ORGANIC LETTERS

2012
Vol. 14, No. 7
1700–1703

Efficient and High Yield One-Pot Synthesis of Cyclometalated Platinum(II) β-Diketonates at Ambient Temperature

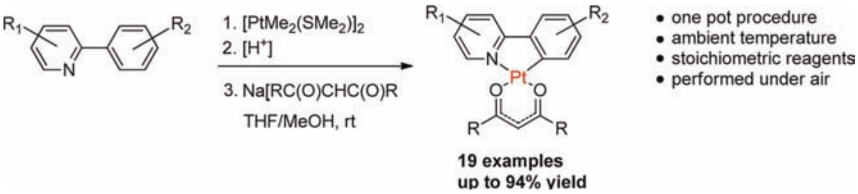
Zachary M. Hudson, Barry A. Blight, and Suning Wang*

Department of Chemistry, Queen's University, 90 Bader Lane, Kingston, Ontario, Canada K7L 3N6

suning.wang@chem.queensu.ca

Received February 1, 2012

ABSTRACT



Cyclometalated Pt(II) β-diketonates are widely used as efficient luminescent materials but are typically prepared at high temperatures in low yields using excess reagents. A one-pot synthesis of these complexes is described employing stoichiometric reagents and short reaction times at ambient temperature, giving yields of up to 94%. The method is applicable to a broad range of substrates including N^C, P^C, and C^C chelate Pt(II) complexes and different β-diketonate ligands.

Cyclometalated platinum complexes are among the most efficient phosphorescent materials and have been widely explored for use in chemical sensors[1] and organic light-emitting diodes (OLEDs).[2] In particular, cyclometalated platinum(II) β-diketonates have been the subject of considerable research[3] due to the excellent stability and high triplet energy level of typical diketonate ancillary ligands. As a result, this moiety has been incorporated into materials with many fascinating structures, including bimetallic complexes,[4] photochromic materials,[5] liquid crystals,[6] and metallahelicenes.[7] Furthermore, the efficient phosphorescence of cyclometalated platinum β-diketonates has led to many applications in biological imaging,[8] nonlinear optics,[9] oxygen sensing,[10] and most notably electroluminescent devices.[2b−h] Despite this broad research activity, however, an efficient synthetic method for producing these compounds has remained elusive. This is of particular concern due to the high cost of platinum-based

---

(1) (a) Thomas, S. W., III; Yagi, S.; Swager, T. M. *J. Mater. Chem.* **2005**, *15*, 2829–2835. (b) Thomas, S. W., III; Venkatesan, K.; Müller, P.; Swager, T. M. *J. Am. Chem. Soc.* **2006**, *128*, 16641–16648. (c) Li, K.; Chen, Y.; Lu, W.; Zhu, N.; Che, C.-M. *Chem.—Eur. J.* **2011**, *17*, 4109–4112. (d) Wong, K. H.; Chan, M. C. W.; Che, C.-M. *Chem.—Eur. J.* **1999**, *5*, 2845–2849. (e) Rao, Y. L.; Wang, S. *Inorg. Chem.* **2009**, *48*, 7698–7713. (f) Hudson, Z. M.; Zhao, S. B.; Wang, R. Y.; Wang, S. *Chem.—Eur. J.* **2009**, *15*, 6131–6137. (g) Albrecht, M.; van Koten, G. *Adv. Mater.* **1999**, *11*, 171–174. (h) Hudson, Z. M.; Sun, C.; Harris, K. J.; Lucier, B. E. G.; Schurko, R. W.; Wang, S. *Inorg. Chem.* **2011**, *50*, 3447–3457. (i) Huo, C.; Zhang, H. D.; Zhang, H. Y.; Zhang, H. Y.; Yang, B.; Zhang, P.; Wang, Y. *Inorg. Chem.* **2006**, *45*, 4735–4742.

(2) For representative examples, see: (a) Cocchi, M.; Virgili, D.; Fattori, V.; Rochester, D. L.; Williams, J. A. G. *Adv. Funct. Mater.* **2007**, *17*, 285–289. (b) Hudson, Z. M.; Sun, C.; Helander, M. G.; Amarne, H.; Lu, Z.; Wang, S. *Adv. Funct. Mater.* **2010**, *20*, 3426–3439. (c) Hudson, Z. M.; Helander, M. G.; Lu, Z.; Wang, S. *Chem. Commun.* **2011**, *47*, 755–757. (d) Yang, X.; Froehlich, J. D.; Chae, H. S.; Harding, B. T.; Li, S.; Mochizuki, A.; Jabbour, G. E. *Chem. Mater.* **2010**, *22*, 4776–4782. (e) Velusamy, M.; Chen, C.; Wen, Y. S.; Lin, J. T.; Lin, C.; Lai, C.; Chou, P. *Organometallics* **2010**, *29*, 3912–3921. (f) He, Z.; Wong, W.; Yu, X.; Kwok, H.; Lin, Z. *Inorg. Chem.* **2006**, *45*, 10922–10937. (g) Zhou, G.; Wang, Q.; Wang, X.; Ho, C.; Wong, W.; Ma, D.; Wang, L.; Lin, Z. *J. Mater. Chem.* **2010**, *20*, 7472–7484. (h) Chi, Y.; Chou, P. *Chem. Soc. Rev.* **2010**, *39*, 638–655 and references therein.

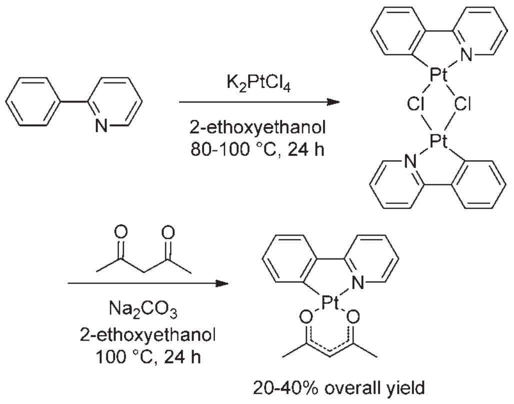
(3) (a) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055–3066. (b) Perez, M. D.; Djurovich, P. I.; Hassan, A.; Cheng, G. Y.; Stewart, T. J.; Aznavour, K.; Bau, R.; Thompson, M. E. *Chem. Commun.* **2009**, 4215–4217. (c) Ghedini, M.; Pugliese, T.; LaDeda, M.; Godbert, N.; Aiello, I.; Amati, M.; Belviso, S.; Lelj, F.; Accorsi, G.; Barigelletti, F. *Dalton Trans.* **2008**, *37*, 4303–4318. (d) Kozhevnikov, D. N.; Kozhevnikov, V. N.; Shafikov, M. Z.; Prokhorov, A. M.; Bruce, D. W.; Williams, J. A. G. *Inorg. Chem.* **2011**, *50*, 3804–3815. (e) Kozhevnikov, D. N.; Kozhevnikov, V. N.; Ustinova, M. M.; Santoro, A.; Bruce, D. W.; Koenig, B.; Czerwieniec, R.; Fischer, T.; Zabel, M.; Yersin, H. *Inorg. Chem.* **2009**, *48*, 4179–4189.

(4) (a) Ma, B.; Djurovich, P. I.; Yousufuddin, M.; Bau, R.; Thompson, M. E. *J. Phys. Chem. C* **2008**, *112*, 8022–8031. (b) Shin, C. H.; Huh, J. O.; Baek, S. J.; Kim, S. K.; Lee, M. H.; Do, Y. *Eur. J. Inorg. Chem.* **2010**, 3642–3651. (c) Kozhevnikov, V. N.; Durrant, M. C.; Williams, J. A. G. *Inorg. Chem.* **2011**, *50*, 6304–6313.

10.1021/ol300242f

starting materials, increasing the cost of research and seriously limiting the commercial viability of these compounds.

Scheme 1. Traditional Preparation Method for Cyclometalated Pt(II) β-Diketonates

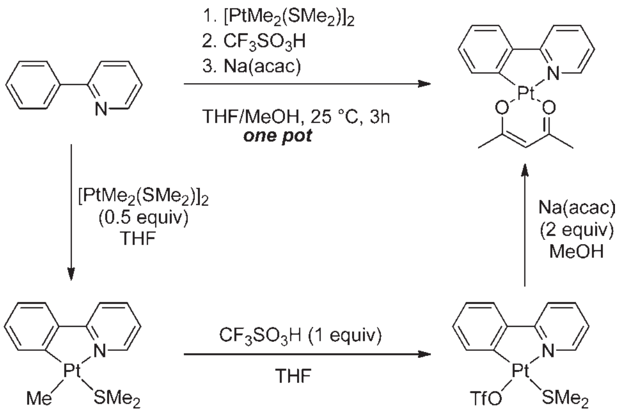


Cyclometalated platinum β-diketonates are typically prepared by a modified method of Lewis and co-workers,[3a,11] a two-step process in which 2 to 2.5 equiv of a cyclometalating ligand are heated with K_2PtCl_4 to give a chloro-bridged platinum dimer, which is then heated with Na_2CO_3 and β-diketone to give the final product (Scheme 1). This process has several disadvantages, such as requiring long reaction times at high temperature and giving typical yields of only 20−40% over two steps. The need for excess ligand is particularly problematic, as the organic ligands used for many applications in advanced materials are often of considerable value themselves. Furthermore, the high temperature reaction conditions limit the scope of cyclometalating ligands that can be used to prepare these complexes. Although recent reports have described stoichiometric reactions of cyclometalating ligands using PtCl(DMSO)(acac) as starting material, long reaction times and low yields are typical of this method as well.[2b,c,12]

Inspired by this challenge, we sought to develop an efficient one-pot synthesis of cyclometalated platinum β-diketonates under mild conditions. We elected to use $[PtMe_2(SMe_2)]_2$ as starting material, which has been widely used as a precursor in C−H activation chemistry[13] and can be easily prepared on a multigram scale from K_2PtCl_4 in 85−90% overall yield.

When treated with stoichiometric quantities of 2-phenylpyridine (ppy) in THF at ambient temperature, this starting material affords the cyclometalated $Pt(ppy)Me(SMe_2)$ complex with irreversible loss of CH_4. Treatment of this solution with 1 equiv of trifluoromethane sulfonic acid (TfOH) leads to rapid loss of a second equivalent of CH_4, giving the corresponding $Pt(ppy)(OTf)(SMe_2)$ complex incorporating two labile ancillary ligands. Addition of a solution of sodium β-diketonate in methanol then gives clean conversion to the desired Pt(ppy)(acac) product, which is isolated as analytically pure material in 87% yield following column chromatography (Scheme 2). This reaction sequence can be conveniently carried out at ambient temperature under an atmosphere of air in less than 3 h.

Scheme 2. An Improved One-Pot Synthesis of Cyclometalated Pt(II) β-Diketonates



This method shows broad substrate scope across N^C-chelate ligands incorporating a variety of structures and functional groups (Table 1). Clean conversion to the cyclometalated diketonate complex is observed for both electron-rich (R = −OMe, −NR_2) and electron-deficient (R = F, Cl) arenes, with little change in overall yields observed in either case. The method is equally successful in the synthesis of heterocyclic N^C-chelate complexes and can be used to synthesize benzofuran, benzothiazole, and

---

(5) (a) Chan, J. C.; Lam, W. H.; Wong, H.; Zhu, N.; Wong, W.; Yam, V. W.-W. *J. Am. Chem. Soc.* **2011**, *133*, 12690–12705. (b) Rao, Y.; Wang, S. *Organometallics* **2011**, *30*, 4453–4458.

(6) (a) Buey, J.; Díez, L.; Espinet, P.; Kitzerow, H.-S.; Miguel, J. A. *Chem. Mater.* **1996**, *8*, 2375–2381. (b) Venkatesan, K.; Kouwer, P. H. J.; Yagi, S.; Müller, P.; Swager, T. M. *J. Mater. Chem.* **2008**, *18*, 400–407. (c) Santoro, A.; Whitwood, A. C.; Williams, J. A. G.; Kozhevnikov, V. N.; Bruce, D. W. *Chem. Mater.* **2009**, *21*, 3871–3882. (d) Wang, Y.; Liu, Y.; Luo, J.; Qi, H.; Li, X.; Nin, M.; Liu, M.; Shi, D.; Zhu, W.; Cao, Y. *Dalton Trans.* **2011**, *40*, 5046–5051.

(7) Norel, L.; Rudolph, M.; Vanthuyne, N.; Williams, J. A. G.; Lescop, C.; Roussel, C.; Autschbach, J.; Crassous, J.; Réau, R. *Angew. Chem., Int. Ed.* **2010**, *49*, 99–102.

(8) Mou, X.; Wu, Y.; Liu, S.; Shi, M.; Liu, X.; Wang, C.; Sun, S.; Zhao, Q.; Zhou, X.; Huang, W. *J. Mater. Chem.* **2011**, *21*, 13951–13962.

(9) (a) Wu, W.; Guo, H.; Wu, W.; Ji, S.; Zhao, J. *Inorg. Chem.* **2011**, *50*, 11446–11460. (b) Wu, W.; Wu, W.; Ji, S.; Guo, H.; Zhao, J. *Dalton Trans.* **2011**, *40*, 5953–5963.

(10) (a) Wu, W.; Wu, W.; Ji, S.; Guo, H.; Song, P.; Han, K.; Chi, L.; Shao, J.; Zhao, J. *J. Mater. Chem.* **2010**, *20*, 9775–9786. (b) Wu, W.; Wu, W.; Ji, S.; Guo, H.; Zhao, J. *J. Organomet. Chem.* **2011**, *696*, 2388–2398.

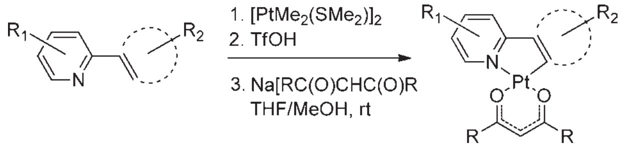
(11) Cockburn, B. N.; Howe, V.; Keating, T.; Johnson, B. F. G.; Lewis, J. *J. Chem. Soc., Dalton Trans.* **1973**, 404–410.

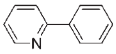
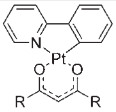
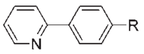
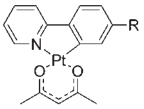
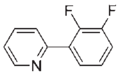
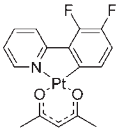
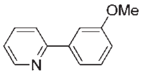
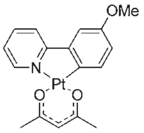
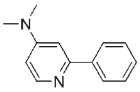
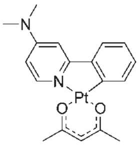
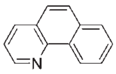
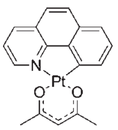
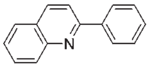
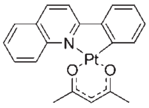
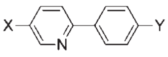
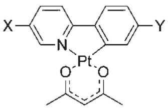
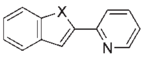
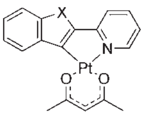
(12) Crespo, M.; Anderson, C. M.; Tanski, J. M. *Can. J. Chem.* **2009**, *87*, 80–87.

(13) (a) Scott, J. D.; Puddephatt, R. J. *Organometallics* **1983**, *2*, 1643–1648. (b) Puddephatt, R. J.; Thomson, M. A.; Manojlovic-Muir, L.; Muir, K. W.; Frew, A. A.; Brown, M. P. *J. Chem. Soc., Chem. Commun.* **1981**, *15*, 805–806. (c) Zhang, F. B.; Kirby, C. W.; Hairsine, D. W.; Jennings, M. C.; Puddephatt, R. J. *J. Am. Chem. Soc.* **2005**, *127*, 14196–14197. (d) Song, D. T.; Wang, S. *Organometallics* **2003**, *22*, 2187–2189. (e) Zhao, S. B.; Song, D. T.; Jia, W. L.; Wang, S. *Organometallics* **2005**, *24*, 3290–3296. (f) Wick, D. D.; Goldberg, K. I. *J. Am. Chem. Soc.* **1997**, *119*, 10235–10236.

(14) Wang, Z. B.; Helander, M. G.; Hudson, Z. M.; Qiu, J.; Wang, S.; Lu, Z. H. *Appl. Phys. Lett.* **2011**, *98*, 213301–213303.

Table 1. Preparation of N^C Chelate Pt(II) β-Diketonates



entry	ligand	complex	yield [%][a]
1			**1a**, R = Me, 87 **1b**, R = *t*-Bu, 87 **1c**, R = Ph, 83
2			**2a**, R = Me, 81 **2b**, R = Cl, 85 **2c**, R = Br, 85
3			76
4			85
5			83
6			76
7			87
8[b]			**8a**, X = BMes$_2$ Y = H, 94 **8b**, X = H, Y = NPh$_2$, 92 **8c**, X = BMes$_2$, Y = NAr$_2$, 88[c]
9			**9a**, X = O, 92 **9b**, X = S, 89 **9c**, X = N-Ph, 83

[a] Yields are of analytically pure material. [b] Mes = Mesityl (2,4,6-trimethylphenyl), Ar$_2$ = Ph(1-Naphthyl).

N-phenylindole derivatives in 92, 89, and 83% yield, respectively (Table 1, entry 9). Incorporation of extended π-systems is equally facile, as platinum β-diketonate complexes of 2-phenylquinoline and benzo[*h*]quinoline (entries 6, 7) are readily prepared in yields of 87 and 76%. Motivated by our own interest in boron chemistry, we also present an improved synthesis of several triarylboron-functionalized platinum phosphors (entry 8a–8c), among the most efficient Pt-based emitter materials incorporated into OLEDs to date.[2b,c,14] The yields of these boryl-functionalized Pt(II) compounds are about 4 to 5 times greater than those (~20%) obtained using the PtCl(DMSO)(acac) precursor method.[2b,c] As applications in phosphorescent materials have been a principal driving force behind research in cyclometalated platinum complexes, the photophysical properties of all complexes reported herein have been determined and are provided in the Supporting Information. Compounds **2b**–**c**, **4**, **5**, **9a**, **9c**, and **10** have not been previously reported and are fully characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis, and the identities of all known compounds were confirmed by ^{1}H NMR and elemental analysis.

While functionalization of Pt(II) β-diketonates on the N^C-chelate backbone is more common, considerable research has also been devoted to the functionalization of Pt complexes on the β-diketonate itself.[2d,e,4a,6a] While acetylacetonate (acac) is by far the most widely used of these, dibenzoylmethane (dbm) and dipivaloylmethane (dpm) have also appeared in numerous studies, with notably different physical properties. Using these as representative examples in the reaction with 2-phenylpyridine, this method is shown to be applicable using alternative β-diketonate ligands with no significant reduction in overall yield (entry 1b,c).

Our initial investigations made use of TfOH, due to the high lability of its conjugate base, when acting as a ligand to metal centers. However, its high toxicity and difficulty in handling make it less than ideal for use on an industrial scale. We therefore studied the use of other strong organic acids, namely *p*-toluenesulfonic acid (TsOH) and trifluoroacetic acid (TFA) in the demethylation of Pt(ppy)Me(SMe$_2$). After reaction with acetylacetonate, these reactions gave product **1a** in 91 and 92% yield respectively, indicating that strong acids that are more easily handled may be used in a similar manner.

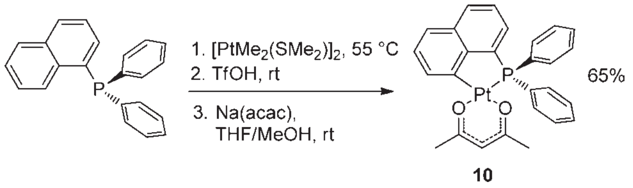
Encouraged by these results, we sought to determine if this method could be applied to other cyclometalated platinum systems. P^C-chelate phosphines have recently found use as highly efficient emitter materials for OLEDs,[2h,15] though platinum-containing examples are comparatively less well studied. In particular, very few reports describe the preparation of platinum β-diketonate P^C-chelate complexes,[16] presenting numerous opportunities for materials research. We thus examined the reaction of (1-naphthyl)-diphenylphosphine with [PtMe$_2$(SMe$_2$)]$_2$, carried out under a nitrogen atmosphere to prevent oxidation of the phosphine. The cyclometalation of this ligand is readily achieved under mild heating at 55 °C for 4 h, and following reaction with acid and acetylacetonate at room temperature, the

---

(15) (a) Hung, J.-Y.; Chi, Y.; Pai, I.-H.; Yu, Y.-C.; Lee, G. H.; Chou, P. T.; Wong, K. T.; Chen, C. C.; Wu, C. C. *Dalton Trans.* **2009**, *38*, 6472. (b) Chiu, Y. C.; Hung, J. Y.; Chi, Y.; Chen, C. C.; Chang, C. H.; Wu, C. C.; Cheng, Y. M.; Yu, Y. C.; Lee, G. H.; Chou, P. T. *Adv. Mater.* **2009**, *21*, 2221–2229.

(16) (a) Cheney, A. J.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1972**, 754–763. (b) Gill, D. F.; Mann, B. E.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1973**, 270–278. (c) Duff, J. M.; Mann, B. E.; Shaw, B. L.; Turtle, B. *J. Chem. Soc., Dalton Trans.* **1974**, 139–145. (d) Empsall, H. D.; Heys, P. N.; Shaw, B. L. *J. Chem. Soc., Dalton Trans.* **1978**, 257–262.

Scheme 3. Synthesis of a P^C Chelate Pt(II) β-Diketonate Complex

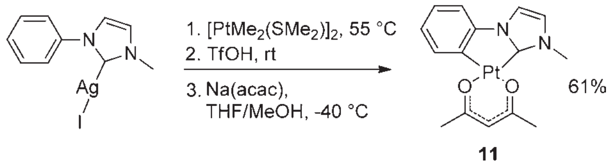


corresponding Pt(P^C)(acac) complex was successfully obtained in 65% yield (Scheme 3).

Similarly, recent years have witnessed a surge of interest in platinum complexes of *N*-heterocyclic carbenes, with applications as broad as catalysis,[17] cancer therapy,[18] and organic electronics.[19] This presented a unique synthetic challenge, and we sought to determine if our methodology could be applied to the synthesis of C^C-chelate carbene complexes of platinum β-diketonates. Few examples of such products have appeared in literature, requiring several days at high temperature to prepare.[19a,b] Literature methods require initial formation of a silver(I) carbene species, followed by transmetalation with $Pt(COD)Cl_2$ (COD = 1,4-cyclooctadiene) at 100 °C for 16 h, followed by reaction with β-diketone and Na(O-*t*-Bu) at 100 °C for a further 16 h.

Using *N*-methyl-*N*′-phenylimidazolium iodide as a representative example, we have found that our synthetic methods can be adapted successfully to give C^C chelate carbene complexes of platinum β-diketonates (Scheme 4). These complexes remain most conveniently prepared *via*

Scheme 4. Synthesis of a Pt(II) β-Diketonate Complex Using a C^C Chelate Carbene Ligand



Ag(I) carbene starting materials, which can be easily isolated after reaction of imidazolium salt with Ag_2O at room temperature.[20] This species is then stirred for 1 h with $[PtMe_2(SMe_2)]_2$ and filtered to remove precipitated AgI. Mild heating is then required for cyclometalation of the pendant phenyl group, with complete reaction observed after 2 h at 55 °C followed by reaction with acid at room temperature.

Surprisingly, addition of Na(acac) as a neat solid or in methanol led to rapid decomposition, giving a complex mixture of products not isolable by column chromatography. This undesired reactivity in the final step is readily avoided by cooling the reaction mixture to -40 °C, and after 2 h the corresponding Pt(C^C)(acac) complex may be successfully isolated in 61% yield (Scheme 4).

In summary, we have described a simple one-pot method for the preparation of cyclometalated platinum β-diketonates in significantly higher yield at lower cost. This method requires only stoichiometric equivalents of the N^C-chelate ligand, with typical yields of 80−90% after a 3 h reaction time at ambient temperature. The method is versatile toward a broad array of functional groups and heterocyclic systems and can be further adapted to the preparation of P^C-chelate phosphine compounds and C^C-chelate complexes of *N*-heterocyclic carbenes.

Acknowledgment. The authors gratefully acknowledge the Natural Sciences and Engineering Council of Canada (NSERC) for financial support.

Supporting Information Available. General experimental information, synthetic and characterization details for all Pt(II) complexes, and their UV−visible absorption and phosphorescence emission spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.

---

(17) (a) Jullien, H.; Brissy, D.; Sylvain, R.; Retailleau, P.; Naubron, J. V.; Gladiali, S.; Marinetti, A. *Adv. Synth. Catal.* **2011**, *353*, 1109–1112. (b) Brissy, D.; Skander, M.; Retailleau, P.; Frison, G.; Marinetti, A. *Organometallics* **2009**, *28*, 140–151. (c) Lu, C.; Gu, S.; Chen, W.; Qiu, H. *Dalton Trans.* **2010**, *39*, 4198–4204.

(18) (a) Sun, R. W.-Y.; Chow, A. L.-F.; Li, X.-H.; Yan, J. J.; Chui, S. S.-Y.; Che., C.-M. *Chem. Sci.* **2011**, *2*, 728–736. (b) Skander, M.; Retailleau, P.; Bourrié, B.; Schio, L.; Mailliet, P.; Marinetti, A. *J. Med. Chem.* **2010**, *53*, 2146–2154.

(19) (a) Haneder, S.; Da Como, E.; Feldmann, J.; Lupton, J. M.; Lennartz, C.; Erk, P.; Fuchs, E.; Molt, O.; Münster, I.; Schildknecht, C.; Wagenblast, G. *Adv. Mater.* **2008**, *20*, 3325–3330. (b) Unger, Y.; Meyer, D.; Molt, O.; Schildknecht, C.; Münster, I.; Wagenblast, G.; Strassner, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 10214–10216. (c) Wu, Y.; Wu, S.; Li, H.; Geng, Y.; Su, Z. *Dalton Trans.* **2011**, *40*, 4480–4488.

(20) Newman, C. P.; Clarkson, G. J.; Rourke, J. P. *J. Organomet. Chem.* **2007**, *692*, 4962–4968. Note: Ag(I) carbenes have been reported as both linear L−Ag−X and ionic $[L_2Ag][AgX_2]$ formulations; for clarity, the former is depicted in this report.