Intermolecular 2+2 Carbonyl-Olefin Photocycloadditions Enabled by Cu(I)-Norbornene MLCT

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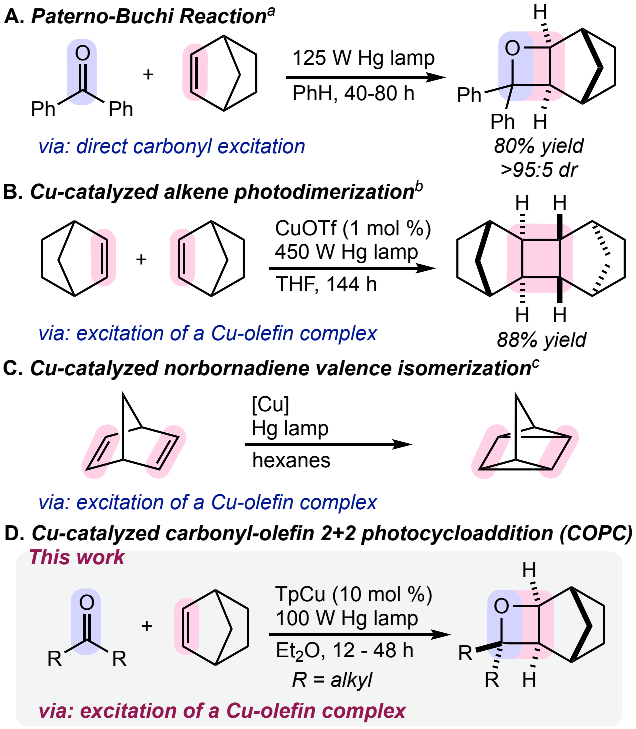
Supporting Information Placeholder

ABSTRACT: Photocycloadditions are often typified by the oxetane forming Paternò-Büchi reaction. However, the mechanistic constraints of carbonyl excitation and olefin interception have limited this attractive oxetane forming pathway. Here we describe the use of a Cu(I) precatalyst that achieves selective olefin activation via coordination to the metal center. Significantly, this intermolecular 2+2 carbonyl-olefin photocycloaddition engages alkyl ketones which are more challenging to accommodate via direct irradiation pathways. Mechanistic investigations support the in situ formation of a Cu-norbornene resting state that undergoes a MLCT leading to oxetane formation.

The photochemically allowed 2+2 cycloaddition of two π-components is a straightforward, atom-economical approach to 4-membered ring construction. The premier example of such a reaction is the photocycloaddition of carbonyl and alkene π-bonds to form oxetanes, known as the Paternò-Büchi reaction (Scheme 1A).[1,2] Despite the name recognition of this reaction and the utility of oxetanes in drug discovery,[3,4] its strategic application to the general synthesis of oxetanes has been mechanistically limited to specific substrate pairings because they proceed via direct carbonyl excitation or photosensitization followed by alkene interception.[5,6] Consequently, the majority of reports feature aryl ketones or aldehydes paired with electron-rich alkenes,[7-9] while examples of alkyl ketone substrates are more limited and rely on UVC irradiation and quartz reaction vessels, reducing their practicality and user friendliness.[10] Catalyst controlled approaches have not been widely developed.

The ability of d^6 octahedral transition metal compounds to undergo metal to ligand charge transfer (MLCT) upon irradiation is the fundamental photophysical property that has propelled the burgeoning field of photoredox catalysis.[11] The geometries, oxidation states, and relatively slow ligand exchange kinetics of these complexes were design features selected to promote MLCT and generate relatively long-lived excited states capable of intermolecular electron or energy transfer.[12] Radical-type reactivity occurring at the highly conjugated ligands is uncommon although recent examples have emerged where the active species that undergoes excitation is a substrate-metal complex.[13-16] We envisioned that inverting many of the properties that make Ru- or Ir-based photoredox catalysts successful could unlock the potential for new mechanistic pathways featuring MLCT and access new reactivity modes.

Scheme 1. Selected Previous 2+2 Photocycloadditions.

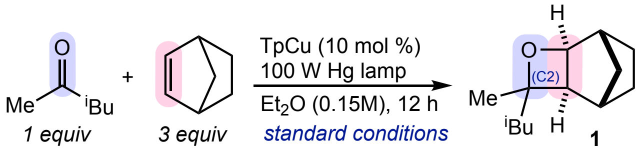


[a]See ref. 2a. [b]See ref. 17b. [c]See ref. 22.

Mackor and Kochi were among the first to report that catalytic copper(I) triflate significantly improved the efficiency of simple alkene photodimerizations via excitation of an in situ formed Cu(I)-olefin complex (Scheme 1B).[17-

[20] These examples required prolonged reaction times (~days) and high wattage (450 W) immersion well photoreactor setups to achieve even moderate reaction efficiencies. Salomon and co-workers initially proposed that excitation of an in situ formed Cu(I)-olefin complex resulted in a charge transfer event between the metal center and the alkene ligand leading to cyclobutane formation.[20] Budzelaar and coworkers later computationally confirmed that the directionality of the charge transfer event is metal (Cu) to ligand (olefin) (MLCT).[21] Analogously, the valence isomerization of norbornadiene to quadricyclane was reported using a range of pre-catalysts[22a] including Cu(I)-halides[22b,c] and other Cu(I) compounds bearing neutral mono- and bi-dentate phosphines,[22d-j] mono-anionic oxoquinolinato[22k] and tris(pyrazolyl)borate[22l] chelates (Scheme 1C). Spectroscopic studies by Kutal and coworkers also confirmed that Cu(I) mediated norbornadiene to quadricyclane valence isomerization occurred by excitation of an in situ generated Cu-η^2-norbornadiene complex and proceeds via a MLCT.[22l]

Table 1. 2+2 COPC Reaction conditions effects.[a]



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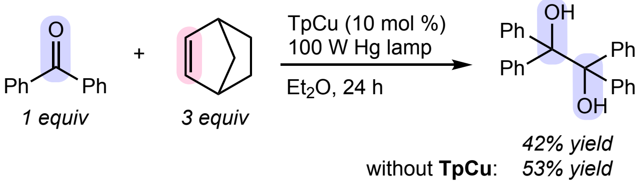
Entry	Deviation from standard conditions	Yield of **1**[a]
1	none	49%[b]
2	No TpCu	*n.d.*
3	No light[c]	*n.d.*
4	1 equiv norbornene	33%[d]
5	CuOTf in place of TpCu	13%[d]
6	CuOTf + KTp (10 mol % each)[e]	31%

[a]Yields determined via ^{1}H-NMR of crude reaction mixtures using durene as an internal standard; a 55:45 diastereomeric ratio was determined via gas chromatography of the crude reaction mixture; OTf = triflate. [b]^{1}H-NMR yield calculated as the average over 3 independent trials, standard deviation >3% yield. [c]In the absence of light, the reaction mixture was heated to 43 °C to replicate the temperatures reached during irradiation. [d]36 h reaction time. [e]11% yield of norbornene dimers were also isolated. [e]CuOTf and KTp were mixed in diethyl ether for 20 min prior to addition of substrates and irradiation.

We envisioned that with an appropriate supporting ligand, excitation of a Cu(I)-olefin compound in the presence of a carbonyl could form an oxetane – inverting the conventional 2+2 photocycloadditive oxetane forming pathway of the Paternò-Büchi reaction (Scheme 1D). By activation of a metal-olefin complex rather than direct excitation of either substrate, this approach could alter the reactivity of the excited state and allow a more diverse range of carbonyls to participate in 2+2 carbonyl-olefin photocycloadditions (2+2 COPC). We selected tris(pyrazolyl)borate (Tp)[23] for our investigations as we anticipated that the monoanionic state could mimic the electronic influences of the weakly coordinating triflate anion commonly used, and the tridentate facial coordination mode could simultaneously allow for olefin coordination[24] and inhibit non-productive quenching via flattening.[25-27]

Irradiation of a 1:3 mixture of methyl isobutyl ketone and norbornene in the presence of 10 mol % tris(pyrazolyl)borate copper(I) (**TpCu**)[28] in diethyl ether with a 100W Hg lamp for 12 h resulted in 49% yield of oxetane **1** as a 55:45 mixture of diastereomers at C2 with exclusive *cis-exo* disposition at the ring junction (Table 1, entry 1). In the absence of **TpCu** or light, **1** was not detected (entries 2 and 3). The reaction efficiency decreased when an equimolar ratio of ketone and alkene were used, requiring a longer 36 h reaction time to produce **1** in only 33% yield (entry 4). Using 10 mol % copper(I) triflate in place of **TpCu** resulted in only 13% yield of **1** and 11% yield of a mixture of norbornene dimers (entry 5). Notably, alkene dimers were not detected when **TpCu** was used. In lieu of using pre-formed **TpCu**, an equimolar mixture of copper(I) triflate and potassium tris(pyrazolyl)borate (10 mol % each) was successful but produced **1** with diminished reaction efficiency (31 vs. 49% yield, entry 6 vs 1).

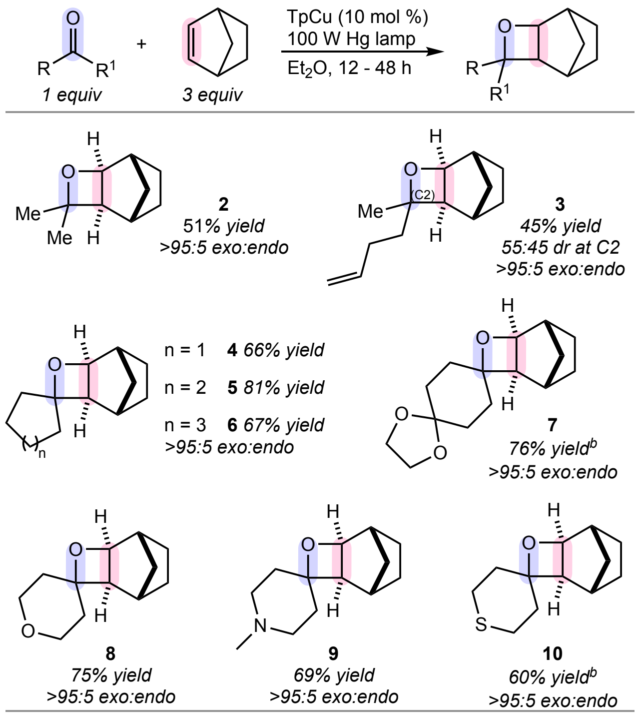
Scheme 2. Aryl ketone dimerization[a]



[a]Yields determined from ^{1}H-NMR of crude reaction mixtures using durene as an internal standard.

Aryl ketones, such as benzophenone, are prototypical carbonyls in Paternò-Büchi reactions. When subjected to our standard conditions, benzophenone with excess norbornene resulted in benzopinacol formation in 42% yield without detection of the corresponding oxetane (Scheme 2). A control experiment without added **TpCu** resulted in similar reaction efficiency and selectivity for ketone dimerization. Selectivity for benzophenone dimerization in ethereal solvents rather than oxetane formation with norbornene in benzene solutions has been previously reported.[2] We attribute the lack of background Paternò-Büchi reactivity to the diethyl ether solvent used and the failure of aryl ketones to produce oxetanes in our study to the inability of the Cu-mediated pathway to outcompete ketone dimerization.[29,30] Also, the excitation of alkyl ketones generally requires the use of quartz reaction vessels to ensure adequate transmission however, we exclusively used borosilicate reaction vessels in our study which significantly block light at wavelengths shorter than 280 nm (see Fig. 1). This suggests that the traditional Paternò-Büchi mechanism of direct carbonyl excitation is not operative in this 2+2 COPC and highlights the opportunities that become available when a suitable catalyst is used.

Scheme 3. 2+2 COPC Scope of alkyl carbonyls.[a]



[a]Yields determined by ^{1}H-NMR of crude reaction mixtures using durene as an internal standard; diastereomeric ratios were determined via ^{1}H-NMR of the crude reaction mixtures with the structure of the major diastereomer shown; see the SI for additional details. [b]Isolated yields following purification via silica gel chromatography.

Next, a variety of alkyl ketones were investigated using these Cu-catalyzed 2+2 COPC conditions (Scheme 3). Irradiation of acetone, a common organic photosensitizer, reacted to form oxetane **2** in 51% yield. 5-Hexen-2-one which contains a terminal alkene was smoothly converted to **3** in 45% yield as a 55:45 mixture of diastereomers at C2. No intra- or intermolecular reactivity was observed as a result of the α-olefin. The absence of reactivity for other alkenes in this 2+2 COPC suggests that norbornene interaction with **TpCu** is preferred and is the source of observed reactivity.[31] Cyclic ketones proved to be outstanding carbonyl substrates, generating oxetanes **4-10** in good to excellent yields and in each case, exclusively as the *cis*-*exo* diastereomers. These examples showcase the tolerance of acid sensitive acetal (**7**), ether (**8**), basic tertiary amine (**9**), and thio-ether (**10**) functionality during 2+2 COPC.

To interrogate the mechanism by which this Cu-catalyzed 2+2 COPC occurs, we carried out a series of spectroscopic studies. We collected the electronic absorption spectra of diethyl ether solutions of **TpCu** (green line, Figure 1) and an equimolar mixture of **TpCu** and methyl isobutyl ketone (gold line). Both spectra are nearly identical and lack any distinct absorption features 200 – 400 nm. Conversely, an ethereal solution of **TpCu** and norbornene (1:1 molar ratio, pink line) has a broad absorption feature with a maximum at 272 nm, suggesting the formation of a new species in solution. A 1:1:1 mixture of **TpCu**, norbornene, and methyl isobutyl ketone (orange line) displays the same absorption features as without added ketone, suggesting that this new species is the resting state species.

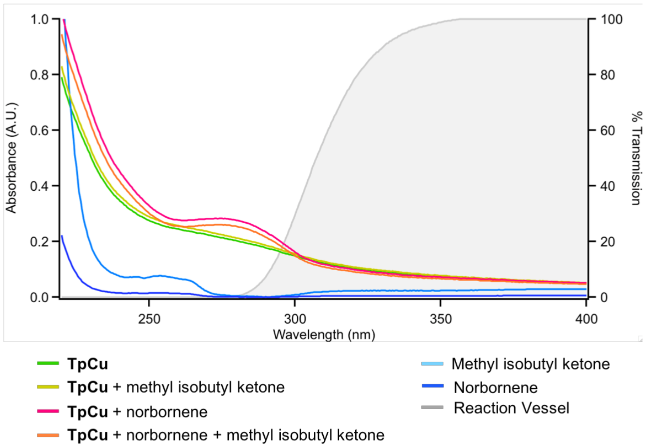


Figure 1. Electronic absorption spectra. All samples were collected at 0.5 mM in diethyl ether and as equimolar mixtures of the compounds indicated with each component being 0.5 mM. The transmission spectrum of the reaction vessels used in this study is overlaid for reference (right vertical axis).

The borosilicate reaction vessels used, transmit very little light <280 nm indicating that oxetane formation is the result of absorption >280 nm (see Figure 1). Oxetane **1** was detected in only 60% conversion after 12 h of irradiation when a long pass 300 nm cut-on filter was applied compared to >98% conversion without the filter. Transmission through the cut-on filter ranges from <1% below 295 nm to >22% above 300 nm. The correlation between the decreased amount of light that reaches the reaction mixture between 280-300 nm and the decreased conversion to **1** suggests that oxetane forming excitation occurs in this region.

In agreement with the electronic absorption data, a mixture of **TpCu** and methyl isobutyl ketone does not result in the appearance of a new compound as determined by ^{1}H-NMR (Figure 2, spectrum C). However, in the presence (spectrum A) or absence of methyl isobutyl ketone (spectrum B), mixtures of **TpCu** and norbornene resulted in the formation of a Cu-olefin compound as evidenced by the downfield chemical shift change from 7.10 to 7.43 ppm of the proton at the C5 pyrazole position and a broadening of the signals corresponding to norbornene (comparing spectra D to B and A). The ^{1}H-NMR spectrum of a 1:10:30 ratio of **TpCu**, methyl isobutyl ketone, and norbornene showed the same characteristic C5 pyrazole proton chemical shift that was observed from stoichiometric mixing of **TpCu** and norbornene, suggesting that **TpCu(Norb)** is formed under the reaction conditions and is the resting state species.

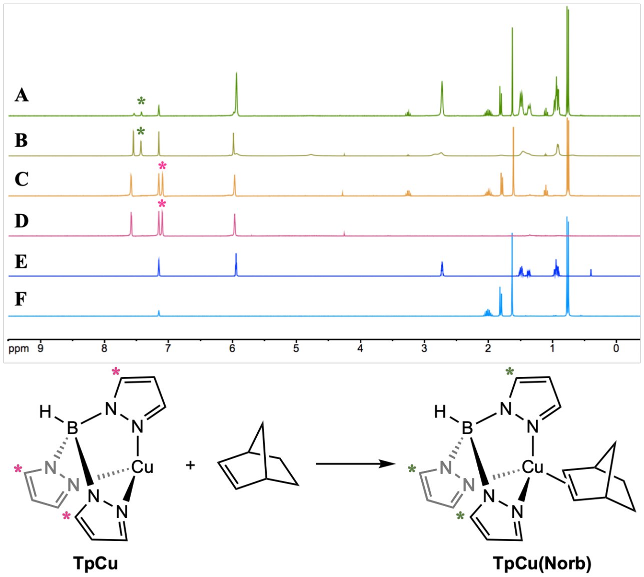
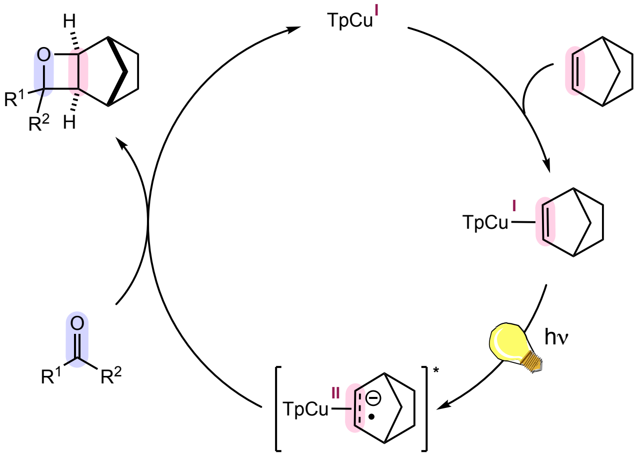


Figure 2. ^{1}H-NMR spectra of reaction components. All samples were prepared in benzene-d_6. **A** shows 1:10:30 mixture of **TpCu**:methyl isobutyl ketone: norbornene (0.11M with respect to ketone). **B** shows **TpCu(Norb)** (0.11M). **C** shows a 1:1 mixture of TpCu and methyl isobutyl ketone (0.11M in each component). **D** shows **TpCu** (0.11M). **E** shows norbornene (0.11 mM). **F** shows methyl isobutyl ketone (0.11M).

In alignment with the previously reported mechanisms of Cu-mediated alkene photodimerization,[18-21] valence isomerization,[22] and our collected data we propose that Cu-catalyzed 2+2 COPC proceeds via initial olefin coordination to **TpCu** to form **TpCu(Norb)** (Scheme 4). Excitation 280-300 nm results in MLCT to generate a Cu(II) metal center and an alkene radical anion. Trapping of this polarized intermediate by the carbonyl unit of the alkyl ketone can result in oxetane formation.[32] Luminescence data collected by excitation 280-300 nm did not exhibit a relationship between the concentration of additional norbornene or methyl isobutyl ketone in the presence of **TpCu(Norb)**.[33] The absence of an observed quenching relationship does not definitively exclude the possibility that an additional sensitization process may contribute to oxetane formation. The spin state of 2+2 photocycloadditions is commonly inferred based on the stereochemistry of the products detected.[34,35] However, the use of norbornene in our present work precludes an analogous interpretation because geometric constraints would result in identical products irrespective of spin state.

Scheme 4. Mechanistic proposal.



In conclusion, we have developed a Cu-catalyzed 2+2 carbonyl-olefin photocycloaddition of alkyl ketones and norbornene that accesses the corresponding oxetanes via a mechanistically distinct pathway from conventional Paternò-Büchi reactions. Our approach allows for traditionally more challenging alkyl ketones to engage in 4-membered ring formation because direct carbonyl excitation is avoided. Mechanistic investigations support that in situ formed **TpCu(Norb)** is the photoactive species that upon excitation leads to oxetane formation. This intermolecular 2+2 COPC process disrupts the traditional Paternò-Büchi oxetane forming mechanistic paradigm and was achieved using a MLCT approach enabled through alkene substrate coordination. Additional examples of substrate dependent MLCT catalysis for use in chemical synthesis are under active investigation in our laboratory and will be disclosed in due course.

ASSOCIATED CONTENT

Supporting Information. The Supporting Information is available free of charge on the ACS Publications website. Experimental details; characterization data including NMR spectra of novel compounds; methods and results (PDF)

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Notes

The authors declare no competing financial interest.

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REFERENCES

(1) Griesbeck, A. G. In Molecular and Supramolecular Photochemistry; Griesbeck, A. G., Mattay, J., Eds.; Marcel Dekker: New York, 2005; Vol. 12: Synthetic Organic Photochemistry, Chapter 4.

(2) (a) Scharf, D.; Korte, F. Photosensibilisierte cyclodimerisierung von norbornen. *Tetrahedron Lett.,* **1963**, *13*, 821-823. https://www.sciencedirect.com/science/article/pii/S0040403901907221. (b) Arnold, D. R.; Hinman, R. L.; Glick, A. H. Chemical properties of the carbonyl n, π state. The photochemical preparation of oxetanes. *Tetrahedron Lett.*, **1964**, *5*, 1425 – 1430. DOI: 10.1016/S0040-4039(00)90493-3.

(3) Burkhard, J. A.; Wuitschik, G.; Rogers-Evans, M.; Müller, K.; Carreira, E. M. Oxetanes as Versatile Elements in Drug Discovery and Synthesis. *Angew. Chem. Int. Ed.,* **2010**, *49*, 9052 – 9067. https://onlinelibrary.wiley.com/doi/full/10.1002/anie.200907155

(4) Delost, M. D.; Smith, D. T.; Anderson, B. J.; Njardarson, J. T. From Oxiranes to Oligomers: Architectures of U.S. FDA Approved Pharmaceuticals Containing Oxygen Heterocycles. *J. Med. Chem.,* **2018**, *61*, 10996 – 11020. https://pubs.acs.org/doi/abs/10.1021/acs.jmedchem.8b00876

(5) Or in substrate controlled, intramolecular settings.

(6) For an example of an intramolecular Paternò-Büchi reaction that proceeds via alkene excitation, see: Kumarasamy, E.; Raghunathan, R.; Kumar Kandappa, S.; Sreenithya, A.; Jockusch, S.; Sunoj, R. B.; Sivaguru, J. Transposed Paternò-Büchi Reaction. *J. Am. Chem. Soc.*, **2017**, *139*, 655-662. DOI: 10.1021/jacs.6b05936

(7) D'Auria, M.; Racioppi, R. Oxetane Synthesis through the Paternò-Büchi Reaction. *Molecules*, **2013**, *18*, 11384-11482. https://www.mdpi.com/1420-3049/18/9/11384/htm

(8) Fréneau, M.; Hoffmann, N. The Paternò-Büchi reaction – Mechanisms and application to organic synthesis. *J. Photochem. Photobio. C: Photochem. Rev.,* **2017**, *33*, 83 – 108. https://www.sciencedirect.com/science/article/pii/S1389556717300886

(9) Bull, J. A.; Croft, R. A.; Davis, O. A.; Doran, R.; Morgan, K. F. Oxetanes: Recent Advances in Synthesis, Reactivity, and Medicinal Chemistry. *Chem. Rev.*, **2016**, *116*, 12150-12233. https://pubs.acs.org/doi/full/10.1021/acs.chemrev.6b00274

(10) Hoffmann, N. Photochemical Reactions as Key Steps in Organic Synthesis. *Chem. Rev.*, **2008**, *108*, 1052 – 1103. https://pubs.acs.org/doi/abs/10.1021/cr0680336?src=recsys

(11) (a) Prier, C. K.; Rankic, D. A.; MacMillan, D. W. C. Visible Light Photoredox Catalysis with Transition Metal Complexes: Applications in Organic Synthesis. *Chem. Rev.*, **2013**, *113*, 5322 – 5363. https://pubs.acs.org/doi/10.1021/cr300503r. (b) Shaw. M. H.; Twilton, J.; MacMillan, D. W. C. Photoredox Catalysis in Organic Chemistry. *J. Org. Chem.*, **2016**, *81*, 6898 – 6926. https://pubs.acs.org/doi/10.1021/acs.joc.6b01449

(12) For a recent examples of Cu-based photoredox catalysis, see: (a) Reiser, O. Shining Light on Copper: Unique Opportunities for Visible-Light-Catalyzed Atom Transfer Radical Addition Reactions and Related Processes. *Acc. Chem. Res.*, **2016**, *49*, 1990 – 1996. DOI: 10.1021/acs.accounts.6b00296. (b) Michelet, B.; Deldaele, C.; Kajouj, S.; Moucheron, C.; Evano, G. A General Copper Catalyst for Photoredox Transformations of Organic Halides. *Org. Lett.*, **2017**, *19*, 3576 – 3579. https://pubs.acs.org/doi/10.1021/acs.orglett.7b01518. (c) Minozzi, C.; Caron, A.; Grenier-Petel, J. C.; Santandrea, J.; Collins, S. K. *Angew. Chem., Int. Ed.*, **2018**, *57*, 5477 – 5481. DOI: 10.1002/anie.201800144. (d) Larsen, C. B.; Wenger, O. S. *Chem. – Eur. J.*, **2018**, *24*, 2039 – 2058. DOI: 10.1002/chem.201703602.

(13) Shields, B. J.; Kudisch, B.; Scholes, G. D.; Doyle, A. G. Long-Lived Charge-Transfer States of Nickell(II) Aryl Halide Complexes Facilitate Bimolecular Photoinduced Electron Transfer. *J. Am. Chem. Soc.*, **2018**, *140*, 3035 – 3039. https://pubs.acs.org/doi/10.1021/jacs.7b13281

(14) Lim, C.-H.; Kudisch, M.; Liu, B.; Miyake, G. M. C-N Cross-Coupling via Photoexcitation of Nickel-Amine Complexes. *J. Am. Chem.,* **2018**, *140*, 7667 – 7673. https://pubs.acs.org/doi/10.1021/jacs.8b03744

(15) Ravetz, B. D.; Wang, J. Y.; Ruhl, K. E.; Rovis, T. Photoinduced Ligand-to-Metal Charge Transfer Enables Photocatalyst-Independent Light-Gated Activation of Co(II). *ACS Catalysis*, **2019**, *9*, 200 – 204. https://pubs.acs.org/doi/full/10.1021/acscatal.8b04326#showReferences

(16) For recent examples where coordination of substrate enables selective excitation of the substrate-metal complex but bond formation does not occur at the coordinated atoms, see: (a) Huang, X.; Quinn, T. R.; Harms, K.; Webster, R. D.; Zhang, L.; Wiest, O.; Meggers, E. Direct Visible-Light-Excited Asymmetric Lewis Acid Catalysis of Intermolecular [2+2] Photocycloadditions. *J. Am. Chem. Soc.*, **2017**, *139*, 9120 – 9123. https://pubs.acs.org/doi/abs/10.1021/jacs.7b04363. (b) Skubi, K. L.; Kidd, J. B.; Jung, H.; Guzei, I. A.; Baik, M.-H.; Yoon, T. P. Enantioselective Excited-State Photoreactions Controlled by a Chiral Hydrogen-Bonding Iridium Sensitizer. *J. Am. Chem. Soc.*, **2017**, *139*, 17186 – 17192. https://pubs.acs.org/doi/10.1021/jacs.7b10586

(17) (a) Trecker, D. J.; Foote, R. S.; Henry, J. P.; McKeon, J. E. Photochemical Reactions of Metal-Complexed Olefins. II. Dimerization of Norbornene and Derivatives. *J. Am. Chem. Soc.,* **1966**, *88*, 3021-3026. https://pubs.acs.org/doi/abs/10.1021/ja00965a024. (b) Salomon, R. G.; Kochi, J. K. Copper(I) triflate: A superior catalyst for olefin photodimerization. *Tetrahedron Lett.*, **1973**, *14*, 2529 – 2532. https://www.sciencedirect.com/science/article/pii/S0040403901961970.

(18) Salomon, R. G. Homogeneous metal-catalysis in organic photochemistry. *Tetrahedron*, **1983**, *39*, 485 – 575. https://www.sciencedirect.com/science/article/pii/S0040402001918307

(19) (a) Salomon, R. G.; Folting, K.; Streib, W. E.; Kochi, J. K. Copper(I) catalysis in photocycloadditions. II. Cyclopentene, cyclohexene, and cycloheptene. *J. Am. Chem. Soc.,* **1974**, *96*, 1145-1152. https://pubs.acs.org/doi/abs/10.1021/ja00811a031. (b) Evers, J. Th. M.; Mackor, A. Photocatalysis (I) copper(I) trifloromethane sulphonate catalyzed photochemical reactions of unsaturated ethers and alcohols. *Tetrahedron Lett.*, **1978**, *19*, 821 – 824. https://www.sciencedirect.com/science/article/pii/S0040403901854071. (c) Sarkar, N.; Nayek, A.; Ghosh, S. Copper(I)-Catalyzed Intramolecular Asymmetric [2+2] Photocycloaddition. Synthesis of Both Enantiomers of Cyclobutane Derivatives. *Org. Lett.*, **2004**, *6*, 1903 – 1905. https://pubs.acs.org/doi/10.1021/ol049696h

(20) Salomon, R. G.; Kochi, J. K. Cationic Olefin Complexes of Copper(I). Structure and Bonding in Group Ib Metal-Olefin Complexes. *J. Am. Chem. Soc.*, **1973**, *95*, 1889-1897. https://pubs.acs.org/doi/abs/10.1021/ja00787a031

(21) Budzelaar, P. H. M.; Timmermans, P. J. J. A.; Mackor, A.; Baerends, E. J. Bonding in the ground state and excited states of copper-alkene complexes. *J. Organomet. Chem.*, **1987**, *331*, 397 – 407. https://www.sciencedirect.com/science/article/pii/0022328X87800116

(22) (a) Kutal, C. Use of Transition Metal Compounds to Sensitize an Energy Storage Reaction. *Adv. Chem. Ser.*, **1978**, *168*, 158 – 173. https://pubs.acs.org/doi/10.1021/ba-1978-0168.ch010. (b) Schwendiman, D. P.; Kutal, C. Catalytic role of copper(I) in the photoassisted valence isomerization of norbornadiene. *J. Am. Chem. Soc.*, **1977**, *99*, 5677 – 5682.

https://pubs.acs.org/doi/abs/10.1021/ja00459a025. (c) Schwendiman, D. P.; Kutal, C. Transition metal photoassisted valence isomerization of norbornadiene. An attractive energy-storage reaction. *Inorg. Chem.*, **1977**, *16*, 719 – 721. https://pubs.acs.org/doi/abs/10.1021/ic50169a047. (d) Onishi, M.; Hiraki, K. Phosphine steric effects on the catalytic activities of a few chloro(tertiary phosphine)copper(I) oligomers in photoisomerizations of norbornadiene and *trans*-stilbene. *Inorg. Chim. Acta.,* **1992**, *202*, 27 – 30. https://www.sciencedirect.com/science/article/pii/S0020169300853451. (e) Onishi, M.; Hiraki, K.; Itoh, H.; Eguchi, H.; Abe, S.; Kawato, T. Syntheses of new ferrocenylphosphinecopper(I) complexes and their application to the valence isomerization of norbornadiene to quadricyclane. *Inorg. Chim. Acta.,* **1988**, *145*, 105 – 109. https://www.sciencedirect.com/science/article/pii/S0020169300820150. (f) Borsub, N.; Chang, S. C.; Kutal, C. Ligand control of the mechanism of photosensitization by copper(I) compounds. *Inorg. Chem.*, **1982**, *21*, 538 – 543. https://pubs.acs.org/doi/10.1021/ic00132a015. (g) Fife, D. J.; Moore, W. M.; Morse, K. W. Photosensitized isomerization of norbornadiene to quadricyclane with (arylphosphine)copper(I) halides. *J. Am. Chem. Soc.*, **1985**, *107*, 7077 – 7083. https://pubs.acs.org/doi/abs/10.1021/ja00310a053. (h) Orchard, S. W.; Kutal, C. Photosensitization of the norbornadiene to quadricyclane rearrangement by an electronically-excited copper(I) compound. *Inorg. Chim. Acta.*, **1982**, *64*, L95 – L96. https://www.sciencedirect.com/science/article/pii/S0020169300902895. (i) Grutsch, P. A.; Kutal, C. Photobehavior of copper(I) compounds. Role of copper(I)-phosphine compounds in the photosensitized valence isomerization of norbornadiene. *J. Am. Chem. Soc.*, **1979**, *101*, 4228 – 4233. https://pubs.acs.org/doi/abs/10.1021/ja00509a031. (j) Grutsch, P. A.; Kutal, C. Use of copper(I) phosphine compounds to photosensitize the valence isomerization of norbornadiene. *J. Am. Chem. Soc.*, **1977**, *99*, 6460 – 4233. https://pubs.acs.org/doi/abs/10.1021/ja00461a059. (k) Franseschi, F.; Guardigli, M.; Solar, E.; Floriana, C.; Chiesi-Villa, A.; Rizzoli, C. Designing Copper(I) Photosensitizers for the Norbornadiene-Quadricyclane Transformation Using Visible Light: An Improved Solar Energy Storage System. *Inorg. Chem.*, **1997**, *36*, 4099 – 4107. https://pubs.acs.org/doi/abs/10.1021/ic9706156. (l) Sterling, R. F.; Kutal, C. Photoconversion of Norbornadiene to Quadricyclene in the Presence of a Copper(I) Carbonyl Compound. *Inorg. Chem.*, **1980**, *19*, 1502-1505. https://pubs.acs.org/doi/abs/10.1021/ic50208a016

(23) (a) Trofimenko, S. Polypyrazolylborates, a new class of ligands. *Acc. Chem. Res.*, **1971**, *4*, 17 – 22. https://pubs.acs.org/doi/abs/10.1021/ar50037a003. (b) Trofimenko, S. Polypyrazolylborates: Scorpionates. *J. Chem. Ed.*, **2005**, *82*, 1715 – 1720. https://pubs.acs.org/doi/abs/10.1021/ed082p1715

(24) Trofimenko, S. Recent advances in poly(pyrazolyl)borate (scorpionate) chemistry. *Chem. Rev.* **1993**, *93*, 943-980. https://pubs.acs.org/doi/10.1021/cr00019a006

(25) Eggleston, M. K.; McMillin, D. R.; Koenig, K. S.; Pallenberg, A. J. Steric Effects in the Ground and Excited States of Cu(NN)2+ Systems. *Inorg. Chem.* **1997**, *36*, 172-176. https://pubs.acs.org/doi/abs/10.1021/ic960698a

(26) Shaw. G. B.; Grant, C. D.; Shirota, H.; Castner Jr., E. W.; Meyer, G. J.; Chen, L. X. Ultrafast Structural Rearrangements in the MLCT Excited State for Copper(I) bis-Phenanthrolines in Solution. *J. Am. Chem. Soc.* **2007**, *129*, 2147-2160. https://pubs.acs.org/doi/abs/10.1021/ja067271f

(27) Gothard, N. A.; Mara, M. W.; Huang, J.; Szarko, J. M.; Rolczynski, B.; Lockard, J. V.; Chen, L. X. Strong Steric Hindrance Effect on Excited State Structural Dynamics of Cu(I) Diimine Complexes. *J. Phys. Chem. A*, **2012**, *116*, 1984-1992. https://pubs.acs.org/doi/10.1021/jp211646p

(28) TpCu can be synthesized via a salt metathesis reaction of $(CuOTf)_2$·PhMe and KTp or CuCl and KTp. See the SI for detailed preparation.

(29) Similar to methyl isobutyl ketone, see Figures 1 and 2 herein, 4-methyl acetophenone did not form an observed coordination compound with **TpCu**, and did not prevent the formation of **TpCu(Norb)** as examined by ^{1}H-NMR and electronic absorption spectroscopies.

(30) Attempted Paternò-Büchi 2+2 photocycloadditions using alkyl ketones carried out in ethereal solvents can undergo radical olefin addition in preference to cycloaddition, see: Reusch, W. A Stereospecific photochemical addition of acetone to norbornene. *J. Org. Chem.*, **1962**, *27*, 1882-1883. https://pubs.acs.org/doi/abs/10.1021/jo01052a505.

(31) For additional substrates that did not result in efficient oxetane formation, see Scheme S1 and S2 of the SI.

(32) For an alternative mechanistic proposal in line with our data involving a Cu(III)-oxametallacycle intermediate, please see the SI, Scheme S3.

(33) See the SI for full experimental data and details.

(34) For examples of spin-state determination in oxetane forming Paternò-Büchi reactions using stereochemistry of observed products, see: (a) Barltrop, J. A.; Carless, H. A. J. Organic photochemistry. XIII. Photocycloaddition of aliphatic ketones to .alpha.,.beta.-unsaturated nitriles. *J. Am. Chem. Soc.*, **1972**, *94*, 1951 – 1959. DOI: 10.1021/ja00761a027.; (b) Turro, N. J.; Wriede, P. A. The Photocycloaddition of Acetone to 1-Methoxy-1-butene. A Comparison of Singlet and Triplet Mechanisms and Singlet and Triplet Biradical Intermediates. *J. Am. Chem. Soc.*, **1970**, *92*, 320 – 329. DOI: 10.1021/ja00705a640.

(35) For examples of spin-state determination in cyclobutene forming 2+2 olefin photocycloadditions using stereochemistry of observed products, see: (a) Lewis, F. D.; Hirsch, R. H. Photochemical cycloaddition of singlet and triplet diphenylvinylene carbonate with conjugated dienes. *J. Am. Chem. Soc.*, **1976**, *98*, 5914 – 5924. DOI: 10.1021/ja00435a028.; (b) Caldwell, R. A.; Díaz, J. F.; Hrncir, D. C.; Unett, D. J. Alkene Triplets as 1,2-Biradicals: The Photocycloaddition of *p*-Acetylstyrene to Styrene. *J. Am. Chem. Soc.*, **1994**, *116*, 8138 – 8145. DOI: 10.1021/ja00097a022.

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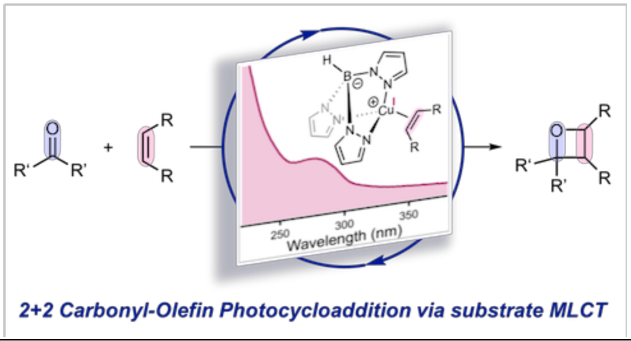

2+2 Carbonyl-Olefin Photocycloaddition via substrate MLCT