ORGANOMETALLICS

pubs.acs.org/Organometallics Article

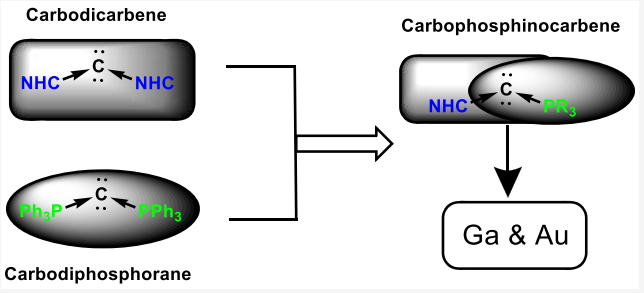
Synthesis of Carbophosphinocarbene and Their Donating Ability: Expansion of the Carbone Class

Shu-kai Liu, Wen-Ching Chen,* Glenn P. A. Yap, and Tiow-Gan Ong*

Cite This: https://dx.doi.org/10.1021/acs.organomet.0c00618 Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

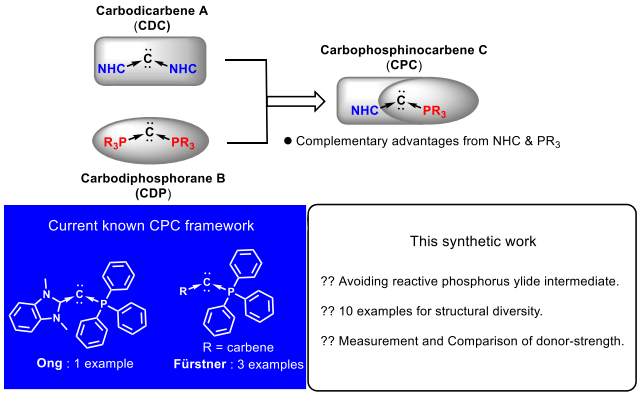
ABSTRACT: In recent years, carbones (CL_2) have established themselves to be reliable ligands in organometallic and catalytic reactions. With its superb donating ability as well as a second lone pair for extra coordination, it distinguishes itself from the widely used carbenes and phosphines. However, a lack of modular structural diversity in carbones has limited its use. A carbophosphinocarbene (CPC), a subclass of carbones containing a carbene and phosphine as flanking groups, offers an easy structural modification. In this work, we report a new modular synthetic procedure for CPCs by using readily available starting materials. In addition, the phosphine moiety can be easily exchanged and directly used out of the bottle. The resulting CPCs offer a strong donating ability. Their electronic properties have been determined using Ga and Au complexes.



INTRODUCTION

Carbodicarbenes **A** (CDCs) are classified in the family of carbones (CL_2) that feature a dicoordinated central carbon (C^0). This C^0 bears two lone electron pairs with N-heterocyclic carbenes (NHCs) as flanking ligands (L) (Scheme 1). Due to the two lone pairs on the central carbon, CDCs have been regarded as ligands with strong σ-donation.[1] Despite sharing some similarities to NHCs as electron-rich scaffolds, CDCs possess low-lying empty p orbitals adjacent to the center carbon containing lone pairs, rendering these two reactive sites capable of undergoing 1,2-addition reactions with a series of organic molecules. This unique property distinguishes CDCs from NHCs in terms of chemical reactivity.[2] Other unique features of CDCs have also been unraveled by the works of England and our laboratory, demonstrating redox and photoactive properties that NHCs are lacking.[3] Definitely, these complementary features should permit CDCs to define their own kind of new conceptual reactivity as opposed to traditional ligands such as NHCs and phosphines.

Scheme 1. General Structures of CDC (A), CDP (B), and CPC (C) and Reported CPCs



The origin of carbones can be historically traced back to the discovery of carbodiphosphorane **B** ($(PPh_3)_2C$ or CDP) by Ramirez around 1965.[4] However, it was Bertrand,[5] Petz,[6] Roesky,[7] Driess,[8] Kira[9] and Frenking[10] who are responsible for putting this octet-defying carbogenic species including silylones and germylones on the map of contemporary chemistry with interest spanning almost all the conventional disciplines of chemistry. Of those carbones, carbodicarbenes and bisylides by Ong,[2,11] Stephan,[12] Meek,[13] Gessner[14] and Fürstner[15] emerged as notable models in their supporting role for main-group chemistry, transition-metal complexes, and catalysis. The success of these cases can be attributed to the presence of framework diversity in these carbone classes, enabling the possibility of modulating the steric and electronic of these ligands for specific reaction conditions.

Special Issue: Organometallic Chemistry of the Main-Group Elements

Received: September 17, 2020

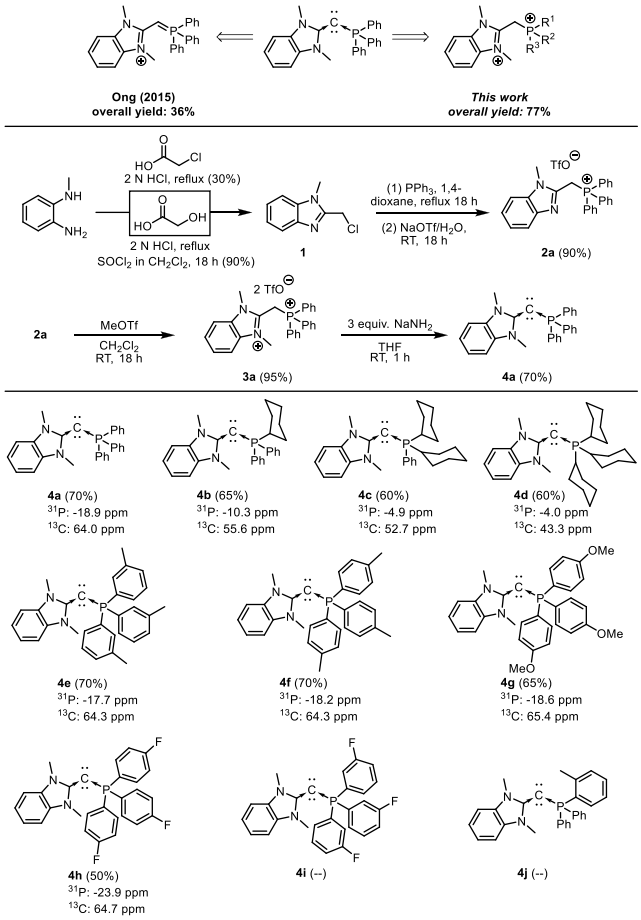
Slightly different from **A** and **B**, the carbophosphinocarbenes **C** (CPCs) are another subset of the C(0) class with their center carbons flanked by NHC and phosphine. The chemical implication invoked by this ligand framework is promising. The two different flanking pendants of CPCs could interplay synergistically, bringing new distinct properties manifested between those of the known CDC and CDP. Most importantly, this platform would allow chemists a great flexibility to tune the electronic and steric environment of this ligand. Unfortunately, the CPC scaffold has been overlooked so far, and only a few known CPCs have been reported, as illustrated in Scheme 1.[11a,15] The lack of a sound synthetic strategy has hampered the expansion of the CPC class. Current known procedures of synthesizing CPCs are ineffective, due to the involvement of overly reactive phosphorus ylide intermediates.[16] In this report, we aim to address the framework diversity of CPCs by creating a simple synthetic strategy based on commercially available starting materials. At the same time, we also investigate and evaluate the donating strength of CPCs by preparing Ga and Au complexes.

RESULTS AND DISCUSSION

There is no library of ligands concerning scaffolds related to the CPC moiety, and thus we began our plan to synthesize ligands. Commercially available *N*-methylphenylenediamine hydrochloride salt and glycolic acid were chosen as starting materials and allowed to react to afford the benzimidazole derivative **1** in excellent yield of 90% (Scheme 2). Chloroacetic acid could also be used as an alternative for making **1**, albeit in lower yield (30%).[17] Subsequently, the highly hygroscopic phosphonium salt **2a** was prepared in 90% yield via refluxing **1** with PPh_3 in 1,4-dioxane solution. An anion exchange with sodium triflate is used to reduce hydromancy and to increase its solubility in organic solvents. A direct methylation using methyl trifluoromethanesulfonate effectively transformed **2a** to the CPC precursor **3a**. As illustrated at the bottom of Scheme 2, a total of 10 different CPC precursors (**3a**−**j**) were successfully obtained in good yields using similar preparation steps (for further details see the Supporting Information). Aryl, alkyl, or a combination of those (**a**−**d**) with certain degrees of steric modulation and electronic variants (**e**−**j**) are possible. As expected, this new preparation route offered a tremendous improvement in the overall yield of the reaction (77%) with step reduction in comparison to our previously reported method (36%).[11a] The key strategy underlying the present achievement is the absence of any formation of a reactive phosphine ylide. In the previous method the phosphine moiety was introduced via a nucleophilic attack of the ylide at the N-heterocyclic thioether derivative to form the precursor. The ylide's absence in combination with the direct use of the phosphine allows the use of alkylated species, which are sensitive to transylidation.[18] In addition, the product purification for more soluble phosphines (e.g., **d**−**g**) can be more effectively carried out.

The free carbone of CPC **4a** in 70% yield could be isolated through a double-deprotonation process using 2 equiv of sodium amide base (Scheme 2). Other analogous precursors **3** could also be converted to free carbone **4** except for **3i,j** (*vide infra*). A ^{31}P NMR study of **4a** shows a large upfield shift, moving from 22.2 to −18.9 ppm with respect to its precursor **3a**. Similarly, the ^{13}C NMR shift of the center carbon of **4a** appears at 64 ppm, substantially upfield with respect to the

Scheme 2. Synthetic Route of CPC and Other Known Derivatives



carbodicarbene (~110 ppm)[1c] but downfield with respect to the carbodiphosphorane **B** (~15 ppm).[18a] We attributed these large NMR shift differences to the π-accepting ability of the flanking ligands embedded within the carbone. The CDC contained two flanking NHCs with vacant p orbitals capable of delocalizing electron density away from the center carbon. This generates a weak shielding effect and thus leads to a downfield shift in ^{13}C resonances. As expected, CPC has a more upfield shift in comparison to CDC, as its flanking phosphine is a poor π-acceptor.[19]

Further closer examination of ^{13}C NMR of CPCs **4e**−**h** containing PAr_3 revealed signals at around 64−65 ppm for the center carbon. The upfield trend of ^{13}C NMR in the CPCs was consistently observed with an increase in number of the alkyl group. For example, **4b** containing one cyclohexyl substituent has a signal at 55.6 ppm, while that of **4d** appears at 43.3 ppm with three cyclohexyl groups (Scheme 2). This upfield phenomenon may be correlated directly to the higher σ-donating strength of PCy_3 in comparison to PPh_3. In contrast to ^{13}C NMR, the phosphine resonance moves oppositely toward the downfield region as the number of alkyl substituents of CPCs increased (**4a** (−18.9 ppm) > **4b** (−10.3 ppm) > **4c** (−4.9 ppm) > **4d** (−4.0 ppm)). This phenomenon in ^{31}P NMR could be rationalized by an electron-withdrawing effect invoked by the aryl group that had pulled the electron density away from the C(0) center to the phosphorus center, generating a stronger shielding effect over the P atom for an upfield shift. This trend of correlation is

https://dx.doi.org/10.1021/acs.organomet.0c00618
Organometallics XXXX, XXX, XXX−XXX

further exemplified by **4h**. Bearing fluorine within the moiety, **4h** has the most upfield signal of all CPCs at −23.9 ppm. In that sense, results obtained from ^{31}P NMR studies could be used to quantify the π-back-bonding ability of the carbones.

X-ray crystal analyses have been carried out for **4c**,**d**,**f**, obtained from a slow evaporation of fluorobenzene at −20 °C or benzene at room temperature (Figure 1). The pertinent

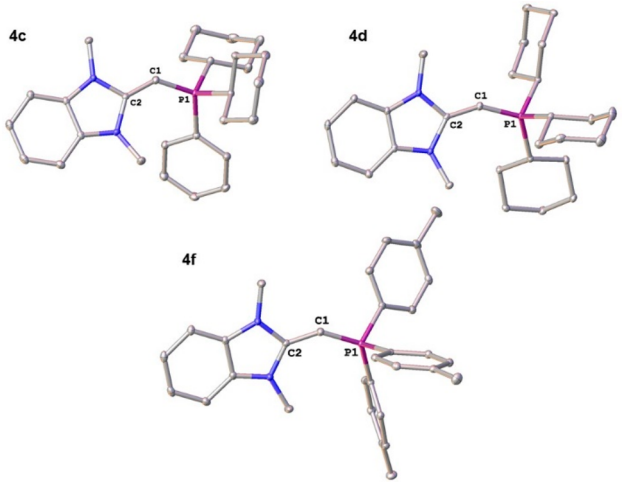


Figure 1. X-ray crystal structures of CPC **4c**,**d**,**f** with thermal ellipsoids drawn at the 30% probability level and hydrogen atoms omitted for clarity.

crystal structure of **4a** was reported previously by Ong's laboratory.[11a] We note that the structure of **4c** flanked with $PPhCy_2$ features two chemically different molecules in a unit cell. Thus, we have averaged the structural parameters for the following discussion. The C1−C2 and C1−P1 bond lengths in **4a**,**c**,**d**,**f** are consistently the same with average values of ∼1.33 and ∼1.65 Å, respectively, suggesting a minimum steric influence of substituents on the topology of the structures. Among these structures, steric bulk invoked by three cyclohexyl groups has resulted in **4d** having the largest C2−C1−P1 angle of 149.25° (Table 1).

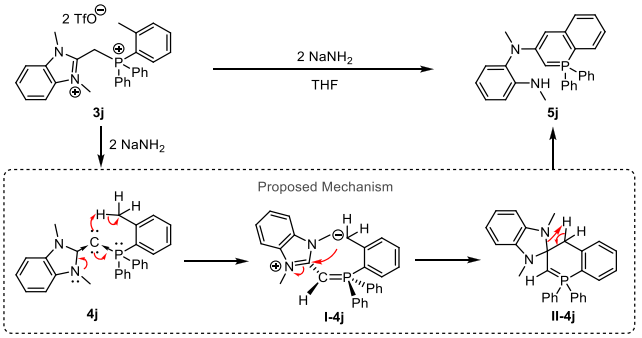
Table 1. Overview of Specific Bond Lengths of CDP, CDC, and CPCs

	C1−C2 (Å)	C1−P1 (Å)	C2−C1−C3/C2−C1−P1 (deg)
CDP[18b]		1.629(3)	143.8(6)
CDC[1c]	1.318−1.346		134.8−146.1
4a[11a]	1.3378(17)	1.6435(12)	143.04(10)
4c[a]	1.3392(19)	1.6629(14)	137.94(11)
4d	1.3262(18)	1.6441(13)	149.25(12)
4f	1.345(2)	1.6454(19)	144.09(15)

[a]There are two chemically distinct molecules in the unit cell; average values are given.

It should be noted that we failed to obtain free carbones **4i**,**j**, in spite of attempts using various kinds of bases for deprotonation. We could not identify products associated with the deprotonation reaction of **3i**, but we successfully isolated the air-stable bright orange compound **5j** (60% yield), which is attributed to the decomposition of the carbone as an intermediate. **5j** is a phosphorine heteroarene, as confirmed by a single-crystal X-ray diffraction experiment and NMR spectroscopy (see the Supporting Information). On the basis of a similar cyclization via carbene CH insertion observed by Bertrand,[20] we propose that the transformation of this reaction occurred via generation of the unstable carbone **4j** as depicted in Scheme 3. Since the methyl group at the *ortho* position of

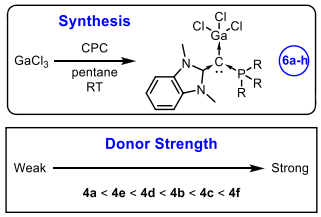
Scheme 3. Proposed Mechanism of the Phosphorine 5j from 3j



the tolyl substituent was in close range with the reactive site of the carbone, a facile intramolecular abstraction occurred to form a six-membered cyclic transition state to give **II-4j**. Rearrangement and concomitant C−N bond cleavage proceeded to generate product **5j**.

To evaluate the electronic properties of the CPC ligands, the synthesis of metal complexes bearing CPCs is necessary. We selected gallium and gold complexes as our target of investigation, because of the experimental simplicity and literature precedent of using these complexes for measuring the donating strength. The CPC-ligated gallium complexes (**6a**−**h**, Scheme 4) were prepared by reacting equimolar

Scheme 4. Formation of Ga-CPC Complex 6: Overview of $\sum_{ClGaCl}$, the Resulting TEP($GaCl_3$), and the TEP[23] of PR_3



TEP of PR_3 (cm^{-1})	PR_3
2068.9	PPh_3
2065.2	PPh_2Cy
2063.1	$PPhCy_2$
2056.4	PCy_3
2067.2	P(*m*-Tol)$_3$
2066.7	P(*p*-Tol)$_3$

TEP and Σ_{ClGaCl} of CPC	Gandon Method (cm^{-1} / °)
4a	2043.3 / 320.00
4b	2032.4 / 313.65
4c	2032.5 / 313.72
4d	2034.1 / 314.64
4e	2036.9 / 316.29
4f	2031.7 / 313.27

amounts of the ligand and $GaCl_3$ in pentane solution. The target main-group complexes precipitated readily out of the solution and were fully characterized by NMR and MS analysis. Single-crystal X-ray structural analyses confirmed the coordination of the CPC **4a**−**f** to $GaCl_3$. Unfortunately, we were unable to get suitable crystals of the complexes with CPCs **4g**,**h**. As expected, $GaCl_3$ changes its geometry from trigonal planar to a trigonal-pyramidal-like geometry. The C1−Ga1 bond length varies from 1.9369(13) to 1.964(2) Å for the CPCs (**6a**−**f**). These bond lengths are shorter in comparison to CAACs (∼2.0463 Å)[21] or NHCs (∼1.994 Å).[22] The electronic variation had no dramatic consequence over the Ga−carbone bond length of the CPC. Because of a decrease in the electron density due to the $GaCl_3$ coordination, the average C1−C2 (∼1.431 Å) and C1−P1 (1.707 Å) bond distances of all these CPCs were lengthened in comparison to the free CPC (1.337 and 1.65 Å). Notably, the C2−C1−P1 angle became

https://dx.doi.org/10.1021/acs.organomet.0c00618
Organometallics XXXX, XXX, XXX−XXX

more acute, an indication of a change of the CPC from sp^2 toward sp^3 hybridization.

Another important structural feature of these Ga complexes of **6** is the sum of the Cl−Ga−Cl angles ($\sum_{ClGaCl}$). The Gandon group recently reported that the degree of the pyramidalization of the L→$GaCl_3$ complex correlated with the TEP (Tolman electronic parameter) donating strength over a wide range of ligands such as phosphines, carbenes (NHC/CAAC), and several CDC/CDPs. It was found that a stronger donor will concentrate the π-character of the gallium orbitals toward the chlorine atoms. This effect leads to the compacting of the three Cl−Ga−Cl angles. As a result, the sum of angles around Cl−Ga provides useful information about the donor strength of CPC ligands.[21] In Scheme 4, the $\sum_{ClGaCl}$ values and their calculated TEP values are given for each CPC-Ga complex. In view of these structural parameters, the complex **6f** (313.3°) bearing the **4f** ligand has the smallest value of $\sum_{ClGaCl}$, while **6a** bearing the **4a** ligand has the largest value (320.0°). Subsequent conversion of the $\sum_{ClGaCl}$ values gives TEP values of 2031.7 and 2043.3 cm^{-1} on the basis of Gandon protocol, respectively (see the Supporting Information). Importantly, the donor strength predicted by the Gandon method showed that the CPCs are more strongly donating ligands (2043−2031 cm^{-1}) in comparison to NHCs and CAACs (2051−2046 cm^{-1}). As shown in Scheme 4, the donation ability strength of CPC is ranked in order of weakest to strongest as **4a** < **4e** < **4d** < **4b** < **4c** < **4f** on the basis of the Gandon protocol. Notwithstanding its accuracy in predicting electronic features for common ligands, we observed an anomaly within the carbone system in this method. For example, **4d** flanked by PCy_3 is supposed to be more electron rich than **4b** (PPh_2Cy), **4c** ($PPhCy_2$), and **4f** (p-$PTol_3$) but the Gandon method predicted otherwise. This is counterintuitive to our conventional chemical electronic knowledge of these ligands, as flanking phosphine fragments should account for most of the donor strength of CPCs.

Gandon and co-workers briefly noted that noncovalent interactions and crystal forces influence the conformation of structures, which might affect the accuracy of the measurement. A detailed examination of these structures revealed a noncovalent interaction between the electronegative chloride atoms and flanking NHC containing an empty p orbital. The nonbonding interaction varies from 3.281 Å (**6c**) to 3.415 Å (**6f**; see Figure 2), which is within the combined van der Waals radii of 3.45 Å. Interestingly, we could not find such a noncovalent interaction in complex **6e** (see Figure 2). This interaction seems to widen the angle of $\sum_{ClGaCl}$, which can cause a deception of the true geometry angle. On the basis of this observation, we concluded that the presence of this noncovalent interaction negatively affects the Gandon method and makes predicting the donor strength of the CPC in a more precise manner harder.

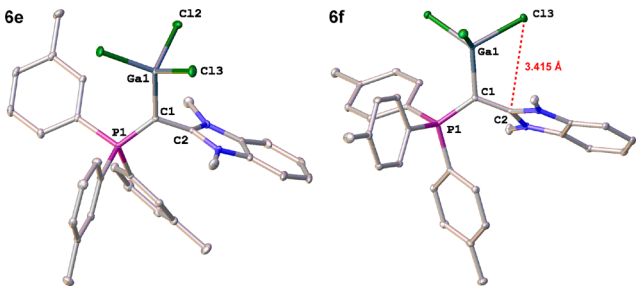
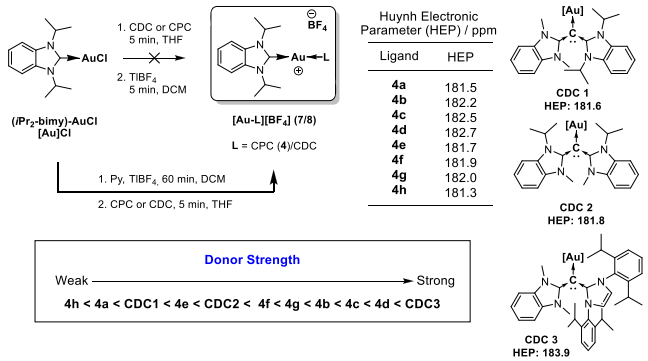


Figure 2. X-ray crystal structures of Ga-CPCs **6e**,**f** with thermal ellipsoids drawn at the 30% probability level. Solvent and hydrogen atoms are omitted for clarity. Selected bond lengths (Å) and angles (deg): **6e**, Ga1−C1 1.9425(15), C1−C2 1.4352(29), C1−P1 1.7017(15), C2−C1−P1 117.03(11); **6f**, Ga1−C1 1.964(2), C1−C2 1.419(3), C1−P1 1.715(2), C2−C1−P1 121.96(15), C2···Cl3 3.415.

To avoid the problem associated with nonbonding interactions in the Gandon method, we needed to find a more effective alternate to quantify each CPC. More importantly, we needed a method that is not dependent on the single-crystal X-ray structures. The Huynh electronic parameter (HEP) seems to be the perfect choice to measure the donating ability of the carbones. Huynh et al. reported a parameter based on the ^{13}C NMR chemical shift of the carbene carbon atom of the complexes *trans*-[$PdBr_2$($i$$Pr_2$-bimy)(L)] and [($i$$Pr_2$-bimy)Au-L]$^+$ as a probe for gauging the donating strength of the ligand L.[24] Similar to Gandon's method, this method mainly measures the σ-donating ability of the ligand. The preparation of [($i$$Pr_2$-bimy)Au-L][$BF_4$] complexes (**7**) was needed, in which L was our CPC ligand. A previously reported synthetic protocol based on the starting compound ($i$$Pr_2$-bimy)Au-Cl was not suitable, as it was plagued by a facile ligand redistribution process leading to the unwanted by-product [($i$$Pr_2$-bimy)$_2$Au]$^+$, which made the purification step unmanageable (Scheme 5). Therefore, an alternative route was developed to prepare [($i$$Pr_2$-bimy)Au-L][$BF_4$].

Scheme 5. Formation of Complexes 7 and 8 and Their Resulting HEPs



The isolable [($i$$Pr_2$-bimy)Au-py][$BF_4$] (**9**; see the Supporting Information for further information) is used as an intermediate in the synthesis step, the desirable complexes **7** were obtained in good yield with full characterization via NMR and MS experiments. Crystals of **7a** suitable for X-ray analyses were grown by diffusion of pentane into a saturated dichloromethane solution at −30 °C. The Au−C bond of **7a** (2.052(2) Å) is slightly long, warranting no further detailed discussion. On the basis of ^{13}C NMR studies of complexes **7**, the HEP revealed the following order of the weakest to the strongest carbone ligands: **4h** < **4a** < **4e** < **4f** < **4g** < **4b** < **4c** < **4d**. Similarly to Gandon's method with $GaCl_3$ we observed **4a** to be the most weakly donating ligand, while **4d** is now seen as the most strongly donating ligand. We were also able to analyze CPCs **4h** (p-P(PhF)$_3$) and **4g** (p-P(Anisyl)$_3$) with this method. These two were missing in the Gandon method due to a lack of crystal structures. Again, the anomaly occurring in

https://dx.doi.org/10.1021/acs.organomet.0c00618
Organometallics XXXX, XXX, XXX−XXX

Gandon's method with alkylated phosphines is not observed here. The more electron rich phosphine PCy_3 in **4d** is the strongest donor among the CPCs, in line with our intuitive thoughts. In addition, the HEP was measured with our previously reported CDCs as well with the following ranking: **CDC1** < **CDC2** < **CDC3**. The result is also in line with our expectation that **CDC3** is the most strongly donating ligand followed by **CDC2** and **CDC1**, which have approximately equal donating strengths. On comparison of the results of CPCs and CDCs, the HEP reveals that **CDC3** is more strongly donating than CPC **4d**. **CDC1** and **CDC2** are ranked in the lower midrange, showing that most of the newly synthesized CPCs are more strongly donating ligands. The reason may be the donating strength of the free ligand itself. Imidazolylidene is known to be a stronger donor than the phosphines and therefore makes **CDC3** the strongest member. On the other hand, the benzimidazolylidene strength is similar to that of the phosphines, leading to a lower rank.

CONCLUSION

In conclusion, we have shown a new, convenient, and efficient synthetic pathway for the gram-scale synthesis of CPCs. This short and highly modular synthesis allows the use of most commercially available alkyl and aryl phosphines out of the bottle without involving the reactive phosphorus ylide. In addition, it can be considered the most customizable ligand next to the current NHCs and phosphines. $TEP(GaCl_3)$ and the HEP studies reveal the excellent donating ability of CPCs, easily surpassing those of CAACs and NHCs. A majority of the presented CPCs are more strongly donating than previously reported CDCs. Our group is currently conducting further research and analysis of the properties of the CPCs and their application.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.0c00618.

Experimental details and characterization data (PDF)

Accession Codes

CCDC 2031833−2031844 contain 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 Authors

Wen-Ching Chen − *Institute of Chemistry, Academia Sinica, Taipei, Taiwan*; Email: cwc590317@gmail.com

Tiow-Gan Ong − *Institute of Chemistry, Academia Sinica, Taipei, Taiwan; The Department of Applied Chemistry, National Chiao Tung University, Hsin-chu, Taiwan; The Department of Chemistry, National Taiwan University, Taipei, Taiwan;* orcid.org/0000-0001-9817-6300; Email: tgong@gate.sinica.edu.tw

Authors

Shu-kai Liu − *Institute of Chemistry, Academia Sinica, Taipei, Taiwan; The Department of Applied Chemistry, National Chiao Tung University, Hsin-chu, Taiwan; Sustainable Chemical Science and Technology, Taiwan International Graduate Program, Academia Sinica and National Chiao Tung University, Hsin-chu, Taiwan;* orcid.org/0000-0002-8627-5253

Glenn P. A. Yap − *The Department of Chemistry and Biochemistry, University of Delaware, Newark, Delaware 19716, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.organomet.0c00618

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was financially supported by the Ministry of Science & Technology of Taiwan (MOST-107-2113-M-001-034-MY2, MOST-109-2113-M-001-038, and MOST-108-2113-M-001-026-MY3 grants) and the grant of an Academia Sinica Investigator Award (AS-IA-108-M04). S.L. thanks Academia Sinica and TIGP for financial and technical support.

REFERENCES

(1) For recent reviews, see: (a) Doddi, A.; Peters, M.; Tamm, M. N-Heterocyclic Carbene Adducts of Main Group Elements and Their Use as Ligands in Transition Metal Chemistry. *Chem. Rev.* **2019**, *119*, 6994−7112. (b) Liu, S.-k.; Shih, W.-C.; Chen, W.-C.; Ong, T.-G. Carbodicarbenes and their Captodative Behavior in Catalysis. *ChemCatChem* **2018**, *10*, 1483−1498. (c) Liu, S.; Chen, W.-C.; Ong, T.-G. Synthesis and Structure of Carbodicarbenes and Their Application in Catalysis. In *Modern Ylide Chemistry: Applications in Ligand Design, Organic and Catalytic Transformations*; Gessner, V. H., Ed.; Springer International: Cham, Switzerland, 2018; pp 51−71.

(2) Chen, W.-C.; Shih, W.-C.; Jurca, T.; Zhao, L.; Andrada, D. M.; Peng, C.-J.; Chang, C.-C.; Liu, S.-k.; Wang, Y.-P.; Wen, Y.-S.; Yap, G. P. A.; Hsu, C.-P.; Frenking, G.; Ong, T.-G. Carbodicarbenes: Unexpected π-Accepting Ability during Reactivity with Small Molecules. *J. Am. Chem. Soc.* **2017**, *139*, 12830−12836.

(3) (a) Chan, S.-C.; Gupta, P.; Engelmann, X.; Ang, Z. Z.; Ganguly, R.; Bill, E.; Ray, K.; Ye, S.; England, J. Observation of Carbodicarbene Ligand Redox Noninnocence in Highly Oxidized Iron Complexes. *Angew. Chem., Int. Ed.* **2018**, *57*, 15717−15722. (b) Chan, S.-C.; Ang, Z. Z.; Gupta, P.; Ganguly, R.; Li, Y.; Ye, S.; England, J. Carbodicarbene Ligand Redox Noninnocence in Highly Oxidized Chromium and Cobalt Complexes. *Inorg. Chem.* **2020**, *59*, 4118−4128. (c) Hsu, Y.-C.; Wang, V. C.-C.; Au-Yeung, K.-C.; Tsai, C.-Y.; Chang, C.-C.; Lin, B.-C.; Chan, Y.-T.; Hsu, C.-P.; Yap, G. P. A.; Jurca, T.; Ong, T.-G. One-Pot Tandem Photoredox and Cross-Coupling Catalysis with a Single Palladium Carbodicarbene Complex. *Angew. Chem., Int. Ed.* **2018**, *57*, 4622−4626.

(4) (a) Ramirez, F.; Desai, N. B.; Hansen, B.; McKelvie, N. Hexaphenylcarbodiphosphorane, $(C_6H_5)_3PCP(C_6H_5)_3$. *J. Am. Chem. Soc.* **1961**, *83*, 3539−3540. (b) Desai, N. B.; McKelvie, N.; Ramirez, F. A New Synthesis of 1,1-Dibromoölefins via Phosphine-Dibromomethylenes. the Reaction of Triphenylphosphine with Carbon Tetrabromide. *J. Am. Chem. Soc.* **1962**, *84*, 1745−1747.

(5) (a) Melaimi, M.; Parameswaran, P.; Donnadieu, B.; Frenking, G.; Bertrand, G. Synthesis and Ligand Properties of a Persistent, All-Carbon Four-Membered-Ring Allene. *Angew. Chem., Int. Ed.* **2009**, *48*, 4792−4795. (b) Fernández, I.; Dyker, C. A.; DeHope, A.; Donnadieu, B.; Frenking, G.; Bertrand, G. Exocyclic Delocalization at the Expense of Aromaticity in 3,5-bis(π-Donor) Substituted Pyrazolium Ions and Corresponding Cyclic Bent Allenes. *J. Am. Chem. Soc.* **2009**, *131*, 11875−11881. (c) Lavallo, V.; Dyker, C. A.; Donnadieu, B.; Bertrand, G. Synthesis and Ligand Properties of Stable Five-Membered-Ring Allenes Containing Only Second-Row Elements. *Angew. Chem., Int. Ed.* **2008**, *47*, 5411−5414. (d) DeHope, A.; Donnadieu, B.; Bertrand,

G. Grubbs and Hoveyda-type ruthenium complexes bearing a cyclic bent-allene. *J. Organomet. Chem.* **2011**, *696*, 2899−2903. (e) Weinstein, C. M.; Martin, C. D.; Liu, L.; Bertrand, G. Cross-Coupling Reactions between Stable Carbenes. *Angew. Chem., Int. Ed.* **2014**, *53*, 6550−6553.

(6) (a) Petz, W. Addition compounds between carbones, CL2, and main group Lewis acids: A new glance at old and new compounds. *Coord. Chem. Rev.* **2015**, *291*, 1−27. (b) Petz, W.; Neumüller, B. New platinum complexes with carbodiphosphorane as pincer ligand via ortho phenyl metallation. *Polyhedron* **2011**, *30*, 1779−1784. (c) Petz, W.; Öxler, F.; Neumüller, B. Syntheses and crystal structures of linear coordinated complexes of Ag^+ with the ligands $C(PPh_3)_2$ and $(HC\{PPh_3\}_2)^+$. *J. Organomet. Chem.* **2009**, *694*, 4094−4099. (d) Petz, W.; Kutschera, C.; Neumüller, B. Reaction of the Carbodiphosphorane Ph_3PCPPh_3 with Platinum(II) and -(0) Compounds: Platinum Induced Activation of C−H Bonds. *Organometallics* **2005**, *24*, 5038−5043.

(7) (a) Mondal, K. C.; Roesky, H. W.; Schwarzer, M. C.; Frenking, G.; Niepötter, B.; Wolf, H.; Herbst-Irmer, R.; Stalke, D. A Stable Singlet Biradicaloid Siladicarbene: $(L:)_2Si$. *Angew. Chem., Int. Ed.* **2013**, *52*, 2963−2967. (b) Li, Y.; Mondal, K. C.; Roesky, H. W.; Zhu, H.; Stollberg, P.; Herbst-Irmer, R.; Stalke, D.; Andrada, D. M. Acyclic Germylones: Congeners of Allenes with a Central Germanium Atom. *J. Am. Chem. Soc.* **2013**, *135*, 12422−12428.

(8) (a) Xiong, Y.; Yao, S.; Inoue, S.; Epping, J. D.; Driess, M. A Cyclic Silylone ("Siladicarbene") with an Electron-Rich Silicon(0) Atom. *Angew. Chem., Int. Ed.* **2013**, *52*, 7147−7150. (b) Xiong, Y.; Yao, S.; Tan, G.; Inoue, S.; Driess, M. A Cyclic Germadicarbene ("Germylone") from Germyliumylidene. *J. Am. Chem. Soc.* **2013**, *135*, 5004−5007. (c) Zhou, Y.-P.; Karni, M.; Yao, S.; Apeloig, Y.; Driess, M. A Bis(silylenyl)pyridine Zero-Valent Germanium Complex and Its Remarkable Reactivity. *Angew. Chem., Int. Ed.* **2016**, *55*, 15096−15099.

(9) (a) Ishida, S.; Iwamoto, T.; Kabuto, C.; Kira, M. A stable silicon-based allene analogue with a formally sp-hybridized silicon atom. *Nature* **2003**, *421*, 725−727. (b) Iwamoto, T.; Masuda, H.; Kabuto, C.; Kira, M. Trigermaallene and 1,3-Digermasilaallene. *Organometallics* **2005**, *24*, 197−199. (c) Iwamoto, T.; Abe, T.; Kabuto, C.; Kira, M. A missing allene of heavy Group 14 elements: 2-germadisilaallene. *Chem. Commun.* **2005**, 5190−5192. (d) Kira, M.; Iwamoto, T.; Ishida, S.; Masuda, H.; Abe, T.; Kabuto, C. Unusual Bonding in Trisilaallene and Related Heavy Allenes. *J. Am. Chem. Soc.* **2009**, *131*, 17135−17144. (e) Kira, M. An isolable dialkylsilylene and its derivatives. A step toward comprehension of heavy unsaturated bonds. *Chem. Commun.* **2010**, *46*, 2893−2903.

(10) (a) Tonner, R.; Frenking, G. $C(NHC)_2$: Divalent Carbon(0) Compounds with N-Heterocyclic Carbene Ligands—Theoretical Evidence for a Class of Molecules with Promising Chemical Properties. *Angew. Chem., Int. Ed.* **2007**, *46*, 8695−8698. (b) Tonner, R.; Frenking, G. Divalent Carbon(0) Chemistry, Part 1: Parent Compounds. *Chem. - Eur. J.* **2008**, *14*, 3260−3272. (c) Tonner, R.; Frenking, G. Divalent Carbon(0) Chemistry, Part 2: Protonation and Complexes with Main Group and Transition Metal Lewis Acids. *Chem. - Eur. J.* **2008**, *14*, 3273−3289. (d) Takagi, N.; Shimizu, T.; Frenking, G. Divalent E(0) Compounds (E = Si−Sn). *Chem. - Eur. J.* **2009**, *15*, 8593−8604. (e) Takagi, N.; Shimizu, T.; Frenking, G. Divalent Silicon(0) Compounds. *Chem. - Eur. J.* **2009**, *15*, 3448−3456. (f) Tonner, R.; Frenking, G. Tolman's Electronic Parameters for Divalent Carbon(0) Compounds. *Organometallics* **2009**, *28*, 3901−3905. (g) Klein, S.; Tonner, R.; Frenking, G. Carbodicarbenes and Related Divalent Carbon(0) Compounds. *Chem. - Eur. J.* **2010**, *16*, 10160−10170. (h) Esterhuysen, C.; Frenking, G. Distinguishing Carbones from Allenes by Complexation to AuCl. *Chem. - Eur. J.* **2011**, *17*, 9944−9956. (i) Himmel, D.; Krossing, I.; Schnepf, A. Dative Bonds in Main-Group Compounds: A Case for Fewer Arrows! *Angew. Chem., Int. Ed.* **2014**, *53*, 370−374. (j) Frenking, G. Dative Bonds in Main-Group Compounds: A Case for More Arrows! *Angew. Chem., Int. Ed.* **2014**, *53*, 6040−6046. (k) Himmel, D.; Krossing, I.; Schnepf, A. Dative or Not Dative? *Angew. Chem., Int. Ed.* **2014**, *53*, 6047−6048. (l) Frenking, G.; Hermann, M.; Andrada, D. M.; Holzmann, N. Donor-acceptor bonding in novel low-coordinated compounds of boron and group-14 atoms C-Sn. *Chem. Soc. Rev.* **2016**, *45*, 1129−1144.

(11) (a) Chen, W.-C.; Shen, J.-S.; Jurca, T.; Peng, C.-J.; Lin, Y.-H.; Wang, Y.-P.; Shih, W.-C.; Yap, G. P. A.; Ong, T.-G. Expanding the Ligand Framework Diversity of Carbodicarbenes and Direct Detection of Boron Activation in the Methylation of Amines with CO_2. *Angew. Chem., Int. Ed.* **2015**, *54*, 15207−15212. (b) Chen, W.-C.; Lee, C.-Y.; Lin, B.-C.; Hsu, Y.-C.; Shen, J.-S.; Hsu, C.-P.; Yap, G. P. A.; Ong, T.-G. The Elusive Three-Coordinate Dicationic Hydrido Boron Complex. *J. Am. Chem. Soc.* **2014**, *136*, 914−917. (c) Chen, W.-C.; Hsu, Y.-C.; Lee, C.-Y.; Yap, G. P. A.; Ong, T.-G. Synthetic Modification of Acyclic Bent Allenes (Carbodicarbenes) and Further Studies on Their Structural Implications and Reactivities. *Organometallics* **2013**, *32*, 2435−2442.

(12) (a) Pranckevicius, C.; Liu, L.; Bertrand, G.; Stephan, D. W. Synthesis of a Carbodicyclopropenylidene: A Carbodicarbene based Solely on Carbon. *Angew. Chem., Int. Ed.* **2016**, *55*, 5536−5540. (b) Dobrovetsky, R.; Stephan, D. W. Catalytic Reduction of CO_2 to CO by Using Zinc(II) and In Situ Generated Carbodiphosphoranes. *Angew. Chem., Int. Ed.* **2013**, *52*, 2516−2519. (c) Pranckevicius, C.; Fan, L.; Stephan, D. W. Cyclic Bent Allene Hydrido-Carbonyl Complexes of Ruthenium: Highly Active Catalysts for Hydrogenation of Olefins. *J. Am. Chem. Soc.* **2015**, *137*, 5582−5589.

(13) (a) Marcum, J. S.; Roberts, C. C.; Manan, R. S.; Cervarich, T. N.; Meek, S. J. Chiral Pincer Carbodicarbene Ligands for Enantioselective Rhodium-Catalyzed Hydroarylation of Terminal and Internal 1,3-Dienes with Indoles. *J. Am. Chem. Soc.* **2017**, *139*, 15580−15583. (b) Roberts, C. C.; Matías, D. M.; Goldfogel, M. J.; Meek, S. J. Lewis Acid Activation of Carbodicarbene Catalysts for Rh-Catalyzed Hydroarylation of Dienes. *J. Am. Chem. Soc.* **2015**, *137*, 6488−6491. (c) Goldfogel, M. J.; Roberts, C. C.; Meek, S. J. Intermolecular Hydroamination of 1,3-Dienes Catalyzed by Bis(phosphine)carbodicarbene−Rhodium Complexes. *J. Am. Chem. Soc.* **2014**, *136*, 6227−6230.

(14) (a) Scherpf, T.; Wirth, R.; Molitor, S.; Feichtner, K.-S.; Gessner, V. H. Bridging the Gap between Bisylides and Methandiides: Isolation, Reactivity, and Electronic Structure of an Yldiide. *Angew. Chem., Int. Ed.* **2015**, *54*, 8542−8546. (b) Scharf, L. T.; Gessner, V. H. Metalated Ylides: A New Class of Strong Donor Ligands with Unique Electronic Properties. *Inorg. Chem.* **2017**, *56*, 8599−8607. (c) Scharf, L. T.; Andrada, D. M.; Frenking, G.; Gessner, V. H. The Bonding Situation in Metalated Ylides. *Chem. - Eur. J.* **2017**, *23*, 4422−4434. (d) Weber, P.; Scherpf, T.; Rodstein, I.; Lichte, D.; Scharf, L. T.; Gooßen, L. J.; Gessner, V. H. A Highly Active Ylide-Functionalized Phosphine for Palladium-Catalyzed Aminations of Aryl Chlorides. *Angew. Chem., Int. Ed.* **2019**, *58*, 3203−3207. (e) Scherpf, T.; Schwarz, C.; Scharf, L. T.; Zur, J.-A.; Helbig, A.; Gessner, V. H. Ylide-Functionalized Phosphines: Strong Donor Ligands for Homogeneous Catalysis. *Angew. Chem., Int. Ed.* **2018**, *57*, 12859−12864. (f) Kroll, A.; Steinert, H.; Scharf, L. T.; Scherpf, T.; Mallick, B.; Gessner, V. H. A diamino-substituted carbodiphosphorane as strong C-donor and weak N-donor: isolation of monomeric trigonal-planar $L{\cdot}ZnCl_2$. *Chem. Commun.* **2020**, *56*, 8051−8054.

(15) (a) Alcarazo, M.; Suárez, R. M.; Goddard, R.; Fürstner, A. A New Class of Singlet Carbene Ligands. *Chem. - Eur. J.* **2010**, *16*, 9746−9749. (b) Alcarazo, M.; Lehmann, C. W.; Anoop, A.; Thiel, W.; Fürstner, A. Coordination chemistry at carbon. *Nat. Chem.* **2009**, *1*, 295−301.

(16) Bestmann, H. J.; Zimmerman, R. 1.6 - Synthesis of Phosphonium Ylides. In *Comprehensive Organic Synthesis*; Trost, B. M., Fleming, I., Eds.; Pergamon: Oxford, 1991; pp 171−202.

(17) Dumat, B.; Bordeau, G.; Faurel-Paul, E.; Mahuteau-Betzer, F.; Saettel, N.; Metge, G.; Fiorini-Debuisschert, C.; Charra, F.; Teulade-Fichou, M.-P. DNA Switches on the Two-Photon Efficiency of an Ultrabright Triphenylamine Fluorescent Probe Specific of AT Regions. *J. Am. Chem. Soc.* **2013**, *135*, 12697−12706.

https://dx.doi.org/10.1021/acs.organomet.0c00618
Organometallics XXXX, XXX, XXX−XXX

(18) (a) Yogendra, S.; Schulz, S.; Hennersdorf, F.; Kumar, S.; Fischer, R.; Weigand, J. J. Reductive Ring Opening of a Cyclo-Tri(phosphonio)methanide Dication to a Phosphanylcarbodiphospho-rane: In Situ UV-Vis Spectroelectrochemistry and Gold Coordination. *Organometallics* **2018**, *37*, 748−754. (b) Vincent, A. T.; Wheatley, P. J. Crystal structure of bis-(triphenylphosphoranylidene)-methane [hexaphenylcarbodiphosphorane, $Ph_3P{:}C{:}PPh_3$]. *J. Chem. Soc., Dalton Trans.* **1972**, 617−622.
(19) Wilson, D. J. D.; Couchman, S. A.; Dutton, J. L. Are N-Heterocyclic Carbenes "Better" Ligands than Phosphines in Main Group Chemistry? A Theoretical Case Study of Ligand-Stabilized E_2 Molecules, L-E-E-L (L = NHC, phosphine; E = C, Si, Ge, Sn, Pb, N, P, As, Sb, Bi). *Inorg. Chem.* **2012**, *51*, 7657−7668.
(20) Weinstein, C. M.; Junor, G. P.; Tolentino, D. R.; Jazzar, R.; Melaimi, M.; Bertrand, G. Highly Ambiphilic Room Temperature Stable Six-Membered Cyclic (Alkyl)(amino)carbenes. *J. Am. Chem. Soc.* **2018**, *140*, 9255−9260.
(21) El-Hellani, A.; Monot, J.; Tang, S.; Guillot, R.; Bour, C.; Gandon, V. Relationship between Gallium Pyramidalization in L·GaCl3 Complexes and the Electronic Ligand Properties. *Inorg. Chem.* **2013**, *52*, 11493−11502.
(22) Marion, N.; Escudero-Adán, E. C.; Benet-Buchholz, J.; Stevens, E. D.; Fensterbank, L.; Malacria, M.; Nolan, S. P. Synthesis, Characterization, and Structure of $[GaCl_3(NHC)]$ Complexes. *Organometallics* **2007**, *26*, 3256−3259.
(23) (a) Tolman, C. A. Steric effects of phosphorus ligands in organometallic chemistry and homogeneous catalysis. *Chem. Rev.* **1977**, *77*, 313−348. (b) Chen, L.; Ren, P.; Carrow, B. P. Tri(1-adamantyl)phosphine: Expanding the Boundary of Electron-Releasing Character Available to Organophosphorus Compounds. *J. Am. Chem. Soc.* **2016**, *138*, 6392−6395. (c) Brink, A.; Roodt, A.; Steyl, G.; Visser, H. G. Steric vs. electronic anomaly observed from iodomethane oxidative addition to tertiary phosphine modified rhodium(i) acetylacetonato complexes following progressive phenyl replacement by cyclohexyl [PR_3 = PPh_3, PPh_2Cy, $PPhCy_2$ and PCy_3]. *Dalton Trans.* **2010**, *39*, 5572−5578.
(24) (a) Huynh, H. V. Electronic Properties of N-Heterocyclic Carbenes and Their Experimental Determination. *Chem. Rev.* **2018**, *118*, 9457−9492. (b) Huynh, H. V.; Han, Y.; Jothibasu, R.; Yang, J. A. 13C NMR Spectroscopic Determination of Ligand Donor Strengths Using N-Heterocyclic Carbene Complexes of Palladium(II). *Organometallics* **2009**, *28*, 5395−5404. (c) Guo, S.; Sivaram, H.; Yuan, D.; Huynh, H. V. Gold and Palladium Hetero-Bis-NHC Complexes: Characterizations, Correlations, and Ligand Redistributions. *Organometallics* **2013**, *32*, 3685−3696. (d) Teng, Q.; Huynh, H. V. A unified ligand electronic parameter based on ^{13}C NMR spectroscopy of N-heterocyclic carbene complexes. *Dalton Trans.* **2017**, *46*, 614−627.

https://dx.doi.org/10.1021/acs.organomet.0c00618
Organometallics XXXX, XXX, XXX−XXX