OL Organic Letters

pubs.acs.org/OrgLett

Letter

Light-Activated CO Donor as a Universal CO Surrogate for Pd-Catalyzed and Light-Mediated Carbonylation

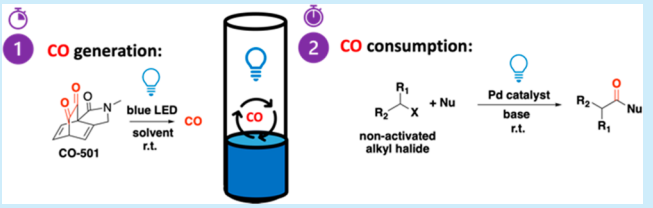
Ladie Kimberly De La Cruz, Nicola Bauer, Alyssa Cachuela, Wing Sze Tam, Ravi Tripathi, Xiaoxiao Yang,* and Binghe Wang*

Cite This: *Org. Lett.* 2022, 24, 4902–4907

Read Online

ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: A low-molecular-weight, solid CO surrogate that only requires a low-power LED for activation to release 2 equiv of CO is reported. The surrogate can be universally implemented in various palladium-catalyzed carbonylative transformations. It is also compatible with protocols that employ blue-light to activate conventionally inaccessible substrates such as nonactivated alkyl halides. Furthermore, we demonstrate that the photolabile CO-releasing scaffold can be installed into polymeric materials, thereby creating new materials with CO-releasing capabilities.



Transition-metal-catalyzed carbonylation, pioneered by Heck and co-workers,[1] is a one-step route to directly introduce molecular complexity in organic synthesis, enabling access to a wide range of carbonyl-containing intermediates.[2] However, the widespread application of carbonylation in small-scale laboratory settings is hindered by the inherent toxicity, storage, and handling issues associated with CO gas tanks. Thus, the development of bench-stable, solid, or liquid reagents to replace the direct use of CO gas is an active research area. CO surrogates developed thus far include a wide array of compounds, ranging from low-molecular-weight compounds such as CO_2,[3] formic acid and its derivatives,[4−7] dimethylformamide,[8] chloroform,[9,10] oxalyl chloride,[11] acyl chlorides,[12] oxalic acid,[13] $Mo(CO)_6$,[14,15] paraformaldehyde, and methanol[16,17] to more complex compounds such as metal carbonyls,[18,19] aldehydes,[20−22] silacarboxylic acids,[23] cyclopropenones,[24] norbornenones,[25] and 9-methyl-fluorene-9-carbonyl chloride,[12,26] among many others. These surrogates have been shown to provide advantages over the use of CO gas. To promote the decarbonylation of the CO surrogates, additional reagents are required. In instances where the condition for CO release is incompatible with the carbonylation chemistry, the spatial separation of the CO surrogate from the carbonylation reaction is necessary. For example, thermal activation or transition-metal-mediated CO release in one vessel is run in parallel with a secondary vessel where carbonylation takes place (Figure 1A). On the other hand, several CO surrogates have been employed in one-pot systems.[27,28] These surrogates have decarbonylation chemistries that can occur concurrently with the carbonylation reaction. For example, phenyl formate is an efficient CO surrogate in one-pot systems that are conducted in the presence of the appropriate base suitable for both decarbonylation and carbonylation.[29,30] Another possible way to achieve

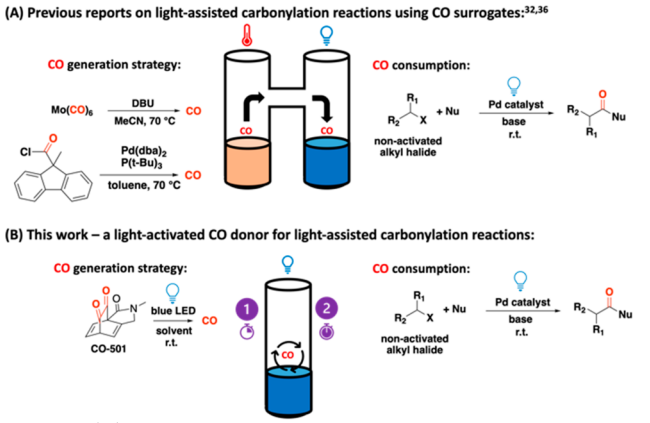


Figure 1. (A) For light-assisted carbonylation reactions using CO surrogates, a two-chamber reaction vessel is needed. (B) A light-activated CO donor simplifies the setup and the protocol.

orthogonal reaction conditions is to use light, instead of other chemicals or heat, to activate the CO surrogate.

Several publications have discussed the inaccessibility of alkyl halides as substrates as one of the challenges in carbonylation.[31−33] One reason for this is the inherently slow oxidative addition step in alkyl halides, coupled with their increased propensity to undergo isomerization via *β*-

Received: May 20, 2022
Published: July 5, 2022

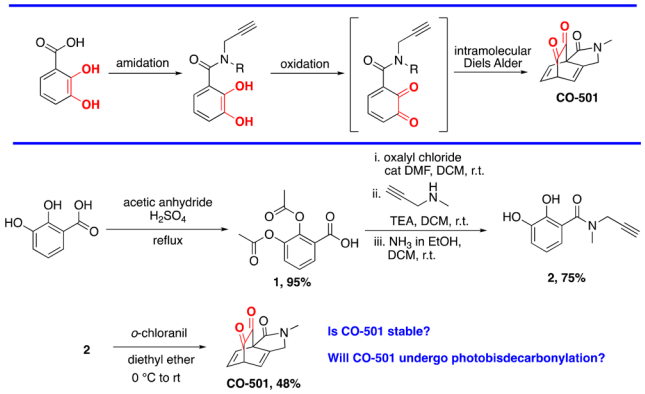
https://doi.org/10.1021/acs.orglett.2c01726
Org. Lett. 2022, 24, 4902−4907

elimination.[34] Recent reports successfully employed light to achieve alternative radical reaction pathways for these challenging substrates.[32,35−37] With the aforementioned challenges in the field, light seems to be a "reagent" that can fulfill two roles by acting as an activator for the release of CO from the surrogate and as a catalyst for nonactivated alkyl halide substrates (Figure 1B).

We describe the design and synthesis of a high-content CO surrogate that utilizes a low-power blue LED as the remote trigger for CO release. This photoactivated CO donor acts as a versatile CO surrogate for various conventional Pd-catalyzed carbonylation reactions. Its utility is further exemplified in carbonylation reactions employing light to access usually restrictive, less-reactive alkyl halides (Figure 1B).[32,35,36] In these examples, the same blue light that activates the CO donor also assists in the catalysis. Furthermore, we showcase an example wherein the photolabile CO releasing unit is built into polymeric scaffolds, affording new materials endowed with CO-releasing capabilities. The polymeric version was shown to be suitable in fully aqueous systems, which could be an entry point for either green chemistry or biological CO applications.

We based our design on the photolabile chemistry of bridged 1,2-diketones. Aromatic 1,2-diketone photoprecursors of polyacenes were previously shown to quantitatively extrude the diketone moiety as 2 equiv of CO.[38,39] We sought to synthesize an aliphatic version of the bridged 1,2-diketone and test if it would still result in the extrusion of 2 equiv of CO under visible-light irradiation. To construct the aliphatic 1,2-diketone moiety, literature precedents describe an intermolecular Diels−Alder reaction between 1,2-quinones and strained alkyne partners,[40] which requires a tedious synthesis. A simplified synthesis (three or four steps) via an intramolecular approach starting from the cheap and readily available catechol, 2,3-dihydroxybenzoic acid was carried out to prepare the photoactivated CO donor, namely, **CO-501** (Scheme 1). Amidation to a propargylic amine installs an

Scheme 1. Strategy to Prepare CO-501



alkyne intramolecular to the latent quinone group formed after the oxidation of the catechol moiety. The diene of the benzoquinone reacts via a Diels−Alder reaction with the tethered alkyne. Echoing our earlier findings,[41,42] tethering a regular alkyne intramolecular to its dienone partner obviated the need for a strained alkyne to drive the Diels−Alder reaction.

The UV−vis spectrum of **CO-501** shows two absorption bands. The absorption between 420 to 500 nm with λ_{max} = 441 nm corresponds to the $\nu-\pi^*$ transition of the carbonyl groups. Irradiating the sample with a blue LED (3W, λ_{max} = 450 nm, power density at the reaction distance of 150 mw/cm^2; see Figure S13 for the detailed spectrum) for 5 min led to the gradual disappearance of the absorption at this wavelength (Figure 2A). Under ambient light (500 lx from the

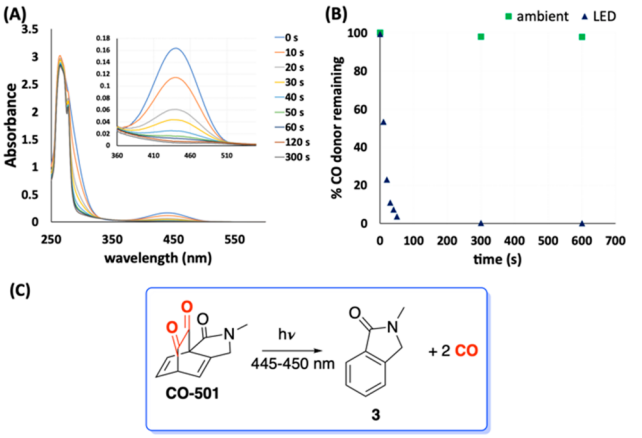


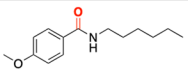
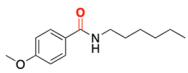
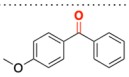
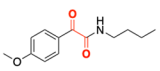
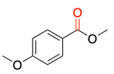
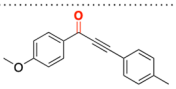
Figure 2. (A) UV−vis spectrum of **CO-501** (1 mM in DMSO) upon exposure to light from a blue LED. (B) **CO-501** is stable under ambient light for at least 2 h but releases CO when exposed to a blue LED. (C) **CO-501** undergoes blue-light-induced decarbonylation to release 2 equiv of CO.

overhanging fluorescence light in the lab), **CO-501** remained stable (Figures 2B and S2) for at least 2 h (stable in the dark for at least 10 months). Furthermore, the GC-TCD headspace analysis of **CO-501** confirmed it unloaded 2 equiv of CO (27 mol wt % CO) upon exposure to the blue LED. These studies indeed show that **CO-501** undergoes bisdecarbonylation quantitatively under irradiation from a blue LED (Figure 2C). Next, we sought to validate the possible use of **CO-501** as a CO surrogate for carbonylation reactions.

However, 1,2-diketones are known to readily and reversibly hydrate in aqueous systems.[43] Liao and co-workers reported that hydration prevents 1,2-diketones from releasing CO, while micellar structures[39,44] and hydrophobic moieties such as *tert*-butyl groups[45] can circumvent this. **CO-501** also undergoes hydration. However, instead of abolishing its CO-releasing capability, hydration merely slows down the process. Figure S4 shows that the diketone $n-\pi^*$ transition at 441 nm present in DMSO also disappears in the presence of water while another peak appears at ∼380 nm. This suggests that one of the carbonyl groups is hydrated, leaving one ketone group intact. NMR studies show that the hydration equilibrium favors the hydrated form in DMSO/water solutions (Figures S8 and 9). After extended irradiation with a LED (440−445 nm) for around 65 min, the hydrated products were converted to compounds with spectra corresponding to that of byproduct **3** (Figure S10). The reversibility of the hydration was further confirmed when the resuspension in DMSO of a lyophilized 1:1 DMSO-d_6/D_2O solution gave an NMR spectrum corresponding to that of intact **CO-501** (Figure S11). The CO yield is also dependent on the water ratio. At 50% DMSO, only 0.8 equiv of CO was recovered after 5 min of irradiation. Increasing the irradiation time to 30 min increased the CO recovery to 1.5 equiv. Further increasing the water content to 98% water in DMSO led to a yield of 1.2 equiv of CO (Figure S3) after 30 min of irradiation, representing a slight decrease in CO production. These findings indicate that these 1,2-

https://doi.org/10.1021/acs.orglett.2c01726
Org. Lett. 2022, 24, 4902−4907

Table 1. Proof-of-Concept Studies on the Applicability of CO-501 as a CO Surrogate for Various Carbonylation Reactions of 4-Methoxyiodobenzene[a] under Different Reaction Conditions

Entry	Carbonylative reactions	Other Starting Material	Catalyst/ Ligand	Base	Solvent	T (°C)	Product		% yield, isolated
1	Aminocarbonylation[12]	hexan-1-amine (2 eq)	$Pd(dba)_2$ (6 mol %), PPh_3 (10 mol %)	Et_3N (2 eq)	dioxane	80		4	89 (98)[#]
2	Aminocarbonylation[36]	hexan-1-amine (2 eq)	$Pd(PPh_3)_4$ (6 mol %)	K_2CO_3 (1 eq)	MeTHF: H_2O	r.t.		4	82
3	Carbonylative Suzuki-Miyaura[47]	phenylboronic acid (1 eq)	$Pd_2(dba)_3$ (1 mol %)	K_2CO_3 (3 eq)	anisole	100		5	80
4	Double Carbonylation[48]	butan-1-amine (3 eq)	$Pd(t\text{-}Bu_3P)_2$ (3 mol %)	DBU (3 eq)	THF	r.t.		6	77
5	Alkoxycarbonylation[49]	methanol (10 eq)	$Pd(OAc)_2$ (5 mol %), Xantphos (5 mol %)	Et_3N (18 eq)	acetonitrile	80		7	56
6	Carbonylative Sonogashira[50]	4-ethynyltoluene (2 eq)	$PdCl_2$ (3 mol %), Xantphos (5 mol %)	Et_3N (3 eq)	dioxane	80		8	79

[a]Performed at *ca.* 0.1 mmol ([#]*ca.* 1 mmol) scale.

diketones are compatible with applications in aqueous systems. Nevertheless, the irradiation time of **CO-501** will need to be adjusted accordingly to achieve maximal CO yields.

Furthermore, due to the vicinal carbonyl moieties, 1,2-diketones such as **CO-501** are more susceptible to attacks by nucleophiles. In control experiments, no carbonylated products were observed when all reaction components were added together with the CO donor (Table S1). This could be explained by the reaction of **CO-501** with the base or amine nucleophiles that are usually added in excess. In the presence of triethylamine and hexylamine, the CO yield decreases and is completely abolished, respectively (Figure S12). Because of this, physically separating the CO-generating reaction from the carbonylation reaction in a two-chamber strategy is one of the possible workarounds to prevent **CO-501** inactivation. Just like in most CO surrogates, the use of commercially available two-chamber gas reactors has been shown to be effective.[46] However, because CO generation is light-activated in **CO-501**, instead of spatial separation, we utilize light as an external trigger to temporally enrich the reaction vessel with CO before adding reaction components that may cause inactivation. Indeed, we find that the chronological separation of the CO generation process and the carbonylation reaction allowed the use of **CO-501** in various carbonylative reactions under a wide range of reaction conditions (Table 1). There is no temperature restriction or partitioning that needs to be factored in with the one-pot setup. With other surrogates that require thermal activation, the CO-generating pot needs to be maintained at a different temperature than the carbonylation pot. Furthermore, in this system, no additional transition-metal catalysts, additives, or bases are needed to activate the CO release. However, for reactions that require a higher CO pressure, a pressure tube with a two-chamber or transparent insert would be needed. With regard to stability, **CO-501** is stable under ambient light for only *ca.* 2 h and needs to be stored in the dark when not in use. **CO-501** left on the benchtop (500 lx ambient light) for one day and seven days slowly decomposed. Using the same conditions to synthesize compound **4** (Table 1, entry 2), the reaction yield decreased by 32% and 44%, respectively. The small difference in yields between these two time points could be attributed to the limited penetration of the ambient light into solid form of **CO-501**. We observed that only the surface of **CO-501** showed color change, indicating partial CO release (Figure S5). Another note is that under the current reaction settings the reaction vessel volume needs to be carefully selected to make sure it will be able to accommodate the accumulated CO. We carried out the reactions in various vessel volumes ranging from 6−20 mL vials to 50 mL round-bottom flasks for larger scale reactions (Figure S15) and found both **CO-501** and this protocol to be widely applicable.

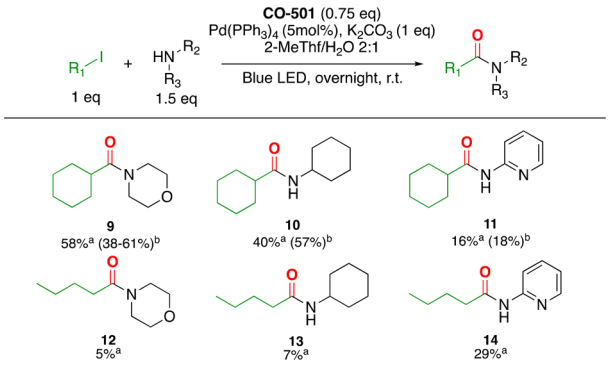
Because **CO-501** releases 2 equiv of CO, a substoichiometric amount of the donor is needed to provide more than 1 equiv of CO to the reaction mixture. The low-power visible light needed for the reaction, coupled with the fast kinetics (Figure 2) associated with the photobisdecarbonylation of **CO-501**, provides CO within 30 min of irradiation. Results also indicate that photoproduct **3** is a stable, benign bystander that does not interfere with the carbonylation process (Tables 1 and S1).

Up to this point, we have shown that **CO-501** is a CO donor that can be used in conventional Pd-catalyzed carbonylation reactions. Next, we demonstrate that the photolysis conditions to release CO from **CO-501** are compatible with the conditions needed for the light-assisted carbonylation of challenging substrates. In prior works utilizing CO surrogates for light-mediated carbonylation, a two-chamber setup was required to accommodate the different reaction conditions employed for CO generation and light-assisted carbonylation reactions.[32,36] The physical separation of the CO generation and carbonylation reactions is necessary because of the incompatibility of the chemistries involved in the two processes. Here, we show that **CO-501** can be used in a simplified one-pot reaction setup that is convenient for light-mediated carbonylation reactions. Cyclohexyl iodide and butyl iodide with either primary or secondary amine nucleophiles

https://doi.org/10.1021/acs.orglett.2c01726
Org. Lett. 2022, 24, 4902−4907

were carbonylated under these reaction conditions (Scheme 2).

Scheme 2. Light-Activated CO Surrogate for Light-Assisted Carbonylation Reactions of Non-Activated Alkyl Iodide Substrates



We explored the immobilization of the photolabile 1,2-diketone core as a way around some of **CO-501**'s limitations. We prepared **CO-502**, a light-activated polymeric version of **CO-501**, as shown in Scheme S3. Using a six-carbon aminocarboxylic acid linker, we first attached the protected propargylic catechol on the aminomethyl polystyrene resin via an amide linkage. Then, subsequent deprotection and oxidation installed the light-activated 1,2-diketone moiety on the resin. **CO-502** was shown to have a CO loading degree of 1.2 mmol CO/g. We demonstrate its utility in the following two scenarios: (1) an improved yield for carbonylation in a fully aqueous system, indicating some protection against hydration, and (2) the simplified workup and purification of a specific carbonylation reaction wherein the desired product coelutes with byproduct **2** (Scheme S4). While these are improvements of the surrogate under specific conditions, the immobilization of this light-sensitive CO-releasing moiety on polymeric structures may potentially open other applications, including biological applications.

In summary, the light-activated CO donors **CO-501** and **CO-502** deliver CO upon activation by a low-power blue LED. To the best of our knowledge, these are the first photoactivated one-pot CO donors that have been demonstrated to be applicable under different carbonylation reaction conditions. More specifically, the use of this light-activated donor has been demonstrated to be compatible with blue light-assisted carbonylation reactions of nonactivated alkyl halide substrates. Furthermore, with **CO-502**, we showed that the photolabile CO-releasing moiety can be installed into polymeric materials to endow them with CO-releasing capabilities. The convenience and practicality of these CO surrogates in various applications have been described herein. Future improvements to this system would be to optimize the synthesis to improve cost-effectiveness, especially for applications beyond research laboratories (*N*-methylprop-2-yn-1-amine is an expensive starting material) and to design ^{13}C- or ^{18}O-labeled 1,2-diketone-based CO surrogates.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.orglett.2c01726.

Experimental details, photographs of the experimental setup, and compound characterization data (PDF)

■ AUTHOR INFORMATION

Corresponding Authors

Xiaoxiao Yang − *Department of Chemistry, Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, Georgia 30303, United States;* orcid.org/0000-0001-9895-9559; Email: xyang20@gsu.edu

Binghe Wang − *Department of Chemistry, Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, Georgia 30303, United States;* orcid.org/0000-0002-2200-5270; Email: wang@gsu.edu

Authors

Ladie Kimberly De La Cruz − *Department of Chemistry, Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, Georgia 30303, United States*

Nicola Bauer − *Department of Chemistry, Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, Georgia 30303, United States*

Alyssa Cachuela − *Department of Chemistry, Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, Georgia 30303, United States*

Wing Sze Tam − *Hong Kong Baptist University, Kowloon Tong, Hong Kong*

Ravi Tripathi − *Department of Chemistry, Center for Diagnostics and Therapeutics, Georgia State University, Atlanta, Georgia 30303, United States*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.orglett.2c01726

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The authors are grateful for financial support from the National Institutes of Health (R01DK119202), the Georgia Research Alliance through an Eminent Scholar fund, and internal resources at Georgia State University.

■ REFERENCES

(1) Schoenberg, A.; Bartoletti, I.; Heck, R. F. Palladium-catalyzed carboalkoxylation of aryl, benzyl, and vinylic halides. *J. Org. Chem.* **1974**, *39*, 3318−3326.

(2) Peng, J.-B.; Geng, H.-Q.; Wu, X.-F. The Chemistry of CO: Carbonylation. *Chem.* **2019**, *5*, 526−552.

(3) Ren, X.; Zheng, Z.; Zhang, L.; Wang, Z.; Xia, C.; Ding, K. Rhodium-Complex-Catalyzed Hydroformylation of Olefins with CO2 and Hydrosilane. *Angew. Chem., Int. Ed. Engl.* **2017**, *56*, 310−313.

(4) Morimoto, T.; Kakiuchi, K. Evolution of Carbonylation Catalysis: No Need for Carbon Monoxide. *Angew. Chem., Int. Ed. Engl.* **2004**, *43*, 5580−5588.

(5) Cao, J.; Zheng, Z.-J.; Xu, Z.; Xu, L.-W. Transition-metal-catalyzed transfer carbonylation with HCOOH or HCHO as non-gaseous C1 source. *Coord. Chem. Rev.* **2017**, *336*, 43−53.

(6) Konishi, H.; Manabe, K. Formic Acid Derivatives as Practical Carbon Monoxide Surrogates for Metal-Catalyzed Carbonylation Reactions. *Synlett* **2014**, *25*, 1971−1986.

(7) Veryser, C.; Van Mileghem, S.; Egle, B.; Gilles, P.; De Borggraeve, W. M. Low-cost instant CO generation at room temperature using formic acid, mesyl chloride and triethylamine. *Reaction Chemistry & Engineering* **2016**, *1*, 142−146.

(8) Panda, B.; Albano, G. DMF as CO Surrogate in Carbonylation Reactions: Principles and Application to the Synthesis of Heterocycles. *Catalysts* **2021**, *11*, 1531.
(9) Grushin, V. V.; Alper, H. Novel palladium-catalyzed carbonylation of organic halides by chloroform and alkali. *Organometallics* **1993**, *12*, 3846−3850.
(10) Mondal, K.; Halder, P.; Gopalan, G.; Sasikumar, P.; Radhakrishnan, K. V.; Das, P. Chloroform as a CO surrogate: applications and recent developments. *Org. Biomol. Chem.* **2019**, *17*, 5212−5222.
(11) Hansen, S. V. F.; Ulven, T. Oxalyl Chloride as a Practical Carbon Monoxide Source for Carbonylation Reactions. *Org. Lett.* **2015**, *17*, 2832−2835.
(12) Hermange, P.; Lindhardt, A. T.; Taaning, R. H.; Bjerglund, K.; Lupp, D.; Skrydstrup, T. Ex Situ Generation of Stoichiometric and Substoichiometric 12CO and 13CO and Its Efficient Incorporation in Palladium Catalyzed Aminocarbonylations. *J. Am. Chem. Soc.* **2011**, *133*, 6061−6071.
(13) Shao, C.; Lu, A.; Wang, X.; Zhou, B.; Guan, X.; Zhang, Y. Oxalic acid as the in situ carbon monoxide generator in palladium-catalyzed hydroxycarbonylation of arylhalides. *Org. Biomol. Chem.* **2017**, *15*, 5033−5040.
(14) Nordeman, P.; Odell, L. R.; Larhed, M. Aminocarbonylations Employing Mo(CO)6 and a Bridged Two-Vial System: Allowing the Use of Nitro Group Substituted Aryl Iodides and Aryl Bromides. *J. Org. Chem.* **2012**, *77*, 11393−11398.
(15) Jana, N.; Zhou, F.; Driver, T. G. Promoting Reductive Tandem Reactions of Nitrostyrenes with Mo(CO)6 and a Palladium Catalyst To Produce 3H-Indoles. *J. Am. Chem. Soc.* **2015**, *137*, 6738−6741.
(16) Liu, Q.; Yuan, K.; Arockiam, P.-B.; Franke, R.; Doucet, H.; Jackstell, R.; Beller, M. Regioselective Pd-Catalyzed Methoxycarbonylation of Alkenes Using both Paraformaldehyde and Methanol as CO Surrogates. *Angew. Chem., Int. Ed. Engl.* **2015**, *54*, 4493−4497.
(17) Natte, K.; Dumrath, A.; Neumann, H.; Beller, M. Palladium-Catalyzed Carbonylations of Aryl Bromides using Paraformaldehyde: Synthesis of Aldehydes and Esters. *Angew. Chem., Int. Ed. Engl.* **2014**, *53*, 10090−10094.
(18) Kaiser, N. F.; Hallberg, A.; Larhed, M. In situ generation of carbon monoxide from solid molybdenum hexacarbonyl. A convenient and fast route to palladium-catalyzed carbonylation reactions. *J. Comb. Chem.* **2002**, *4*, 109−11.
(19) Åkerbladh, L.; Odell, L. R.; Larhed, M. Palladium-Catalyzed Molybdenum Hexacarbonyl-Mediated Gas-Free Carbonylative Reactions. *Synlett* **2019**, *30* (02), 141−155.
(20) Morimoto, T.; Fuji, K.; Tsutsumi, K.; Kakiuchi, K. CO-Transfer Carbonylation Reactions. A Catalytic Pauson−Khand-Type Reaction of Enynes with Aldehydes as a Source of Carbon Monoxide. *J. Am. Chem. Soc.* **2002**, *124*, 3806−3807.
(21) Ueda, T.; Konishi, H.; Manabe, K. Palladium-Catalyzed Reductive Carbonylation of Aryl Halides with N-Formylsaccharin as a CO Source. *Angew. Chem., Int. Ed. Engl.* **2013**, *52*, 8611−8615.
(22) Konishi, H. Creation of Novel Toxic Gas Surrogates and the Development of Safe and Facile Catalytic Reactions. *Chem. Pharm. Bull. (Tokyo)* **2018**, *66*, 1−19.
(23) Friis, S. D.; Taaning, R. H.; Lindhardt, A. T.; Skrydstrup, T. Silacarboxylic Acids as Efficient Carbon Monoxide Releasing Molecules: Synthesis and Application in Palladium-Catalyzed Carbonylation Reactions. *J. Am. Chem. Soc.* **2011**, *133*, 18114−18117.
(24) Poloukhtine, A.; Popik, V. V. Highly Efficient Photochemical Generation of a Triple Bond: Synthesis, Properties, and Photodecarbonylation of Cyclopropenones. *J. Org. Chem.* **2003**, *68*, 7833−7840.
(25) Payne, C. M.; Cho, K.; Larsen, D. S. 5-Bromo-norborn-2-en-7-one derivatives as a carbon monoxide source for palladium catalyzed carbonylation reactions. *RSC Adv.* **2019**, *9*, 30736−30740.
(26) Zoller, B.; Zapp, J.; Huy, P. H. Rapid Organocatalytic Formation of Carbon Monoxide: Application towards Carbonylative Cross Couplings. *Chem. Eur. J.* **2020**, *26*, 9632−9638.
(27) Konishi, H.; Manabe, K. Recent progress on catalytic Heck carbonylations using carbon monoxide surrogates. *Tetrahedron Lett.* **2019**, *60*, 151147.
(28) Gautam, P.; Bhanage, B. M. Recent advances in the transition metal catalyzed carbonylation of alkynes, arenes and aryl halides using CO surrogates. *Catal. Sci. Technol.* **2015**, *5*, 4663−4702.
(29) Formenti, D.; Ferretti, F.; Ragaini, F. Synthesis of N-Heterocycles by Reductive Cyclization of Nitro Compounds using Formate Esters as Carbon Monoxide Surrogates. *ChemCatChem.* **2018**, *10*, 148−152.
(30) Gatlik, B.; Chaładaj, W. Pd-Catalyzed Perfluoroalkylative Aryloxycarbonylation of Alkynes with Formates as CO Surrogates. *ACS Catal.* **2021**, *11*, 6547−6559.
(31) Wu, L.; Fang, X.; Liu, Q.; Jackstell, R.; Beller, M.; Wu, X.-F. Palladium-Catalyzed Carbonylative Transformation of C(sp3)−X Bonds. *ACS Catal.* **2014**, *4*, 2977−2989.
(32) Roslin, S.; Odell, L. R. Palladium and visible-light mediated carbonylative Suzuki−Miyaura coupling of unactivated alkyl halides and aryl boronic acids. *Chem. Commun.* **2017**, *53*, 6895−6898.
(33) Frisch, A. C.; Beller, M. Catalysts for Cross-Coupling Reactions with Non-activated Alkyl Halides. *Angew. Chem., Int. Ed. Engl.* **2005**, *44*, 674−688.
(34) Sumino, S.; Fusano, A.; Fukuyama, T.; Ryu, I. Carbonylation Reactions of Alkyl Iodides through the Interplay of Carbon Radicals and Pd Catalysts. *Acc. Chem. Res.* **2014**, *47*, 1563−1574.
(35) Torres, G. M.; Liu, Y.; Arndtsen, B. A. A dual light-driven palladium catalyst: Breaking the barriers in carbonylation reactions. *Science* **2020**, *368*, 318−323.
(36) Sardana, M.; Bergman, J.; Ericsson, C.; Kingston, L. P.; Schou, M.; Dugave, C.; Audisio, D.; Elmore, C. S. Visible-Light-Enabled Aminocarbonylation of Unactivated Alkyl Iodides with Stoichiometric Carbon Monoxide for Application on Late-Stage Carbon Isotope Labeling. *J. Org. Chem.* **2019**, *84*, 16076−16085.
(37) Sargent, B. T.; Alexanian, E. J. Palladium-Catalyzed Alkoxycarbonylation of Unactivated Secondary Alkyl Bromides at Low Pressure. *J. Am. Chem. Soc.* **2016**, *138*, 7520−7523.
(38) Mondal, R.; Okhrimenko, A. N.; Shah, B. K.; Neckers, D. C. Photodecarbonylation of α-Diketones: A Mechanistic Study of Reactions Leading to Acenes. *J. Phys. Chem. B* **2008**, *112*, 11−15.
(39) Peng, P.; Wang, C.; Shi, Z.; Johns, V. K.; Ma, L.; Oyer, J.; Copik, A.; Igarashi, R.; Liao, Y. Visible-light activatable organic CO-releasing molecules (PhotoCORMs) that simultaneously generate fluorophores. *Org. Biomol. Chem.* **2013**, *11*, 6671−6674.
(40) Escorihuela, J.; Das, A.; Looijen, W. J. E.; van Delft, F. L.; Aquino, A. J. A.; Lischka, H.; Zuilhof, H. Kinetics of the Strain-Promoted Oxidation-Controlled Cycloalkyne-1,2-quinone Cycloaddition: Experimental and Theoretical Studies. *J. Org. Chem.* **2018**, *83*, 244−252.
(41) Ji, X.; Wang, B. Strategies toward Organic Carbon Monoxide Prodrugs. *Acc. Chem. Res.* **2018**, *51*, 1377−1385.
(42) Ji, X.; Zhou, C.; Ji, K.; Aghoghovbia, R. E.; Pan, Z.; Chittavong, V.; Ke, B.; Wang, B. Click and Release: A Chemical Strategy toward Developing Gasotransmitter Prodrugs by Using an Intramolecular Diels−Alder Reaction. *Angew. Chem., Int. Ed. Engl.* **2016**, *55*, 15846−15851.
(43) Poziomek, E. J.; Kronenberg, M. E.; Havinga, E. Chemical consequences of the hydration of 1,2-diketones. *Recl. Trav. Chim. Pays-Bas* **1966**, *85*, 791−792.
(44) Wright, M. A.; Wright, J. A. PhotoCORMs: CO release moves into the visible. *Dalton Trans* **2016**, *45*, 6801−6811.
(45) Elgattar, A.; Washington, K. S.; Talebzadeh, S.; Alwagdani, A.; Khalil, T.; Alghazwat, O.; Alshammri, S.; Pal, H.; Bashur, C.; Liao, Y. Poly(butyl cyanoacrylate) nanoparticle containing an organic photo-CORM. *Photochem. Photobiol. Sci.* **2019**, *18*, 2666−2672.
(46) Friis, S. D.; Lindhardt, A. T.; Skrydstrup, T. The Development and Application of Two-Chamber Reactors and Carbon Monoxide Precursors for Safe Carbonylation Reactions. *Acc. Chem. Res.* **2016**, *49*, 594−605.

https://doi.org/10.1021/acs.orglett.2c01726
Org. Lett. 2022, 24, 4902−4907

(47) Li, H.; Yang, M.; Qi, Y.; Xue, J. Ligand-Free Pd-Catalyzed Carbonylative Cross-Coupling Reactions under Atmospheric Pressure of Carbon Monoxide: Synthesis of Aryl Ketones and Heteroaromatic Ketones. *Eur. J. Org. Chem.* **2011**, *2011*, 2662−2667.
(48) Iizuka, M.; Kondo, Y. Remarkable ligand effect on the palladium-catalyzed double carbonylation of aryl iodides. *Chem. Commun.* **2006**, 1739−1741.
(49) Martinelli, J. R.; Watson, D. A.; Freckmann, D. M. M.; Barder, T. E.; Buchwald, S. L. Palladium-Catalyzed Carbonylation Reactions of Aryl Bromides at Atmospheric Pressure: A General System Based on Xantphos. *J. Org. Chem.* **2008**, *73*, 7102−7107.
(50) Neumann, K. T.; Laursen, S. R.; Lindhardt, A. T.; Bang-Andersen, B.; Skrydstrup, T. Palladium-Catalyzed Carbonylative Sonogashira Coupling of Aryl Bromides Using Near Stoichiometric Carbon Monoxide. *Org. Lett.* **2014**, *16*, 2216−2219.

https://doi.org/10.1021/acs.orglett.2c01726
Org. Lett. 2022, 24, 4902−4907