized (Figure S6-9, and Table S6-S7). According to those data, we can see that the activation energy for the reaction of complex **1** with carbonato group is 20.11 kJ mol^{-1} (4.81 kcal mol^{-1}), which is much lower than the free energy change released from the reaction (ΔG = -38.5 kcal mol^{-1}). On the other words, only an initial energy should be supplied to the reaction, and then, it will go forwards automatically.

As we know that the dissociation energy of C═O bond in CO_2 is quite high (~750 kJ mol^{-1}), this is a robust chemical bond and could be hardly cleaved. In general, a high processing temperature is needed for the releasing of carbonyl group from carbon dioxide or carbonato group. In most of case, some high-energy reactants such as hydrogen or unsaturated compounds should be used to supply chemical energy, and some stoichiometric amounts of sacrificial materials should be supplied to the systems. It is a marvel that, by using diiridium bimetallic complexes as redox switch, the activation energy needed is quite low, the reaction is exergonic, and does not need any sacrificial material. The activation energy needed is so low that the reaction can take place at room temperature (Supporting Information).

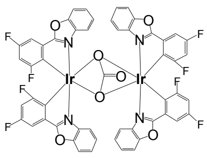
An apparatus was set up to evaluate the performance of this redox switch for splitting carbonato (Supporting Information), where complex **1** reacted with silver carbonate or potassium carbonate, and the carbon monoxide evolved was collected and identified by the reaction of the gas collected with cuprous chloride solution or with Tollens's reagent. The reaction progress for the reaction of complex **1** with silver carbonate was showed in Figure 5a, and for complex **1** with potassium carbonate was also showed in Figure 5b. According to the reaction progresses, we can see that no matter what kind of carbonate was used, 99 % of carbonate could be split to carbon monoxide in a 60 minute of reaction time. That is a quite good outcome.

In summary, a simple but important reaction system was discovered, where a pair of diiridium bimetallic complexes can act as a redox switch to split carbonate into carbon monoxide and oxygen by a pathway with a low energy barrier. The activation energy needed for the reaction system is quite low and the performance of the redox switch is quite good. The reaction system is quite stable in inert solvents, in which the degradation has not been observed. This redox switch could be used to combine with traditional technology to build up a self-contained system for absorbing carbon dioxide and releasing carbon monoxide and oxygen, which could be a promising strategy to develop sustainable energy and treat the troublesome problems resulting from the greenhouse effect of the Earth.



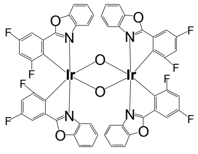
[(dfpbo)$_2$Ir^{III}(£g-Cl)$_2$Ir^{III}(dfpbo)$_2$]

1



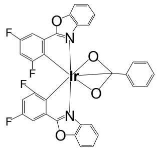
[(dfpbo)$_2$Ir^{III}]$_2$ (£g-CO$_3$)

2



[(dfpbo)$_2$Ir^{IV}(£g-O)$_2$Ir^{IV}(dfpbo)$_2$]

3



(dfpbo)$_2$Ir(benzoyl)

4

Figure 1. The molecular structures of iridium complexes **1~4**

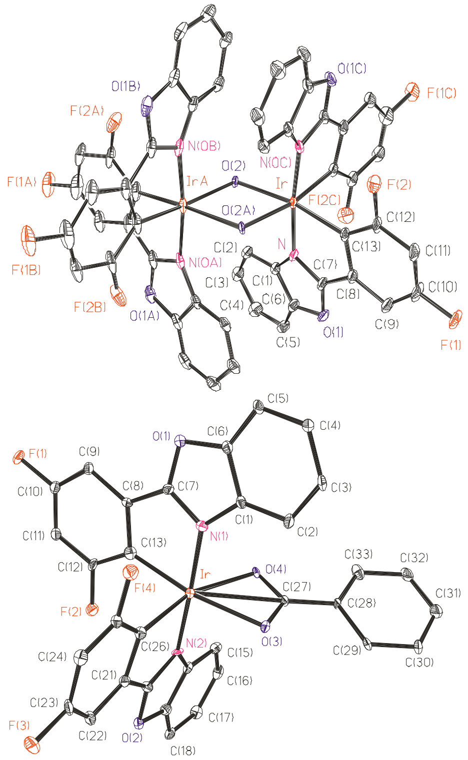


Figure 2. ORTEP diagrams of (a) [(dfpbo)$_2$Ir^{III}]$_2$ (μ-CO$_3$), and (b) (dfpbo)$_2$Ir(benzoyl)], with thermal ellipsoids drawn at 20 % probability level. The hydrogen atoms have been omitted for clarity.

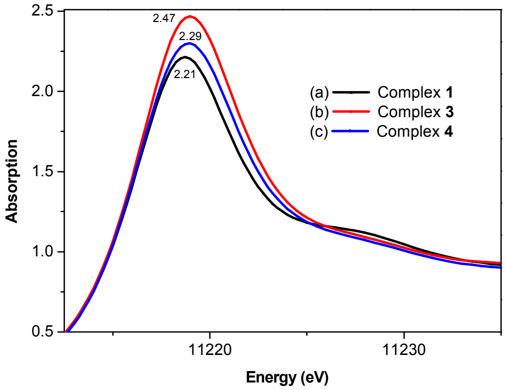


Figure 3. Ir L3-edge XANES of crystalline (a) [(dfpbo)$_2$Ir^{IV}(μ-Cl)$_2$Ir^{IV}(dfpbo)$_2$] (**1**), (b) [(dfpbo)$_2$Ir^{IV}(μ-O)$_2$Ir^{IV}(dfpbo)$_2$] (**3**), and (c) [(dfpbo)$_2$Ir (benzoyl)] (**4**). A Si (111) double crystal monochromator was employed for energy scanning. Fluorescence data were obtained at room temperature using an Ar-filled ionization chamber detector, each sample was scanned 3 times for averaging.

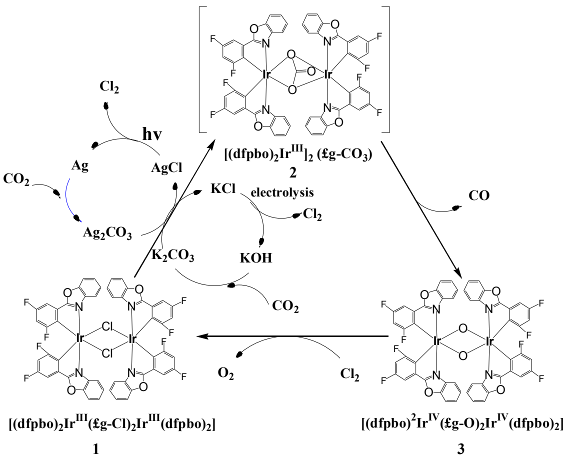


Figure 4. A catalytic system for splitting carbon dioxide into carbon monoxide and oxygen.

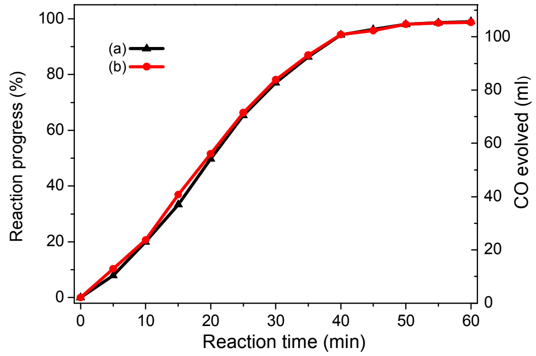


Figure 5. The reaction progress for the reaction of complex **1** with silver carbonate (▲) and for the reaction of complex **1** with potassium carbonate (●), where the reaction progress in percentage was calculated based on the ratio of the volume of carbon monoxide collected to the maximum volume (theoretically).

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website

Synthesis, characterization data, calculation detail, crystalrefinements (PDF)
Crystallographic data for 3 (TXT)
Crystallographic data for 4 (TXT)

AUTHOR INFORMATION

Corresponding Author

trchen@mail.nptu.edu.tw.

Notes

The authors declare no competing financial interest.

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REFERENCES

1. Bertoni, G.; Ciuchini, C.; Tappa, R. ; *Atmos. Environ*. **2004**, *38*, 1625.
2. Cox, P. M.; Betts, R. A.; Jones, C. D.; Spall, S. A.; Totterdell, I. J. *Nature* **2000**, *408*, 184.
3. Alexander, J. M. M.; Jay, A. L.; John, E. B. *Organometallics* **2011**, *30*, 4308**.**
4. William, R. M.; Zhiji, H.; Paul, J. A.; William, W. B.; Patrick, L. H.; Richard, E. *J. Am. Chem. Soc.* **2011,** *133*, 15368.
5. David, C. L.; Charles, C. L. M.; Jonas, C. P. *Inorg. Chem.* **2014**, *53*, 4980**.**
6. Stephen, C. C.; Christine, A. B.; Michael, G. H.; Kent, R. M. *Inorg. Chem.* **1996**, *35*, 7704**.**
7. Peng, K.; Chen, C.; Zuofeng, C.; Cynthia, K. S.; Thomas, J. M.; Maurice, B. *J. Am. Chem. Soc.* **2012**, *134*, 5500.
8. Qiang, Z.; Joanne, T.; František, H. *Organometallics* **2014,** *33*, 5002**.**
9. Arnau, B.; Christophe,r M.; David, W. W.; Erwin, R.; Judy, H. *J. Am. Chem. Soc.* **2014**, *136*, 15473.
10. Jesse, D. F.; Clifford, P. K. *J. Am. Chem. Soc.* **2015**, *137*, 3565.
11. Frank, P. A. J.; Michael, W. G.; Frantisek, H.; James J. T. *Organometallics* **1996**, *15*, 3374.
12. John, A. K.; Kyle, A. G.; Clifford, P. K.; Emily, A. C. *J. Am. Chem. Soc.* **2013**, *135*, 15823.
13. Jay, A.; Richard, P. J.; Gonghu, L. *J. Phys. Chem. A* **2011**, *115*, 2877.
14. Jeffrey, A. T.; Michael, O. W.; Brian, O. P. *Inorg. Chem.* **2014**, *53*, 12962.
15. John, L. D.; Joel, R. *J. Am. Chem. Soc.* **2013**, *135*, 8798.
16. Wenlei, Z.; Ronald, M.; Önder, M.; Haifeng, L.; Shaojun, G.; Christopher, J. W.; Xiaolian, S.; Andrew, A. P.; Shouheng, S. *J. Am. Chem. Soc.* **2013**, *135*, 16833.
17. James, W. R.; Jeffrey, W. T.; Bruce, C. N.; Calvin, J. C.; Alex, M.; Brian, C.; Daniel, L. D. *Organometallics* **2006**, *25*, 3345.
18. Jonathan, R.; Gregory, S. H.; Qi L.; Robert, V. F.; Alex, M.; Feng, J. *ACS Catal.* **2015**, *5*, 4586.
19. Qi, S.; Zuofeng, C.; Xiaofeng, H.; Meichuan, L.; Guohua, Z. *Environ. Sci. Technol.* **2015**, *49*, 5828.
20. Indrajit, S.; Hsu, H.-Ch.; Chang, Y.-C.; Lin, C.-H.; Pradip, K. R.; Abhijit, G.; Wang, C.-H.; Chang, J.-K.; Wu, C.-I.; Chen, L.-C.; Chen, K.-H. *Nano Lett.* **2014**, *14*, 6097.
21. Bhupendra, K.; Jonathan, M. S.; Clifford, P. K. *J. Phys. Chem. C.* **2010**, *114*, 14220.
22. Andreas, B.;Samuel, H.; Stephen, W. R.; Fraser, A. A. *J. Am. Chem. Soc.* **2014**, *136*, 13518.
23. Shunji, X.; Yu, W.; Qinghong, Z.; Weiping, D.; Ye, W. *ACS Catal.* **2014**, *4*, 3644.
24. Jared, S. S.; Christopher, C. C. *J. Am. Chem. Soc.* **2010**, *132*, 2169.
25. Camille, L.; Dennis, U. N.; Ilya, S. M.; Anders, T. L.; Kim, D.; Troels, S. *J. Am. Chem. Soc.* **2014**, *136*, 6142.
26. Jonnathan, M.-R.; Rachel, C. P.; Thomas, P. K.; John, L. D.; Joel, R. *J. Am. Chem. Soc.* **2015**, *137*, 5021.
27. Chen, T.-R. *J. Organomet. Chem.* **2008**, *693*, 3117.
28. Lee, H.-P.; Hsu, Y.-F.; Chen,T.-R.; Chen, J.-D.; Chen, K. H.-C.; Wang, J.-C. *Inorg. Chem.* **2009**, *48*, 1263.
29. Matthew, C. L.; Dale, R. P.; Joseph, M. M.; Roge,r D.; Sommer, D.; Michael, H.; Thomas, R. C.; Elon, A. I. *J. Am. Chem. Soc.* 2015, *137*, 3574.
30. (a) Tolman, C.A. *Chem. SOC. Rev.*. **1972**, *1*, 337. (b) Parkin, G. *Organometallics* **2006**, *25*, 4744. (c) Mingos, D. M. P. *J. Organometal. Chem.* **2004**, *689*, 4420.
31. Chen, T.-R.; Lee H.-P.; Chen J.-D.; Chen K. H.-C. *Dalton Trans.* 2010, *39*, 9458.

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