JOC The Journal of Organic Chemistry

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N-Heterocyclic Carbene Catalyzed Carba-, Sulfa-, and Phospha-Michael Additions with NHC·CO_2 Adducts as Precatalysts

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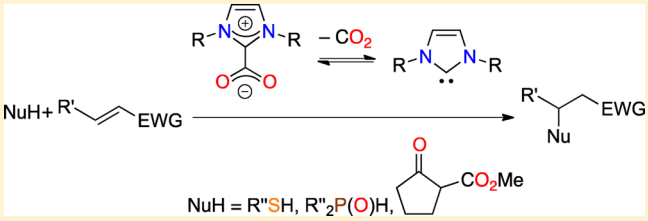
Supporting Information

ABSTRACT: N-heterocyclic carbene catalyzed Michael additions have been revisited with 1,3-dialkyl- or 1,3-diarylimidazol(in)ium-2-carboxylates, that is, NHC·CO_2 adducts, as the source of the free NHC catalysts in solution. Using these precatalysts, a number of efficient carba-, sulfa-, and phospha-Michael additions were achieved very conveniently, without the need for an external strong base to generate the NHC by deprotonation of an azolium salt. To further expand the scope of the procedure, some NHC-catalyzed sulfa-Michael/aldol organocascades were also investigated.



N-heterocyclic carbenes (NHCs) have found widespread applications in organometallic chemistry and organic synthesis. Because of their excellent σ-donor properties, NHCs have primarily been used as ancillary ligands in transition-metal complexes for homogeneous catalysis, which resulted in the development of a number of metal-based catalysts with enhanced and unique properties.[1,2] Alternatively, NHCs have also been used on their own as organocatalysts in a variety of transformations.[3−5] In this field, three distinct organocatalytic activation modes were identified: (1) ambiphilic activation, which results from the simultaneous σ-donor and π-acceptor properties of NHCs and allows them to trigger catalytic "umpolung" reactivity with aldehydes and enals,[6,7] (2) nucleophilic activation when NHCs are used as Lewis base (σ-donor) catalysts, for example in NHC-catalyzed transesterification reactions,[8] Morita−Baylis−Hillman reactions,[9] formal cycloadditions of zwitterionic enolate equivalents,[10,11] and polymerization reactions,[12] and (3) Brønsted base activation, the least studied path, which relies on the ability of NHCs to operate as catalytic proton shuttles as in the case of NHC-catalyzed Michael additions (Scheme 1). Of course, the reactivity and organocatalytic properties of NHCs are strongly dependent on their steric and electronic properties.[13] Among the four common classes of NHCs (Figure 1), imidazolinylidenes and imidazolylidenes are the most potent Brønsted bases, with pK_a values of the corresponding azolium salts ranging between 20 and 25 in aqueous solutions,[14,15] while thiazolylidenes and triazolylidenes exhibit significantly lower Brønsted basicity with pK_a values of ca. 15−19 for thiazolium and triazolium salts in water.[16]

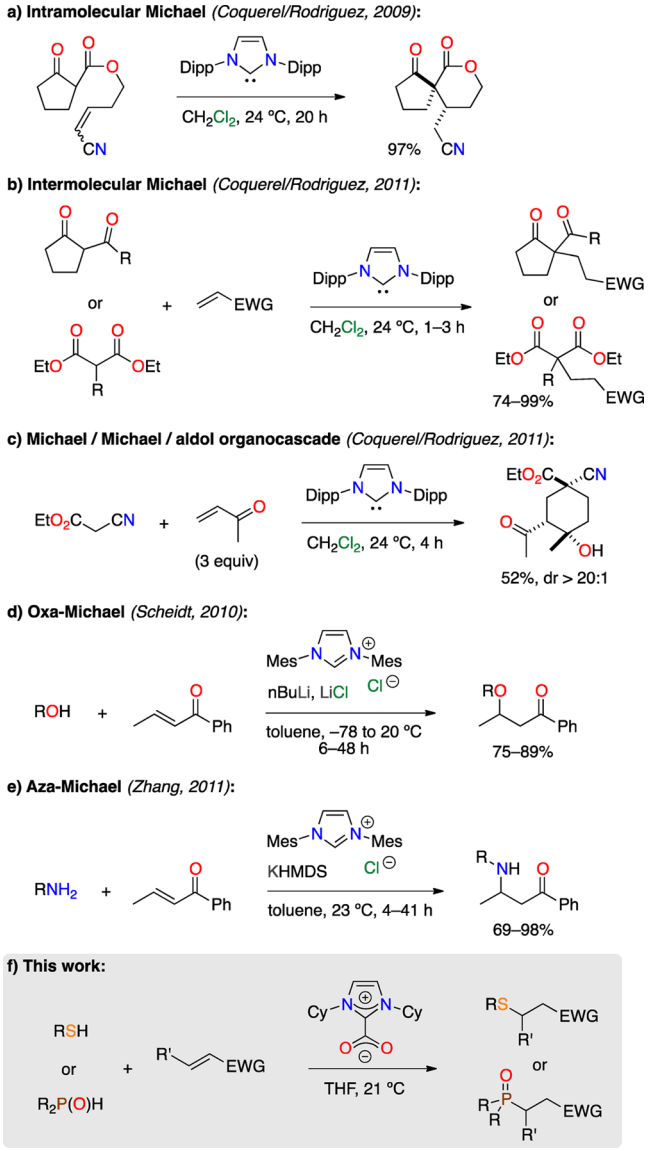
In 2009, stable and isolated imidazolylidenes were found to catalyze intramolecular Michael additions with high efficiency for the stereoselective synthesis of spiro compounds (Scheme 1a).[17] This organocatalytic system was successfully extended to intermolecular reactions and some stereoselective Michael/Michael/aldol organocascades with various kinds of Michael acceptors (Scheme 1b,c).[18] Concurrently, NHC-catalyzed oxa-Michael[19] and aza-Michael[20] additions were performed using imidazolium salt precatalysts in the presence of a strong base and in some cases a stoichiometric additive (Scheme 1d,e). Because sulfa-[21] and phospha-Michael[22,23] additions are among the most effective methods to synthesize organo-sulfur and organo-phosphorus compounds, the development of general, practical, and efficient catalytic systems to ease these reactions is of great importance. Herein, we disclose that NHC-catalyzed carba-, sulfa-, and phospha-Michael additions were efficiently accomplished with readily available and very convenient to use imidazol(in)ium-2-carboxylate (NHC·CO_2) precatalysts (Scheme 1f).

Relatively air-stable NHC·CO_2 zwitterions can be prepared by trapping either preformed or in situ generated 1,3-disubstituted imidazol(in)-2-ylidenes with carbon dioxide (Scheme 2).[24,25] The reaction is reversible in solution, and the carboxylate adducts were shown to act as convenient sources of free NHC ligands for the stoichiometric preparation of NHC−transition-metal complexes with concomitant release of carbon dioxide.[26−29] In contrast, only a few NHC-catalyzed organocatalytic transformations taking advantage of NHC·CO_2 precatalysts have been described so far. Known examples include transesterification reactions,[30−32] the cyclotrimerization of isocyanates,[33] the benzoin condensation,[31,32] the cyanosilylation of carbonyl compounds,[32] and some related polymerization reactions.[32,34,35] In 2012, it was also demonstrated that imidazol(in)ium hydrogen carbonates behaved as alternate sources of NHCs upon formal loss of H_2CO_3.[32,36]

Received: January 21, 2014
Published: February 25, 2014

dx.doi.org/10.1021/jo500108a | J. Org. Chem. 2014, 79, 2758−2764

Scheme 1. NHC-Catalyzed Michael Additions[a]



[a]Abbreviations: Dipp, 2,6-(iPr)$_2$-C$_6$H$_3$; Mes, 2,4,6-(Me)$_3$-C$_6$H$_2$; Cy, cyclohexyl; EWG, electron-withdrawing group; KHMDS, potassium hexamethyldisilazide.

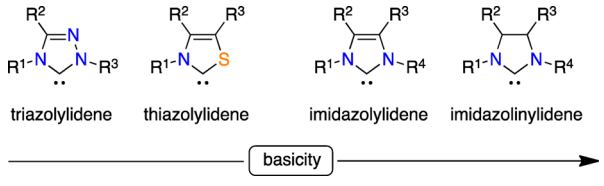


Figure 1. The four common classes of NHCs and their relative Brønsted basicities.

The present study was initiated with the assessment of the organocatalytic activities of five representative NHC·CO$_2$ adducts in model carba-Michael additions (Table 1). It was shown earlier that the reversible decomposition of NHC·CO$_2$ adducts into the corresponding NHCs and carbon dioxide was relatively rapid in polar aprotic solvents,[28] and a brief screening of solvents allowed us to identify THF as a suitable and convenient medium for the studied transformations. Notably,

Scheme 2. NHC·CO$_2$ Adducts Used in This Study

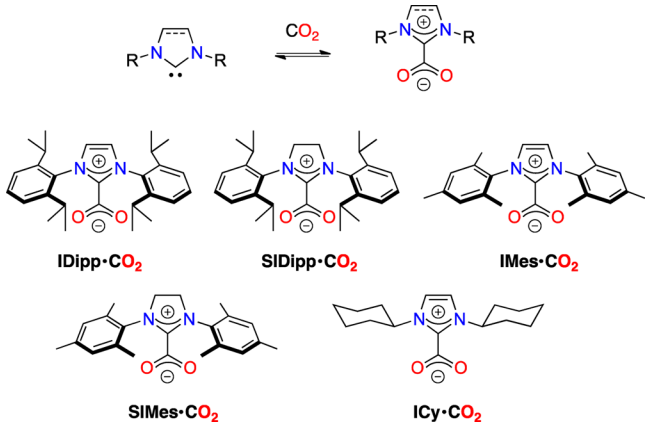
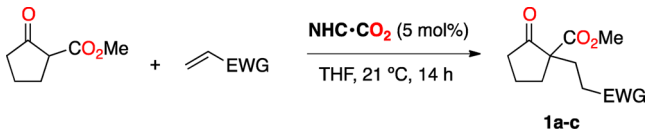


Table 1. NHC-Catalyzed Michael Additions with NHC·CO$_2$ Precatalysts[a]



entry	EWG	NHC·CO$_2$	product	yield (%)[b]
1	CO$_2$Me		**1a**	≤1
2	CO$_2$Me	**IDipp·CO$_2$**	**1a**	80
3	CO$_2$Me	**SIDipp·CO$_2$**	**1a**	47
4	CO$_2$Me	**IMes·CO$_2$**	**1a**	64
5	CO$_2$Me	**SIMes·CO$_2$**	**1a**	6
6	CO$_2$Me	**ICy·CO$_2$**	**1a**	100
7	SO$_2$Ph	**IDipp·CO$_2$**	**1b**	88
8	SO$_2$Ph	**ICy·CO$_2$**	**1b**	93
9	CN	**IDipp·CO$_2$**	**1c**	21
10	CN	**ICy·CO$_2$**	**1c**	88

[a]Reaction conditions: methyl 2-oxocyclopentanecarboxylate (0.25 mmol), electrophile (0.30 mmol), NHC·CO$_2$ (5 mol %), anhydrous THF (2.5 mL), 14 h at 21 °C. [b]Determined by ^{1}H NMR analysis (single-scan experiments) with naphthalene as internal standard.

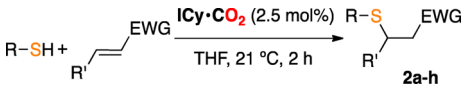
and in sharp contrast with previous results obtained for Michael additions catalyzed by free NHCs,[18] a test reaction in dichloromethane with **IDipp·CO$_2$** (2.5 mol %) failed to afford the Michael adduct **1a** after 12 h at room temperature (no reaction), reflecting the greater stability of the carboxylate precatalyst in this solvent. A control experiment also confirmed that the reaction did not proceed in the absence of any catalyst (Table 1, entry 1). Further investigations showed that imidazolylidene·CO$_2$ adducts were better promoters of the Michael addition than the corresponding imidazolinylidene·CO$_2$ adducts (compare entry 2 with 3, and 4 with 5) and that the *N*,*N*′-dialkyl NHC·CO$_2$ adduct **ICy·CO$_2$** was more efficient than the *N*,*N*′-diaryl derivatives (compare entry 6 with entries 2−5, entry 8 with entry 7, and entry 10 with entry 9). Previous work had established that isolated imidazolylidenes were better catalysts for the Michael addition than the corresponding saturated NHCs (imidazolinylidenes)[17,18] and that imidazolylidene·CO$_2$ adducts were less stable, and thus more prone to release the free carbenes, than the corresponding imidazolinylidene·CO$_2$ adducts.[25,28] Results in Table 1 (entries 2−5) are fully consistent with these earlier findings. In addition, it was also reported that *N*,*N*′-dialkylimidazol(in)ylidenes were better Brønsted bases than *N*,*N*′-diarylimidazol(in)ylidenes.[15] Hence,

dx.doi.org/10.1021/jo500108a | J. Org. Chem. 2014, 79, 2758−2764

the superior catalytic activity of the NHC derived from **ICy·CO$_2$** in the Michael addition (entries 6, 8, and 10) was attributed to the enhanced basicity of **ICy** in comparison to the other NHCs under investigation. For the sake of comparison, a mixture of 1,3-dicyclohexylimidazolium tetrafluoroborate and potassium hexamethyldisilazide was also employed to generate the NHC **ICy** (5 mol %). This system afforded product **1a** quantitatively, as did **ICy·CO$_2$** under similar conditions (Table 1, entry 6). No attempt was made to perform the reaction with the free carbene **ICy**, because this NHC is particularly difficult to isolate in pure form.[37] Overall, these results demonstrate that NHC·CO$_2$ adducts are indeed good precatalysts for NHC-catalyzed Michael additions and **ICy·CO$_2$** was singled out as the most potent one among the five representative zwitterions investigated. The advantages of using an NHC·CO$_2$ adduct instead of an azolium salt precatalyst or an isolated free carbene are essentially practical: the carboxylate inner salts can be easily prepared on a 10 g scale, stored for extended periods of time, and used directly without additives when needed. With an azolium salt precatalyst, the corresponding NHC must be generated by in situ deprotonation, which is particularly inconvenient when a base-free or salt-free reaction medium is required, while the free carbenes are usually much more sensitive to oxygen and moisture and require stringent conditions.

Next, the attention was turned to the NHC-catalyzed sulfa-Michael addition using **ICy·CO$_2$** as the precatalyst in THF (Table 2). In these experiments, thiophenol served as a model

Table 2. NHC-Catalyzed Sulfa-Michael Additions with the ICy·CO$_2$ Precatalyst[a]



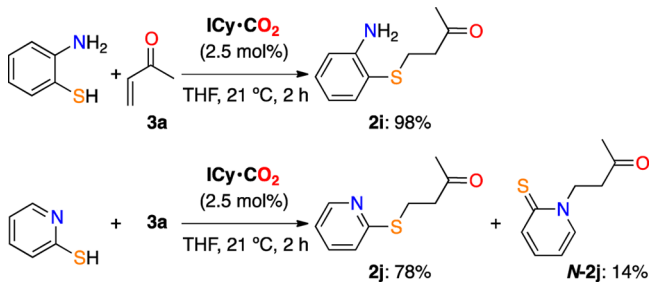
2a-h

entry	R	R'	EWG	product	yield (%)[b]
1[c]	Ph	H	CO_2tBu	**2a**	≤1[d]
2	Ph	H	CO_2tBu	**2a**	90
3	Ph	H	CN	**2b**	99[e]
4	Ph	H	SO_2Ph	**2c**	90
5[f]	Ph	H	$CONH_2$	**2d**	78
6	Ph	H	COMe	**2e**	98
7[g]	Ph	Ph	COPh	**2f**	99
8	2-naphthyl	H	COMe	**2g**	99
9	allyl	H	COMe	**2h**	93

[a]Reaction conditions: thiol (0.25 mmol), electrophile (0.30 mmol), **ICy·CO$_2$** (2.5 mol %, except for entries 1, 5, and 7), anhydrous THF (2.5 mL), 2 h at 21 °C. [b]After silica gel chromatography (except for entry 1). [c]Reaction performed without precatalyst. [d]Based on ^{1}H NMR analysis of the crude reaction mixture. [e]A gram-scale reaction afforded product **2b** in 96% yield. [f]Reaction performed with 10 mol % of **ICy·CO$_2$**. [g]Reaction performed with 5 mol % of **ICy·CO$_2$**.

nucleophile, whose reaction was investigated with a variety of electrophiles (entries 1−7). A blank test performed without any precatalyst confirmed that the uncatalyzed reaction did not occur (or proceeded very slowly) under the experimental conditions adopted (entry 1). In the presence of a catalytic amount of **ICy·CO$_2$**, however, generally high yields of the sulfa-Michael adducts **2a−f** were obtained under the standard conditions used throughout this study (21 °C, 2 h) with α,β-unsaturated ester, nitrile, sulfone, amide, and ketone derivatives. Reactions with naphthalene-2-thiol and propene-1-thiol also provided the corresponding sulfa-Michael adducts **2g,h** in high yields (entries 8 and 9, respectively). To demonstrate the scalability of the process, a gram-scale synthesis of product **2b** was carried out starting from thiophenol (10 mmol) and acrylonitrile (12 mmol) in the presence of ICy·CO$_2$ (2.5 mol %). With no other modification to the procedure outlined above than the substrate concentration (1 M instead of 0.1 M), 3-(phenylsulfanyl)propanenitrile was isolated in 96% yield after chromatographic purification. Also particularly worth noting are the reactions of 2-aminobenzenethiol and pyridine-2-thiol with methyl vinyl ketone (**3a**), which chemoselectively afforded the corresponding sulfa-Michael adducts **2i,j** in 98% and 78% yields, respectively (Scheme 3). In the latter case, however, a

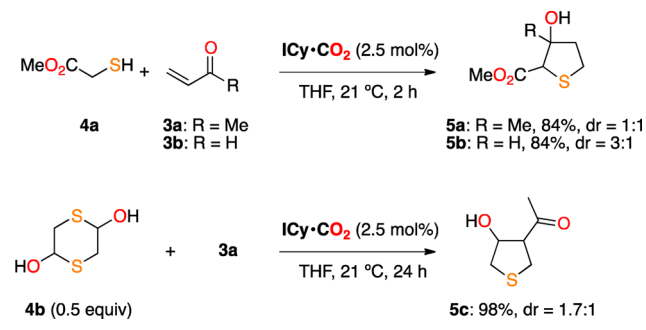
Scheme 3. *S/N* Chemoselectivity in NHC-Catalyzed Hetero-Michael Additions



minor amount (ca. 15%) of the aza-Michael addition product ***N*-2j** was produced. It was shown previously that the NHC-catalyzed hetero-Michael addition of 2-aminoethanol to an α,β-unsaturated ketone led only to the aza-Michael addition product.[20] Thus, the chemoselectivity of NHC-catalyzed hetero-Michael additions follows the order RSH > RNH$_2$ > ROH.

Some sulfa-Michael/aldol organocascades were previously reported under aminocatalytic conditions.[38] Hence, with an efficient catalytic system at hand for the sulfa-Michael addition, NHC-catalyzed sulfa-Michael-initiated organocascades were investigated. The reaction of methyl 2-mercaptoacetate (**4a**) with methyl vinyl ketone (**3a**) or acrolein (**3b**) in the presence of **ICy·CO$_2$** (2.5 mol %) in THF gave the expected tetrahydrothiophenes **5a,b** in good yields, albeit with a poor diastereoselectivity (Scheme 4). Another type of sulfa-Michael/aldol organocascade also proved possible using 1,4-dithiane-2,5-diol (**4b**), a dimeric surrogate of 2-mercaptoacetaldehyde, in combination with methyl vinyl ketone (**3a**). In the presence of **ICy·CO$_2$** (2.5 mol %) in THF, the corresponding tetrahy-

Scheme 4. NHC-Catalyzed Sulfa-Michael/Aldol Organocascades with the ICy·CO$_2$ Precatalyst

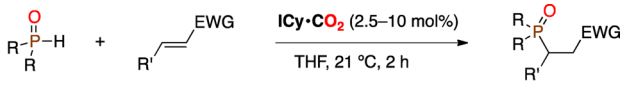


dx.doi.org/10.1021/jo500108a | J. Org. Chem. 2014, 79, 2758−2764

drothiophene **5c** was isolated in excellent yield, but the diastereoselectivity remained modest (Scheme 4).

The same catalytic system was also applied to the phospha-Michael addition of two prototypical phosphorus-based pronucleophiles, namely diphenylphosphine oxide (**6a**) and diethylphosphonic acid (**6b**). It was recently demonstrated that diphenylphosphine oxide (**6a**) could undergo phospha-Michael additions to terminal and internal activated alkenes upon thermal activation (neat, microwave-assisted heating at ca. 125−200 °C).[39,40] Indeed, the uncatalyzed reaction of **6a** with *tert*-butyl acrylate at 21 °C for 2 h afforded only traces of the corresponding phospha-Michael adduct **7a** (Table 3, entry 1).

Table 3. NHC-Catalyzed Phospha-Michael Additions with the ICy·CO_2 Precatalyst[a]



6a: R = Ph
6b: R = OEt

7a-f: R = Ph
8a-e: R = OEt

entry	R	R'	EWG	ICy·CO_2 (mol %)	product	yield (%)[b]
1	Ph	H	CO_2tBu	0	**7a**	≤2[c]
2	Ph	H	CO_2tBu	10	**7a**	76
3	Ph	H	CN	5	**7b**	82
4	Ph	H	SO_2Ph	5	**7c**	84
5	Ph	H	$CONH_2$	10	**7d**	0[c]
6	Ph	H	COMe	5	**7e**	81
7	Ph	Ph	COPh	10	**7f**	75
8	OEt	H	CO_2tBu	0	**8a**	0[c]
9	OEt	H	CO_2tBu	2.5	**8a**	99
10	OEt	H	CN	2.5	**8b**	99
11	OEt	H	SO_2Ph	2.5	**8c**	97
12	OEt	H	$CONH_2$	10	**8d**	0[c]
13	OEt	H	COMe	2.5	**8e**	98

[a]Reaction conditions: diphenylphosphine oxide (**6a**) or diethylphosphonic acid (**6b**, 0.25 mmol), electrophile (0.30 mmol), **ICy·CO_2** (2.5 mol %), anhydrous THF (2.5 mL), 2 h at 21 °C. [b]After silica gel chromatography (except for entries 1, 5, 8, and 12). [c]Based on ^{1}H NMR analysis of the crude reaction mixture.

Gratifyingly, the same reaction performed in the presence of a catalytic amount of **ICy·CO_2** (10 mol %) afforded product **7a** in 76% yield (entry 2). The screening of other representative electrophiles in the presence of 5−10 mol % of **ICy·CO_2** helped define the scope of the reaction. Thus, activation of the alkene with a cyanide (entry 3), a sulfone (entry 4), or a ketone moiety (entries 6 and 7) were successful, but the reaction with acrylamide, a generally poor electrophile for (hetero)Michael addition reactions, failed to afford the desired product **7d** (entry 5). With **6b** as the pronucleophile, the reactions with the same representative electrophilic alkenes were found to be even more efficient than with **6a**, requiring only 2.5 mol % of the precatalyst to obtain nearly quantitative yields of the isolated phospha-Michael adducts **8a−c,e** after 2 h at 21 °C (entries 9−11 and 13, respectively). Again, acrylamide was found to be inert under these experimental conditions (entry 12).

In summary, the scope of NHC-catalyzed Michael additions has been extended to their sulfa and phospha analogues, which nicely complements the organocatalytic applications of NHCs involving a Brønsted base activation mode. The simplicity and efficiency of the method makes it an attractive alternative to known procedures for sulfa-[21] and phospha-Michael[22,23] additions. Additionally, some NHC-catalyzed sulfa-Michael-initiated organocascades were also carried out. Importantly, it was demonstrated that zwitterionic imidazolium carboxylates, the so-called NHC·CO_2 adducts, are excellent and very convenient sources of the corresponding free NHCs in solution for NHC-catalyzed Michael additions. The main advantages of using NHC·CO_2 adducts are that they can be easily prepared on a multigram scale and stored for extended periods of time, they can be handled and weighed in the air, and most importantly, they do not require the use of an external strong base or any additive to generate the corresponding NHCs. This last feature proved critical in the present study because, unlike the NHC **IDipp** used in the early NHC-catalyzed Michael additions (see Scheme 1), its **ICy** congener, which was found most efficient at promoting the (hetero)Michael additions detailed herein, is difficult to isolate in pure form and is usually generated in situ by deprotonation of an imidazolium salt. From a broader perspective, it is our belief that NHC·CO_2 adducts will soon be recognized as attractive precatalysts for the development of organocatalysis with NHCs.

EXPERIMENTAL SECTION

General Information. Reactions were performed under an air atmosphere using 10 mL tubular oven-dried reaction vessels equipped with a Teflon-coated magnetic stirring bar and capped with a rubber septum. Imidazol(in)ium-2-carboxylates were prepared according to the literature.[28] All other reagents were obtained from commercial sources and were used as supplied unless otherwise specified. Anhydrous THF was obtained from a solvent purification system. Thiophenol and 2-propene-1-thiol were dried over $CaCl_2$ and distilled prior to use. All acrylic acid derivatives were filtered through a short pad of silica gel prior to use, except phenyl vinyl sulfone, acrylamide, and *trans*-chalcone. All reagents and precatalysts were weighed and handled in air at room temperature. The reactions were monitored by TLC visualized by UV (254 nm) and/or with *p*-anisaldehyde/H_2SO_4 in EtOH and/or molybdophosphoric acid in EtOH. Column chromatography was performed with silica gel. Petroleum ether refers to the fraction distilled at 40−60 °C. ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra were recorded at 298 K in $CDCl_3$ or CD_2Cl_2, using either tetramethylsilane (δ 0.00 ppm) or the residual nondeuterated solvent signal for ^{1}H NMR (δ 7.26 ppm for $CHCl_3$ and δ 5.32 for CD_2Cl_2) and the deuterated solvent signal for ^{13}C NMR (δ 77.16 ppm for $CHCl_3$ and δ 53.84 for CD_2Cl_2) as internal standards or H_3PO_4 (δ 0.00 ppm) as external reference for ^{31}P NMR. Coupling constants (J) are given in hertz, and the classical abbreviations are used to describe the signal multiplicity. For ^{13}C{^{1}H} NMR experiments, the signal multiplicity with hydrogen atoms (C, CH or CH_3, CH_2) was determined by DEPT-135 experiments.

General Procedure for Carba-Michael Additions (Table 1). The reaction vessel was charged with the NHC·CO_2 adduct (0.0126 mmol, 5 mol %; see Table 1) and naphthalene (0.25 mmol, 32 mg). Anhydrous THF (2.5 mL), methyl 2-oxocyclopentanecarboxylate (0.25 mmol, 31 μL), and the acrylic acid derivative (0.30 mmol) were then added in that order. The reaction mixture was stirred at 21 °C for 14 h and concentrated under vacuum, and the resulting material was directly analyzed by NMR spectroscopy (in $CDCl_3$). The yield of Michael addition products **1a−c** was determined by comparing the integrals of the product resonances (single-scan experiments) with those of naphthalene (7.63 and 7.26 ppm). The NMR data recorded for products **1a−c** were identical with previously reported data.[18]

Control Experiment with an Imidazolium Precatalyst. An NMR tube was charged with ICy·HBF_4 (0.005 mmol, 1.6 mg), potassium bis(trimethylsilyl)amide (0.005 mmol, 1.0 mg), and naphthalene (0.10 mmol, 12.8 mg) as an internal standard. Anhydrous deuterated THF (1 mL) was added, and the mixture was shaken at 21 °C for 5 min. Methyl 2-oxocyclopentanecarboxylate (0.10 mmol, 12.4 μL) and methyl acrylate (0.12 mmol, 10.8 μL) were then added in that order. The NMR tube was shaken periodically. After 14 h, the ^{1}H

dx.doi.org/10.1021/jo500108a | J. Org. Chem. 2014, 79, 2758−2764

NMR analysis of the reaction mixture indicated full conversion (no more starting material) and a quantitative yield of **1a** by comparing the integrals of the product resonances with those of naphthalene.

General Procedure for Sulfa-Michael Additions (Table 2 and Scheme 3). The reaction vessel was charged with **ICy·CO$_2$** (0.0063 mmol, 2.5 mol %, 1.7 mg). Anhydrous THF (2.5 mL), the thiol (0.25 mmol), and the acrylic acid derivative (0.30 mmol) were then added in that order. The reaction mixture was stirred at 21 °C for 2 h and concentrated under vacuum, and the resulting material was directly purified by silica gel chromatography with petroleum ether/EtOAc (7/3 v/v) as eluent to afford the pure products **2a**–**j**.

*tert-Butyl 3-(Phenylsulfanyl)propanoate (**2a**).* Colorless oil (54 mg, 90%) obtained from thiophenol (26 μL) and *tert*-butyl acrylate (44 μL). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.28–7.08 (m, 5H), 3.04 (t, *J* = 7.4 Hz, 2H), 2.44 (t, *J* = 7.4 Hz, 2H), 1.36 (s, 9H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 171.1 (C), 135.7 (C), 130.0 (CH or CH_3), 129.1 (CH or CH_3), 126.5 (CH or CH_3), 81.0 (C), 35.6 (CH_2), 29.3 (CH_2), 28.2 (CH or CH_3). These NMR data matched previously reported data.[41]

*3-(Phenylsulfanyl)propanenitrile (**2b**).* Colorless oil (41 mg, 99%) obtained from thiophenol (26 μL) and acrylonitrile (20 μL). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.35–7.18 (m, 5H), 3.03 (t, *J* = 7.3 Hz, 2H), 2.50 (t, *J* = 7.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 133.3 (C), 131.5 (CH or CH_3), 129.4 (CH or CH_3), 127.8 (CH or CH_3), 118.0 (C), 30.3 (CH_2), 18.3 (CH_2). These NMR data matched previously reported data.[42] A gram-scale experiment was also performed as follows: a 50 mL oven-dried round-bottom flask was charged with **ICy·CO$_2$** (0.25 mmol, 69 mg), anhydrous THF (10 mL), thiophenol (10.0 mmol, 1.03 mL), and acrylonitrile (12 mmol, 0.79 mL), in that order. The reaction mixture was stirred at 21 °C for 2 h and concentrated under vacuum, and the resulting material was directly purified by silica gel chromatography with petroleum ether/EtOAc (7/3 v/v) as eluent to afford the pure product **2b** (1.57 g, 96%).

*2-(Phenylsulfanyl)ethyl Phenyl Sulfone (**2c**).* White solid (62 mg, 90%) obtained from thiophenol (26 μL) and phenyl vinyl sulfone (50 mg). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.78 (m, 2H), 7.57 (m, 1H), 7.47 (m, 2H), 7.20–7.10 (m, 5H), 3.25–3.16 (m, 2H), 3.13–3.04 (m, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 138.7 (C), 134.1 (CH or CH_3), 133.5 (C), 130.2 (CH or CH_3), 129.5 (CH or CH_3), 129.4 (CH or CH_3), 128.1 (CH or CH_3), 127.3 (CH or CH_3), 55.7 (CH_2), 26.5 (CH_2). These NMR data matched previously reported data.[43]

*3-(Phenylsulfanyl)propanamide (**2d**).* White solid (35 mg, 78%) obtained from thiophenol (26 μL) and acrylamide (17.8 mg) using 10 mol % of catalyst (6.8 mg, 0.0252 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.37–7.34 (m, 2H), 7.31–7.26 (m, 2H), 7.22–7.17 (m, 1H), 5.75 (br s, 2H), 3.19 (t, *J* = 7.3 Hz, 2H), 2.51 (t, *J* = 7.3 Hz, 2H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 173.2 (C), 135.2 (C), 129.9 (CH or CH_3), 129.3 (CH or CH_3), 126.7 (CH or CH_3), 35.5 (CH_2), 29.4 (CH_2). These NMR data matched previously reported data.[42]

*4-(Phenylsulfanyl)butan-2-one (**2e**).* Colorless oil (44 mg, 98%) obtained from thiophenol (26 μL) and methyl vinyl ketone (**3a**, 24 μL). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.36–7.27 (m, 4H), 7.22–7.17 (m, 1H), 3.14 (t, *J* = 7.3 Hz, 2H), 2.76 (t, *J* = 7.3 Hz, 2H), 2.14 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 206.6 (C), 135.8 (C), 129.6 (CH or CH_3), 129.1 (CH or CH_3), 126.4 (CH or CH_3), 43.1 (CH_2), 30.1 (CH or CH_3), 27.5 (CH_2). These NMR data matched previously reported data.[44]

*1,3-Diphenyl-3-(phenylsulfanyl)propan-1-one (**2f**).* White solid (79 mg, 99%) obtained from thiophenol (26 μL) and *trans*-chalcone (52 mg) using 5 mol % of catalyst (3.4 mg, 0.0126 mmol). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.87–7.84 (m, 2H), 7.53–7.48 (m, 1H), 7.42–7.31 (m, 6H), 7.26–7.14 (m, 6H), 4.96 (dd, *J* = 6.4 Hz, *J* = 7.8 Hz, 1H), 3.65 (dd, *J* = 17.2 Hz, *J* = 7.8 Hz, 1H), 3.56 (dd, *J* = 17.2 Hz, *J* = 6.4 Hz, 1H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 197.0 (C), 141.3 (C), 136.8 (C), 134.3 (C), 133.3 (CH or CH_3), 132.8 (2 CH or CH_3), 128.9 (2 CH or CH_3), 128.7 (2 CH or CH_3), 128.5 (2 CH or CH_3), 128.1 (2 CH or CH_3), 127.9 (2 CH or CH_3), 127.6 (CH or CH_3), 127.4 (CH or CH_3), 48.3 (CH_2), 44.8 (CH or CH_3). These NMR data matched previously reported data.[42]

*4-(Naphthylsulfanyl)butan-2-one (**2g**).* Off-white solid (57 mg, 99%) obtained from naphthalene-2-thiol (40 mg) and methyl vinyl ketone (**3a**, 24 μL). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.81–7.74 (m, 4H), 7.51–7.41 (m, 3H), 3.24 (t, *J* = 7.3 Hz, 2H), 2.79 (t, *J* = 7.3 Hz, 2H), 2.13 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 206.6 (C), 133.8 (C), 133.3 (C), 131.9 (C), 128.6 (CH or CH_3), 127.8 (CH or CH_3), 127.5 (CH or CH_3), 127.3 (CH or CH_3), 127.1 (CH or CH_3), 126.7 (CH or CH_3), 125.9 (CH or CH_3), 43.1 (CH_2), 30.1 (CH or CH_3), 27.3 (CH_2). These NMR data matched previously reported data.[45]

*4-(Allylsulfanyl)butan-2-one (**2h**).* Colorless oil (34 mg, 93%) obtained from 2-propene-1-thiol (21 μL) and methyl vinyl ketone (**3a**, 24 μL). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 5.82–5.72 (m, 1H), 5.13–5.07 (m, 2H), 3.13 (d, *J* = 7.1 Hz, 2H), 2.68 (m, 4H), 2.15 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): δ 206.9 (C), 134.4 (CH or CH_3), 117.3 (CH_2), 43.6 (CH_2), 35.2 (CH_2), 30.2 (CH or CH_3), 24.6 (CH_2). These NMR data matched previously reported data.[46]

*4-(2-Aminophenylsulfanyl)butan-2-one (**2i**).* Light yellow oil (48 mg, 98%) obtained from 2-aminothiophenol (27 μL) and methyl vinyl ketone (**3a**, 24 μL). ^{1}H NMR (300 MHz, CD_2Cl_2, ppm): δ 7.35 (m, 1H), 7.12 (m, 1H), 6.74–6.64 (m, 2H), 4.44 (br s, 2H), 2.92 (t, *J* = 7.0 Hz, 2H), 2.66 (t, *J* = 7.0 Hz, 2H), 2.09 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, CD_2Cl_2, ppm): δ 207.1 (C), 149.4 (C), 136.6 (CH or CH_3), 130.5 (CH or CH_3), 118.7 (CH or CH_3), 117.3 (C), 115.3 (CH or CH_3), 43.6 (CH_2), 30.3 (CH or CH_3), 28.8 (CH_2). HRMS (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_{10}H_{14}NOS^+$ 196.0791, obsd 196.0791.

*4-(2-Pyridinesulfanyl)butan-2-one (**2j**) and 4-(2-Thiopyridinyl)-butan-2-one (**N-2j**).* Yellow oil (42 mg, 92%) obtained from pyridine-2-thiol (28 mg) and methyl vinyl ketone (**3a**, 24 μL) containing a 5.7:1 mixture of **2j** and ***N*-2j** that could not be separated by silica gel chromatography. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): major isomer (**2j**), δ 8.37 (m, 1H), 7.43 (m, 1H), 7.11 (m, 1H), 6.94 (m, 1H), 3.34 (t, *J* = 7.0 Hz, 2H), 2.88 (t, *J* = 7.0 Hz, 2H), 2.13 (s, 3H); minor isomer (***N*-2j**), δ 7.90 (m, 1H), 7.61 (m, 1H), 7.13 (m, 1H), 6.59 (m, 1H), 4.67 (t, *J* = 5.8 Hz, 2H), 3.22 (t, *J* = 5.8 Hz, 2H), 2.11 (s, 3H). $^{13}C\{^1H\}$ NMR (75 MHz, $CDCl_3$, ppm): major isomer (**2j**), δ 207.1 (C), 158.6 (C), 149.5 (CH or CH_3), 135.9 (CH or CH_3), 122.4 (CH or CH_3), 119.4 (CH or CH_3), 43.8 (CH_2), 30.1 (CH or CH_3), 23.7 (CH_2); minor isomer (***N*-2j**), δ 206.4 (C), 179.6 (C), 142.4 (CH or CH_3), 136.4 (CH or CH_3), 134.2 (CH or CH_3), 113.2 (CH or CH_3), 52.0 (CH_2), 40.8 (CH_2), 30.4 (CH or CH_3). HRMS (ESI+): *m*/*z* $[M + H]^+$ calcd for $C_9H_{12}NOS^+$ 182.0634, obsd 182.0634.

General Procedure for Sulfa-Michael/Aldol Organocascades (Scheme 4). The reaction vessel was charged with **ICy·CO$_2$** (1.7 mg, 0.0063 mmol). Anhydrous THF (2.5 mL), methyl 2-mercaptoacetate (**4a**, 22 μL, 0.25 mmol) or 1,4-dithiane-2,5-diol (**4b**, 18.9 mg, 0.125 mmol), and methyl vinyl ketone (**3a**, 24 μL, 0.30 mmol) or acrolein (**3b**, 20 μL, 0.30 mmol) were then added in that order. The reaction mixture was stirred at 21 °C for 2 h (with **4a**) or 24 h (with **4b**). After concentration under vacuum, the resulting material was purified by filtration through a pad of silica gel with CH_2Cl_2/EtOAc (1/1 v/v) as eluent to afford the pure compounds **5a**–**c** as mixtures of diastereomers.

*Methyl 3-Hydroxy-3-methyltetrahydrothiophene-2-carboxylate (**5a**).* Pale yellow oil (37 mg, 84%) obtained from methyl 2-mercaptoacetate (**4a**, 22 μL) and methyl vinyl ketone (**3a**, 24 μL) as a 1/1 mixture of diastereomers. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 3.81 (s, 1H), 3.74 (s, 3H), 3.70 (s, 3H), 3.68 (s, 1H), 3.17–3.09 (m, 1H), 3.06–3.00 (m, 2H), 2.86–2.79 (m, 1H), 2.37–2.25 (m, 2H), 2.10–2.02 (m, 1H), 1.94–1.85 (m, 1H), 1.45 (s, 3H), 1.41 (s, 3H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 173.2 (C), 172.9 (C), 82.9 (C), 81.0 (C), 59.0 (CH or CH_3), 54.2 (CH or CH_3), 52.6 (CH or CH_3), 52.4 (CH or CH_3), 43.3 (CH_2), 41.4 (CH_2), 29.2 (CH_2), 28.9 (CH_2), 25.4 (CH or CH_3), 22.1 (CH or CH_3). HRMS (ESI+): *m*/*z* $[M + Li]^+$ calcd for $C_7H_{12}O_3SLi^+$ 183.0662, obsd 183.0661. See the Supporting Information for NMR spectra.

*Methyl 3-Hydroxytetrahydrothiophene-2-carboxylate (**5b**).* Pale yellow oil (34 mg, 84%) obtained from methyl 2-mercaptoacetate (**4a**,

dx.doi.org/10.1021/jo500108a | J. Org. Chem. 2014, 79, 2758–2764

22 μL) and acrolein (**3b**, 20 μL) as a 3/1 mixture of diastereomers. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): major diastereomer, δ 4.60 (m, 1H), 3.98 (d, *J* = 4.4 Hz, 1H), 3.76 (s, 3H), 3.20−3.10 (m, 1H), 2.98−2.90 (m, 1H), 2.36−2.26 (m, 1H), 2.06−1.94 (m, 1H); minor diastereomer, δ 4.68 (m, 1H), 3.82 (d, *J* = 3.4 Hz, 1H), 3.71 (s, 3H), 3.25−3.15 (m, 1H), 2.95−2.86 (m, 1H), 2.33−2.23 (m, 1H), 2.02−1.92 (m, 1H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): major diastereomer, δ 172.8 (C), 75.0 (CH or CH_3), 52.7 (CH or CH_3), 51.1 (CH or CH_3), 37.0 (CH_2), 29.2 (CH_2); minor diastereomer, δ 172.7 (C), 76.7 (CH or CH_3), 54.5 (CH or CH_3), 52.6 (CH or CH_3), 37.3 (CH_2), 28.8 (CH_2). HRMS (ESI+): *m*/*z* $[M + Li]^+$ calcd for $C_6H_{10}O3SLi^+$ 169.0505, obsd 169.0506.

*3-Acetyl-4-hydroxytetrahydrothiophene (**5c**).* Pale yellow oil (36 mg, 98%) obtained from 1,4-dithiane-2,5-diol (**4b**, 18.9 mg) and methyl vinyl ketone (**3a**, 24 μL) as a 1.7/1 mixture of diastereomers. ^{1}H NMR (250 MHz, $CDCl_3$, ppm): major diastereomer, δ 4.82 (br s, 1H), 3.24−2.71 (m, 6H), 2.27 (s, 3H); minor diastereomer, δ 4.62−4.49 (m, 1H), 3.24−2.71 (m, 6H), 2.23 (s, 3H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): major diastereomer, δ 207.6 (C), 75.0 (CH or CH_3), 60.8 (CH or CH_3), 39.6 (CH_2), 30.3 (CH or CH_3), 28.9 (CH_2); minor diastereomer, δ 207.8 (C), 76.0 (CH or CH_3), 61.0 (CH or CH_3), 37.0 (CH_2), 29.6 (CH or CH_3), 29.1 (CH_2). HRMS (ESI+): *m*/*z* $[M + Li]^+$ calcd for $C_6H_{10}O_2SLi^+$ 153.0556, obsd 153.0555.

General Procedure for Phospha-Michael Additions (Table 3). The reaction vessel was charged with **ICy·CO$_2$** (1.7, 3.4, or 6.8 mg, 0.0063, 0.0126, or 0.0252 mmol, respectively; see Table 3). Anhydrous THF (2.5 mL), diphenylphosphine oxide (**6a**, 50.5 mg, 0.25 mmol) or diethylphosphonic acid (**6b**, 32 μL, 0.25 mmol), and the acrylic acid derivative (0.30 mmol) were then added in that order. The reaction mixture was stirred at 21 °C for 2 h and concentrated under vacuum, and the resulting material was directly purified by silica gel chromatography with CH_2Cl_2/EtOAc (1/1 v/v) as eluent to afford the pure product **7a**−**c**,**e**,**f** from **6a** or with EtOAc to isolate **8a**−**c**,**e** from **6b**.

*tert-Butyl 3-(Diphenylphosphinyl)propanoate (**7a**).* White solid (63 mg, 76%) obtained from diphenylphosphine oxide (**6a**, 50.5 mg) and *tert*-butyl acrylate (44 μL) using **ICy·CO$_2$** (6.8 mg). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.78−7.69 (m, 4H), 7.51−7.45 (m, 6H), 2.62−2.46 (m, 4H), 1.38 (s, 9H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 171.7 (d, *J* = 17.2 Hz, C), 132.6 (d, *J* = 99.4 Hz, C), 132.0 (d, *J* = 2.8 Hz, CH or CH_3), 130.9 (d, *J* = 9.4 Hz, CH or CH_3), 128.8 (d, *J* = 11.7 Hz, CH or CH_3), 81.2 (s, C), 28.1 (s, CH or CH_3), 27.6 (d, *J* = 2.1 Hz, CH_2), 25.1 (d, *J* = 73.1 Hz, CH_2). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 31.52. These NMR data matched previously reported data.[47]

*3-(Diphenylphosphinyl)propanenitrile (**7b**).* White solid (52 mg, 82%) obtained from diphenylphosphine oxide (**6a**, 50.5 mg) and acrylonitrile (20 μL) using **ICy·CO$_2$** (3.4 mg). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.77−7.69 (m, 4H), 7.60−7.46 (m, 6H), 2.73−2.54 (m, 4H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 132.6 (d, *J* = 2.7 Hz, CH or CH_3), 131.1 (d, *J* = 101.3 Hz, C), 130.8 (d, *J* = 9.6 Hz, CH or CH_3), 129.1 (d, *J* = 12.0 Hz, CH or CH_3), 118.6 (d, *J* = 18.3 Hz, C), 26.3 (d, *J* = 70.1 Hz, CH_2), 10.5 (d, *J* = 0.8 Hz, CH_2). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 28.27. These NMR data matched previously reported data.[39]

*2-(Diphenylphosphinyl)ethyl Phenyl Sulfone (**7c**).* White solid (79 mg, 84%) obtained from diphenylphosphine oxide (**6a**, 50.5 mg) and phenyl vinyl sulfone (50 mg) using **ICy·CO$_2$** (3.4 mg). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.87−7.84 (m, 2H), 7.73−7.62 (m, 5H), 7.57−7.44 (m, 8H), 3.33−3.24 (m, 2H), 2.74−2.63 (m, 2H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 138.4 (s, C), 134.2 (s, CH or CH_3), 132.5 (d, *J* = 2.8 Hz, CH or CH_3), 131.4 (d, *J* = 101.9 Hz, C), 130.8 (d, *J* = 9.6 Hz, CH or CH_3), 129.6 (s, CH or CH_3), 129.1 (d, *J* = 12.0 Hz, CH or CH_3), 128.2 (s, CH or CH_3), 49.5 (d, *J* = 2.0 Hz, CH_2), 23.3 (d, *J* = 68.4 Hz, CH_2). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 28.05. HRMS (ESI+): *m*/*z* $[M + Li]^+$ calcd for $C_{20}H_{19}O_3PSLi^+$ 377.0947, obsd 377.0944.

*4-(Diphenylphosphinyl)butan-2-one (**7e**).* Colorless oil (55 mg, 81%) obtained from diphenylphosphine oxide (**6a**, 50.5 mg) and methyl vinyl ketone (**3a**, 24 μL) using **ICy·CO$_2$** (3.4 mg). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.74−7.67 (m, 4H), 7.50−7.41 (m, 6H), 2.79−2.69 (m, 2H), 2.56−2.46 (m, 2H), 2.08 (s, 3H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 206.2 (d, *J* = 13.4 Hz, C), 132.4 (d, *J* = 100.0 Hz, C), 132.1 (d, *J* = 2.7 Hz, CH or CH_3), 130.8 (d, *J* = 9.4 Hz, CH or CH_3), 128.8 (d, *J* = 11.7 Hz, CH or CH_3), 35.3 (d, *J* = 2.4 Hz, CH_2), 29.8 (s, CH or CH_3), 23.3 (d, *J* = 73.7 Hz, CH_2). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 31.55. These NMR data matched previously reported data.[39]

*1,3-Diphenyl-3-(diphenylphosphinyl)propan-1-one (**7f**).* White solid (67 mg, 65%) obtained from diphenylphosphine oxide (**6a**, 50.5 mg) and *trans*-chalcone (52.1 mg) using **ICy·CO$_2$** (6.8 mg). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 8.03−7.94 (m, 2H), 7.85−7.82 (m, 2H), 7.54−7.27 (m, 10H), 7.26−7.09 (m, 6H), 4.51−4.43 (m, 1H), 4.08−3.95 (m, 1H), 3.45−3.32 (m, 1H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 196.8 (d, *J* = 13.3 Hz, C), 136.5 (d, *J* = 0.6 Hz, C), 136.1 (d, *J* = 5.6 Hz, C), 133.5 (s, CH or CH_3), 132.1 (d, *J* = 2.7 Hz, CH or CH_3), 131.6 (d, *J* = 94.4 Hz, C), 131.55 (s, CH or CH_3), 131.5 (s, CH or CH_3), 131.4 (s, CH or CH_3), 131.1 (d, *J* = 8.9 Hz, CH or CH_3), 130.0 (d, *J* = 5.7 Hz, CH or CH_3), 129.1 (d, *J* = 11.2 Hz, CH or CH_3), 128.7 (s, CH or CH_3), 128.4 (s, CH or CH_3), 128.3 (s, CH or CH_3), 128.2 (s, CH or CH_3), 128.1 (s, CH or CH_3), 127.2 (d, *J* = 2.4 Hz, CH or CH_3), 41.2 (d, *J* = 69.1 Hz, CH or CH_3), 39.2 (s, CH_2). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 34.27. These NMR data matched previously reported data.[48]

*tert-Butyl 3-(Diethoxyphosphinyl)propanoate (**8a**).* Colorless oil (66 mg, 99%) obtained from diethylphosphonic acid (**6b**, 32 μL) and *tert*-butyl acrylate (44 μL) using **ICy·CO$_2$** (1.7 mg). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 4.04 (m, 4H), 2.45 (m, 2H), 1.97 (m, 2H), 1.39 (s, 9H), 1.27 (t, *J* = 7.0 Hz, 6H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 171.3 (d, *J* = 18.9 Hz, C), 81.0 (s, C), 61.7 (d, *J* = 6.4 Hz, CH_2), 28.7 (d, *J* = 3.8 Hz, CH_2), 28.1 (s, CH or CH_3), 21.1 (d, *J* = 144.3 Hz, CH_2), 16.5 (d, *J* = 6.0 Hz, CH or CH_3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 31.16. These NMR data matched previously reported data.[49]

*3-(Diethoxyphosphinyl)propanenitrile (**8b**).* Colorless oil (47.3 mg, 99%) obtained from diethylphosphonic acid (**6b**, 32 μL) and acrylonitrile (20 μL). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 4.11 (m, 4H), 2.60 (m, 2H), 2.05 (m, 2H), 1.32 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 118.4 (d, *J* = 17.6 Hz, C), 62.4 (d, *J* = 6.5 Hz, CH_2), 22.2 (d, *J* = 145.9 Hz, CH_2), 16.5 (d, *J* = 5.9 Hz, CH or CH_3), 11.6 (d, *J* = 4.0 Hz, CH_2). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 25.90. These NMR data matched previously reported data.[50]

*2-(Diethoxyphosphinyl)ethyl Phenyl Sulfone (**8c**).* White solid (74 mg, 97%) obtained from diethylphosphonic acid (**6b**, 32 μL) and phenyl vinyl sulfone (50 mg). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 7.86 (m, 2H), 7.69−7.53 (m, 3H), 4.05 (m, 4H), 3.26 (m, 2H), 2.10 (m, 2H), 1.26 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 138.2 (s, C), 134.2 (s, CH or CH_3), 129.6 (s, CH or CH_3), 128.2 (s, CH or CH_3), 62.4 (d, *J* = 6.6 Hz, CH_2), 50.3 (d, *J* = 3.5 Hz, CH_2), 19.7 (d, *J* = 143.5 Hz, CH_2), 16.4 (d, *J* = 5.9 Hz, CH or CH_3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 26.28. These NMR data matched previously reported data.[51]

*4-(Diethoxyphosphinyl)butan-2-one (**8e**).* Colorless oil (51 mg, 98%) obtained from diethylphosphonic acid (**6b**, 32 μL) and methyl vinyl ketone (**3a**, 24 μL). ^{1}H NMR (250 MHz, $CDCl_3$, ppm): δ 4.13−4.01 (m, 4H), 2.77−2.67 (m, 2H), 2.16 (s, 3H), 2.06−1.91 (m, 2H), 1.30 (t, *J* = 7.1 Hz, 6H). $^{13}C\{^1H\}$ NMR (63 MHz, $CDCl_3$, ppm): δ 205.9 (d, *J* = 15.0 Hz, C), 61.8 (d, *J* = 6.4 Hz, CH_2), 36.5 (d, *J* = 3.8 Hz, CH_2), 29.8 (s, CH or CH_3), 19.5 (d, *J* = 144.7 Hz, CH_2), 16.5 (d, *J* = 6.1 Hz, CH or CH_3). $^{31}P\{^1H\}$ NMR (101.3 MHz, $CDCl_3$, ppm): δ 31.49. These NMR data matched previously reported data.[52]

■ ASSOCIATED CONTENT

Supporting Information

Figures giving ^{1}H and ^{13}C NMR spectra for all compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

dx.doi.org/10.1021/jo500108a | J. Org. Chem. 2014, 79, 2758−2764

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Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Financial support from the European CMST COST Action CM0905 on organocatalysis, the Université de Liège, Aix-Marseille Université, and the Centre National de la Recherche Scientifique (CNRS) is gratefully acknowledged.

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