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Reductive functionalization of carbon dioxide to methyl acrylate at zerovalent tungsten[†]

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Alkali metal reduction of tungsten tetrachloride in the presence of excess trimethylphosphite and ethylene affords moderate yields of *trans*-tetrakis(trimethylphosphite)tungsten bis(ethylene). This easily prepared species bearing inexpensive ancillary ligands promotes the oxidative coupling of carbon dioxide and ethylene at ambient temperature to produce two isomeric tetrakis(trimethylphosphite)tungsten acrylate hydride complexes. These isomers vary by the κ^2 -O,O and κ^3 -C,C,O coordination mode of the acrylate ligand, and swiftly interconvert in solution as detected by 2D NMR spectroscopy. The CO₂-derived acrylate fragment may be released from the tungsten coordination sphere by treatment with methyl iodide to afford modest quantities of free methyl acrylate.

Introduction

The growing scarcity and expense of petroleum resources has motivated numerous endeavors to exploit renewable carbon sources in the production of industrially desirable chemicals.¹ Among these efforts, carbon dioxide has emerged as a promising small molecule carbon source owing to its incredible abundance, relative ease of transport and low toxicity.² Unfortunately, the substantial stability of CO2 has thus far limited its thermochemical utilization to a small set of commodities including urea, salicylic acid and carbonates,³ despite the feasibility of many other reductive functionalization reactions.⁴ The prospect of reducing CO₂ with light olefins to generate acrylates is one such example which has garnered attention since the early 1980s when Hoberg and Carmona reported some of the first carbon dioxide-ethylene couplings at zerovalent nickel and molybdenum species, respectively (Fig. 1).⁵

Acrylates are widely employed polar monomers integral to a range of materials applications, such as super absorbent polymers, and thus present alluring targets for CO₂ functionalization. However, among the now numerous transition metal complexes observed to mediate C-C bond formation between CO2 and ethylene,⁶ only a select few are known to produce acrylate structures.5b,7 Furthermore, liberation of CO2-derived acrylate products from these metal species has seen limited success. Carmona and co-workers have demonstrated that [(PMe₃)₂-(C2H4)MoH(CO2CH=CH2)]2 may be deprotonated by butyllithium to afford lithium acrylate,^{5b} and more recently Rieger and others found adding large excesses of methyl iodide to nickelalactone complexes produces 29-56% yields of methyl acrylate

Hoberg's CO2-Ethylene Coupling



Carmona's Acrylate Formation



Fig. 1 Reductions of CO₂ with ethylene reported by Hoberg and Carmona.

(Fig. 2).⁸ The extrusion of functionalized CO_2 from the nickel complex also represents one of the few cases where a late transition metallalactone has induced β -hydride elimination to create the salient C=C bond of acrylate.⁹ Our laboratory has recently investigated acrylate formation mechanisms at group VI metal centers which appear to engender more facile β-hydride elimination pathways.¹⁰ Herein we report the coupling of carbon dioxide with ethylene at a simple tungsten(0) complex and the subsequent extrusion of methyl acrylate derived from reductive CO₂ functionalization.

Experimental

General considerations

All manipulations were carried out using standard vacuum, Schlenk, cannula or glovebox techniques. Ethylene and carbon dioxide were purchased from Corp Brothers and stored over 4 Å molecular sieves in heavy walled glass vessels prior to use.

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Fig. 2 Methyl iodide induced β -H elimination and methyl acrylate liberation from nickelalactones.

Argon and nitrogen were purchased from Corp Brothers and used as received. WCl₄ was prepared according to literature procedures.¹¹ All other chemicals were purchased from Aldrich, VWR, Strem, Fisher Scientific or Cambridge Isotope Laboratories. Volatile, liquid chemicals were dried over 4 Å molecular sieves and distilled prior to use. Solvents were dried and deoxygenated using literature procedures.¹²

¹H, ¹³C, and ³¹P NMR spectra were recorded on Bruker DRX 400 Avance and 300 Avance MHz spectrometers. ¹H and ¹³C chemical shifts are referenced to residual solvent signals; ³¹P chemical shifts are referenced to an external standard of H₃PO₄. Probe temperatures were calibrated using ethylene glycol and methanol as previously described. ¹³ Unless otherwise noted, all NMR spectra were recorded at 23 °C. IR spectra were recorded using a Hewlett-Packard (Agilent) GCD 1800C GC-MS spectrometer. Elemental analyses were performed at Robertson Microlit Laboratories, Inc., in Madison, NJ or Atlantic Microlab, Inc., in Norcross, GA.

Preparation of trans-[P(OMe)₃]₄W(C₂H₄)₂ (2-C₂H₄)

A 100 mL heavy walled glass reaction vessel was charged with 0.245 g (0.76 mmol) of WCl₄, 0.281 g (2.26 mmol) of P(OMe)₃ and approximately 10 mL of tetrahydrofuran. The resulting mixture was stirred at ambient temperature for two days. The volatiles were removed to afford a dark solid presumed to be (P(OMe)₃)₂WCl₄. The material was rinsed with pentane. To this solid 15 mL tetrahydrofuran, 24.0 g (5.23 mmol) of 0.5% sodium amalgam and 0.216 g (1.74 mmol) of P(OMe)₃ were added. On a vacuum line approximately 20 equiv of ethylene were admitted at -196 °C. The reaction mixture was stirred at ambient temperature for two days. The volatiles were removed in vacuo from the dark solution. The residue was extracted with approximately 15 mL of diethyl ether and filtered through Celite. Removal of the ether and washing with 5 mL of hexamethyldisiloxane afforded 0.307 g (55%) of $2-C_2H_4$ as a light brown solid of good purity. Further purification may be conducted by recrystallization from pentane to yield nearly colorless flakes. Anal. Calcd for C16H44O12P4W: C, 26.10; H, 6.02. Found: C, 26.55; H, 5.76. ¹H NMR (23 °C, C₆D₆): δ 3.50 (br s, 36H, P(OCH₃)₃), 1.97 (quintet, 5.8 Hz, 8H, C₂H₄). ¹³C{¹H} NMR (23 °C, C₆D₆): δ 18.2 (C₂H₄), 51.4 (P(OCH₃)₃). ³¹P{¹H} NMR (23 °C, C₆D₆): δ 133.2 (s, ¹J_{W-P} = 411 Hz).

Preparation of [P(OMe)₃]₄W(CO₂CH=CH₂)H (2-C₃H₃O₂)

A 100 mL heavy-walled glass reaction vessel was charged with 0.142 g (0.193 mmol) of $2-C_2H_4$ and approximately 10 mL of diethyl ether. On a vacuum line approximately 20 equiv of CO₂ were admitted to the vessel at -196 °C. The resulting reaction

mixture was stirred at ambient temperature for two days to afford a pale orange solution. The volatiles were removed in vacuo and the residue rinsed with hexamethyldisiloxane, extracted with pentane and diethyl ether, and filtered through a Pasteur pipette. Chilling the orange solution at -35 °C for several days afforded 0.061 g (41%) of $2-C_3H_3O_2$ as a beige powder. Anal. Calcd for C15H40O14P4W: C. 23.95: H. 5.36. Found: C. 23.98: H. 4.93. κ^2 -2-C₃H₃O₂ isomer: ¹H NMR (23 °C, C₆D₆): δ -8.13 (tt, 13.1, 68.0 Hz, W-H), 3.66 (virtual t, 4.9 Hz, 18H, P(OCH₃)₃), 3.69 (d, 10.9 Hz, 18H, P(OCH₃)₃), 5.15 (dd, 2.1, 10.4 Hz, CO₂CH=CH₂), 5.89 (dd, 10.4, 17.3 Hz, CO₂CH=CH₂), 6.12 (dd, 2.1, 17.4 Hz, CO₂CH=CH₂). ¹³C{¹H} NMR (23 °C, toluene-d₈): δ 47.7, 48.2 (P(OCH₃)₃), 121.2 (CO₂CH=CH₂), 128.6 (CO₂CH=CH₂), 174.3 (CO₂CH=CH₂). ³¹P{¹H} NMR (23 °C, C₆D₆): δ 173.70 (t, ²J_{P-P} = 76 Hz, 2P, ¹J_{W-P} = 486 Hz), 149.41 (t, ${}^{2}J_{P-P} = 76$ Hz, 2P, ${}^{1}J_{W-P} = 486$ Hz). κ^{3} -2-C₃H₃O₂ isomer: ¹H NMR (23 °C, C₆D₆): δ -4.47 (quintet, 1H, W-H), 2.21 (br, 1H, CO₂CH=CH₂), 2.75 (br, 1H, CO₂CH=CH₂), 4.38 (br, 1H, CO₂CH=CH₂), 3.67 (br, 36H, P(OCH₃)₃). ¹H NMR (-60 °C, toluene-d₈): δ -4.69 (m, 1H, W-H), 2.19 (br, 1H, CO₂CH=CH₂), 2.73 (br, 1H, CO₂CH=CH₂), 4.33 (br dd, 8.5, 8.7 Hz, 1H, CO₂CH=CH₂), 3.09 (d, 9H, P(OCH₃)₃), 3.42 (d, 9H, P(OCH₃)₃) 3.50 (d, 9H, P(OCH₃)₃) 3.59 (d, 9H, P(OCH₃)₃). ¹³C{¹H} NMR (23 °C, toluene-d₈): δ 35.0 (CO₂CH=CH₂), 48.6 (P(OCH₃)₃), 49.8 (CO₂CH=CH₂), 179.0 $(CO_2CH=CH_2)$. ³¹P{¹H} NMR (23 °C, C₆D₆): δ 147.47 (br s, 4P). ${}^{31}P{}^{1}H{}$ NMR (-60 °C, toluene-d₈): δ 141.02 (m, 1P), 142.05 (m, 1P), 143.95 (m, 1P), 146.13 (m, 1P). IR for both isomers (KBr): $v_{C-O} = 1638$, 1618, 1367 cm⁻¹; $v_{13C-O} = 1621$, $1587, 1355 \text{ cm}^{-1}.$

Treatment of 2-C₃H₃O₂ with iodomethane

A J. Young NMR tube was charged with 0.020 g (0.027 mmol) of $2-C_3H_3O_2$ and approximately 400 µL of benzene-d₆. On a vacuum line, 5 equiv of methyl iodide were admitted at -196 °C *via* a calibrated gas bulb (85 torr in 28.9 mL). The reaction mixture was thawed, shaken and allowed to sit at ambient temperature for 2 days. The conversion of $2-C_3H_3O_2$ and methyl iodide to methyl acrylate was monitored by ¹H NMR spectroscopy *versus* an internal standard of hexamethyldisiloxane which indicated a yield of 31%. The identity of methyl acrylate was confirmed by GC-MS analysis of the reaction volatiles which afforded a *m*/*z* peak of 85 at a retention time identical to that of an authentic sample.

Results and discussion

Within the relatively few examples of CO₂-ethylene coupling to acrylates at transition metals, zerovalent molybdenum and



Fig. 3 Oxidative coupling of carbon dioxide and ethylene at molyb-denum(0) supported by trimethylphosphite ligands.

tungsten complexes have afforded some of the most promising examples reported thus far.^{5b,7,10} However, most of these complexes either require expensive phosphine ligands to stabilize the low-valent metal or produce functionalized carbon dioxide complexes in rather low total yields from the commercially available precursors. This has directed our efforts toward identifying easily prepared group VI metal complexes supported by simple, inexpensive donor ligands which could serve as more practical platforms to study the reductive functionalization of CO₂ to acrylates and methodologies for extrusion of the acrylate fragment. One complex which shares some of these desired features is trans- $[P(OMe)_3]_4Mo(C_2H_4)_2$ (1-C₂H₄) (Fig. 3) which was previously described by Galindo and co-workers in 1998.7b Encouragingly, complex 1-C₂H₄ mediates acrylate ligand formation upon treatment with carbon dioxide, but was itself synthesized in relatively low yield (~15%). We sought to leverage this attractive, inexpensive ancillary ligand by employing a tungsten metal center which should provide enhanced reduction potential for functionalizing carbon dioxide, possibly afford zerovalent metal ethylene compounds in greater yields and conveniently accommodate further study of acrylate liberation from the metal.

The tungsten congener of $1-C_2H_4$ was prepared by alkali metal reduction of WCl₄ in the presence of trimethylphosphite and excess ethylene (Fig. 4). Best results were obtained when WCl₄ was treated with trimethylphoshite in tetrahydrofuran to generate [P(OMe)₃]₂WCl₄ prior to addition of sodium amalgam, ethylene and more phosphite. Extraction of the reduction mixture with diethyl ether afforded trans- $[P(OMe)_3]_4W(C_2H_4)_2$ (2-C₂H₄) in moderate yield. Complex 2-C₂H₄ was characterized by a combination of combustion analysis and multinuclear NMR spectroscopy. ¹H NMR spectra of the bis(ethylene) species exhibited a quintet signal at 1.97 ppm (${}^{3}J_{P-H} = 5.8$ Hz) assigned to the protons of the bound olefin, with a corresponding ¹³C NMR resonance located at 18.2 ppm (confirmed by ¹H–¹³C HSQC NMR). Both these ¹H and ¹³C chemical shift values are typical of ethylene bound to zerovalent tungsten,^{7a} though slightly upfield of those reported for the molybdenum analogue, $1-C_2H_4$.^{7b}

Treatment of ethereal or hydrocarbon solutions of $2-C_2H_4$ with 1 atm of carbon dioxide over two days resulted in complete conversion to a mixture of two tungsten acrylate hydride isomers, [P(OMe)_3]_4W(H)(CO_2CH=CH_2-\kappa^2-O,O) and [P(OMe)_3]_4W(H)(CO_2CH=CH_2-\kappa^3-C,C,O) (collectively denoted $2-C_3H_3O_2$) (Fig. 5).¹⁴ The coupling reaction with $2-C_2H_4$ proceeded with no observable intermediates and with a qualitatively slower rate than $1-C_2H_4$, suggesting a sluggish ligand dissociation may be key to starting the reaction. The functionalized



Fig. 4 Preparation of tetrakis(trimethylphosphite)tungsten bis-(ethylene).

carbon dioxide products were isolated together as a beige powder from pentane or diethyl ether in modest yield, and were consistently obtained in an approximate 2 : 1 ratio over multiple synthetic trials, with [P(OMe)₃]₄W(H)(CO₂CH=CH₂- κ^2 -*O*,*O*) as the major species. The persistence of two isomeric forms of **2-C₃H₃O₂** hindered our ability to obtain single crystals of suitable quality for X-ray diffraction, and suggested that the two acrylate species may interconvert in solution. This prompted a series of isotopic labeling studies, infrared analyses and multidimensional/variable temperature NMR experiments to confirm the equilibration of the κ^2 and κ^3 coordination modes and verify the structural assignments.

The ambient temperature ¹H and ³¹P NMR spectra of 2-C₃H₃O₂ display multiple signals as expected for a mixture of two tungsten acrylate hydride species. In the upfield region of the ¹H NMR spectrum an apparent triplet of triplets resonance was observed at -8.13 ppm (${}^{2}J_{P-H} = 13.1$, 68.0 Hz) consistent with the metal hydride of κ^2 -2-C₃H₃O₂ coupling to two pairs of phosphorus nuclei (Fig. 6). Additionally, three downfield vinylic protons were observed, resonating at 5.15, 5.89, and 6.12 ppm, similar to the signals of free acrylic acid. A corresponding pair of triplet peaks observed at 173.70 and 149.41 ppm in the ³¹P NMR spectrum is also consistent with the proposed structure of κ^2 -2-C₃H₃O₂, and is analogous to the report of the isostructural molybdenum congener.7b In addition to these NMR signals for κ^2 -2-C₃H₃O₂, a second set of resonances were evident for the κ^3 -2-C₃H₃O₂ isomer. These included vinylic resonances observed at 2.13, 2.23, and 2.77 ppm and a metal hydride at -4.47 ppm. ¹H COSY NMR spectra indicated coupling between these vinylic peaks and the tungsten hydride, confirming that these resonances correspond to one isomer. The upfield shifting of the vinylic signals is consistent with olefin coordination to the metal.¹⁵ Notably, the κ^3 -2-C₃H₃O₂ resonances were all distinctly broadened with respect to those of the κ^2 -2-C₃H₃O₂ isomer, suggesting that κ^3 -2-C₃H₃O₂ may undergo an intramolecular process which interchanges the four P(OMe)₃ ligands (vide infra). This hypothesis is supported by the quintet splitting pattern (${}^{2}J_{P-H} = 49.0$ Hz) exhibited by the W-H signal and a broad singlet at 147.47 ppm observed in the ³¹P NMR spectrum (Fig. 6).

Variable temperature and two-dimensional exchange NMR spectroscopy were employed to assess the intra- and intermolecular dynamics of κ^2 -2-C₃H₃O₂ and κ^3 -2-C₃H₃O₂ in solution. ¹H NOESY NMR experiments (27 °C; mixing time 350 ms) exhibited exchange correlations between the two isomers' metal hydride and olefinic resonances.¹⁶ Additional exchange between



Fig. 5 CO₂-ethylene coupling at tungsten and isomerization of 2-C₃H₃O₂.



Fig. 6 Partial ¹H NMR spectrum of $2-C_3H_3O_2$.

the P(OMe)₃ signals was anticipated, but could not be resolved due poor signal separation. The observations clearly establish an isomerization between κ^2 -2-C₃H₃O₂ and κ^3 -2-C₃H₃O₂ at a rate slightly slower than the 1D NMR acquisition timescale. Acquiring 1D NMR spectra at lower temperatures in toluene-d₈ resolved and sharpened some of the resonances of κ^3 -2-C₃H₃O₂ while leaving those of κ^2 -2-C₃H₃O₂ essentially unchanged.¹⁵ At temperatures around -20 °C, the peaks of κ^3 -2-C₃H₃O₂ appear to undergo decoalescence, distorting the signals into broad, nearfeatureless peaks in the ¹H and ³¹P NMR spectra. At -60 °C, the resonances of κ^3 -2-C₃H₃O₂ sharpen considerably, and exhibit four separate doublet peaks in the P(OMe)₃ region of the ¹H NMR spectrum, confirming that all four phosphite ligands are inequivalent in the static structure. The concurrent observation of four multiplet signals in the ³¹P NMR spectrum supports this characterization. Additionally, the tungsten hydride signal observed in the ¹H NMR spectrum devolves into an unresolved multiplet, as may be anticipated for coupling with four inequivalent phosphorus nuclei with similar chemical shifts. Although a more detailed mechanism of the intramolecular dynamic process in κ^3 -2-C₃H₃O₂ cannot be made solely from the variable temperature NMR data, a rapid site change of the P(OMe)₃ ligands does appear to be the origin of its broadened spectral features.

Confirmation of the incorporation of carbon dioxide into $2-C_3H_3O_2$ was obtained by ¹³C isotopic labeling studies. Treatment of a benzene solution of $2-C_2H_4$ with one atmosphere of ¹³CO₂ afforded two enhanced resonances in the ¹³C NMR spectrum at 179.0 and 174.3 ppm assigned to κ^3 -2-C₃H₃O₂ and κ^2 -2-C₃H₃O₂, respectively. These assignments were established by a ¹H-¹³C HMBC NMR spectrum which showed correlation between the labeled carbons, the respective metal hydride and vinylic resonances. Incorporation of the ¹³C labels also altered to the bands in the infrared spectrum, shifting signals at 1638, 1618 and 1367 cm⁻¹ observed for unlabeled **2-C₃H₃O₂** to 1621, 1587 and 1355 cm⁻¹, respectively. The intense bands in the 1600–1650 cm⁻¹ region suggest that the carboxylates are not bound in bridging modes within dimeric structures.¹⁷ Additionally, the presence of four P(OMe)₃ ligands about each metal (as indicated by ¹H and ³¹P NMR spectroscopy) strongly implies that $2-C_3H_3O_2$ is monomeric as it is coordinately saturated.

The monomeric aggregation state of the molybdenum and tungsten acrylate species $1-C_3H_3O_2$ and $2-C_3H_3O_2$ differ from most of the other of group VI acrylate complexes reported, which typically adopt a dimeric form with a bridging acrylate ligand.^{5b,7a,10} The preference for the monomer may originate from the modest π -acid character of P(OMe)₃. The PMe₃-supported molybdenum and tungsten acrylate species have both



Fig. 7 Liberation of methyl acrylate from 2-C₃H₃O₂ using methyl iodide.

been crystallographically characterized as dimeric structures.^{5b} The modest back-bonding with P(OMe)₃ should strengthen the metal-ligand bond, preventing its loss (as observed for PMe₃; Fig. 1) and thus blocking access to a coordinatively unsaturated species necessary for a bridging acrylate. The modest steric perturbation of switching from the smaller PMe₃ to the larger P(OMe)₃ ligand may also influence the observed differences.¹⁸ Given the parallel in aggregation state of 1-C₃H₃O₂ and 2-C₃H₃O₂, the subtle variation in acrylate coordination mode between these two congeners was somewhat surprising. The spectroscopic data indicate that the tungsten acrylate complex can adopt a κ^2 -coordination mode identical to that described for molybdenum; however, an alternative κ^3 -coordination mode is sufficiently near in energy to permit its observation as the minor isomer of 2-C₃H₃O₂. In general, the κ^3 -acrylate coordination geometry is less common for transition metals compared to the κ^2 -mode.^{7a,19} Its presence here may originate from a competing preference to bind the π -acidic olefin ligand at the more reducing tungsten center.

Following the successful preparation of a CO₂-ethylene derived tungsten acrylate complex, our laboratory was eager to employ this easily prepared complex in studies to liberate a desirable acrylate product from the metal center. Given the strong oxophilicity of tungsten, this presented a considerable challenge. Fortunately, addition of a small excess of methyl iodide to the mixture of the 2-C3H3O2 isomers afforded quantities of methyl acrylate (Fig. 7). The yield of free methyl acrylate (judged by ¹H NMR) was comparable to those achieved by nickelalactone complexes, but under more mild additions of electrophile.⁸ Addition of greater excesses of methyl iodide did not significantly alter or improve the yield of acrylate product. As with the liberation for methyl acrylate from the nickel complexes, the tungsten species convert into an intractable mixture of organometallic products, including at least three metal hydride-containing species as observed by ¹H NMR spectroscopy.²⁰ The formation of methyl acrylate was confirmed by GC-MS and ¹³C isotopic labeling, using both ¹³CO₂ and ¹³CH₃I. Interestingly, while the doubly ¹³C-labeled experiment produced enhanced peaks in the ¹³C NMR spectrum for methyl acrylate (doublets at 166.4 and 51.4 ppm; ${}^{2}J_{C-C} = 2.6$ Hz), it also produced a second set of doublet resonances of comparable intensity at 174.2 and 56.6 ppm $({}^{2}J_{C-C} = 2.8 \text{ Hz}).^{15}$ The similarity of this second set of resonances to free methyl acrylate and the observation of C-C coupling suggests that one of the tungsten byproducts retains a methyl acrylate fragment, and the actual yield of methyl acrylate formed during electrophilic addition may be substantially higher than the 31% observed as free organic. However, attempts to liberate this second portion of methyl acrylate by carbon monoxide addition did not afford additional free acrylate. Similar attempts to liberate the carboxylate fragment by addition of alternative electrophiles including methyl triflate and trimethylsilyl iodide to $2-C_3H_3O_2$ did not afford detectable quantities (¹H NMR) of free acrylate. Although limited in yield, this example of obtaining free acrylate products from CO₂-ethylene coupling is one of rather few examples.

Concluding remarks

The direct coupling of carbon dioxide and ethylene at a transition metal to afford acrylate remains a challenging transformation, but one which offers promise for the chemical reduction of CO₂ to commodity chemicals. To date, most platforms which are known to mediate acrylate formation on group VI metals are somewhat limited from broader exploration by the poor yields of the necessary organometallic species or by the cost of the ancillary ligands. Since considerable advancements are still needed to master both acrylate formation at transition metals and their reductive removal to complete catalytic cycles, we have sought inexpensive, easily prepared acrylate complexes which are obtained from CO₂-ethylene coupling. Reported here is one such tungsten complex supported by trimethyphosphite ligands which functionalizes CO₂ to acrylate. In solution, the acrylate hydride complex 2-C₃H₃O₂ quickly interconverts between two isomeric forms as judged by 2D NMR spectroscopy. This equilibration affords access to both the κ^2 -O,O and κ^3 -C,C,O monomeric acrylate coordination modes, in contrast to observations made with the exact molybdenum congener as well as the closely related trimethylphosphine-tungsten counterpart. These finding suggests that the electrophilicity of the complex imparted by metal and ligand selection may be used to attenuate both the aggregation state and coordination mode of the functionalized CO₂ fragment. Such features should be of interest in the removal of acrylate products. Using 2-C₃H₃O₂, free methyl acrylate derived from CO2-ethylene coupling was obtained by treatment with methyl iodide. While the yields of functionalized CO₂ remain modest, the tungsten acrylate hydride species affords methyl acrylate in comparable quantities and with considerably milder additions of electrophiles than those obtained using late metal CO₂ activation agents. The electrophilic addition in this case as much slower than acrylate isomer interconversion, obscuring the role of acrylate coordination mode. In on-going investigations, our laboratory seeks to employ this readily accessible tungsten acrylate hydride complex in efforts to synthesize other CO2-derived acrylate products, identify the role that acrylate coordination mode may play in product removal, as well as

study reductive acrylate elimination techniques which may ultimately yield new catalytic CO_2 fixation methods.

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