Ancillary Ligand and Base Influences on Nickel-Catalyzed Coupling of CO_2 and Ethylene to Acrylate

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ABSTRACT: The coupling of CO_2 and ethylene to produce acrylates has been an area of increasing interest in recent years following a number of studies which have empirically improved catalytic turnover. Notably, the incorporation of moderately Brønsted and Lewis basic sodium phenoxide salts, as well as zinc dust, and Lewis acidic lithium salts were found to facilitate acrylate formation in batch catalysis. Despite these advances, there has been limited investigation into the effect of the catalyst ancillary ligand and phenoxide base structure on catalytic performance. Here, a collection of 1,2-bis(dialkylphosphino)benzene and related diphosphine ligands were used to show that the influence of steric environs has a marked effect on turnover. Ancillary diphosphine ligands featuring at least two smaller alkyl substituents are needed for strong activity, while the oft-used benzene annulation of the diphosphine does not appear to be determinant in achieving high turnover values. Additionally, the investigation of a collection of substituted sodium phenoxide bases suggests that a subtle balance of basicity and steric factors must be satisfied to obtain optimal catalytic performance. These trends appear to result from competitive, deleterious nucleophilic reactions between base and CO_2 to produce carbonate and the need to maintain sufficient basicity and access to the metal coordination sphere to drive the endergonic CO_2−ethylene coupling reaction.
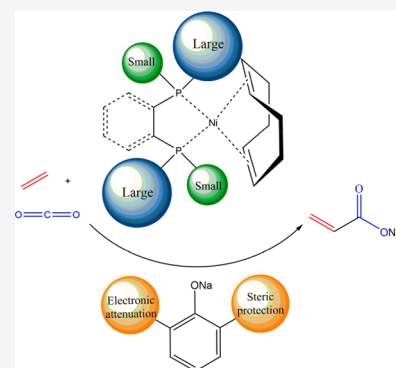
INTRODUCTION

Anthropogenic emissions of greenhouse gases such as carbon dioxide (CO_2) are recognized to have significant adverse effects on the environment and human health.[1] Furthermore, the increasing demand for petroleum-based materials as a primary carbon source is unsustainable, given the finite nature of these resources.[2] The utilization of CO_2 as a carbon feedstock is a promising, sustainable alternative to petroleum for the production of select commodity chemicals.[3] However, the thermodynamic and kinetic stability of CO_2 has limited its large-scale utilization as a carbon source.[3] Notable examples of industrial utilization involve coupling CO_2 with other small molecules such as amines, epoxides, and dihydrogen to yield urea, carbonates, and formates, respectively.[4] Another potential method of CO_2 utilization is its coupling with light olefins for the production of acrylates, a valuable group of commodity chemicals used in adhesives, fabrics, coatings, superabsorbent polymers, and detergents.[5]

Investigations into transition-metal-mediated acrylate synthesis from CO_2 first found promise in the 1980s following reports from Hoberg and Schaefer.[6] These initial findings were seminal in identifying a few zerovalent metal complexes capable of forming a C−C bond between CO_2 and ethylene.[7] The resulting nickelalactone was first characterized in 1983, but despite this progress, catalytic activity remained elusive for several decades. Only recently have low-valent group 10 metal species provided the first evidence for catalytic acrylate formation from CO_2−ethylene coupling.[8]

The first successful catalytic production of acrylate was achieved by Limbach and co-workers using a diphosphine nickel(0) complex in the presence of NaO^{t}Bu, resulting in a turnover number (TON) of 10. However, the catalytic cycle had to be divided into separate steps to prevent deleterious reactions between CO_2 and the strong base (Figure 1).[8] The
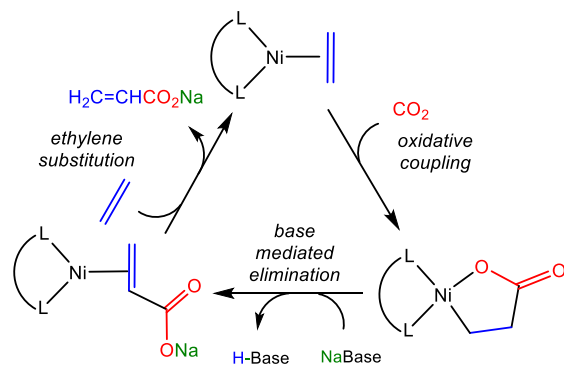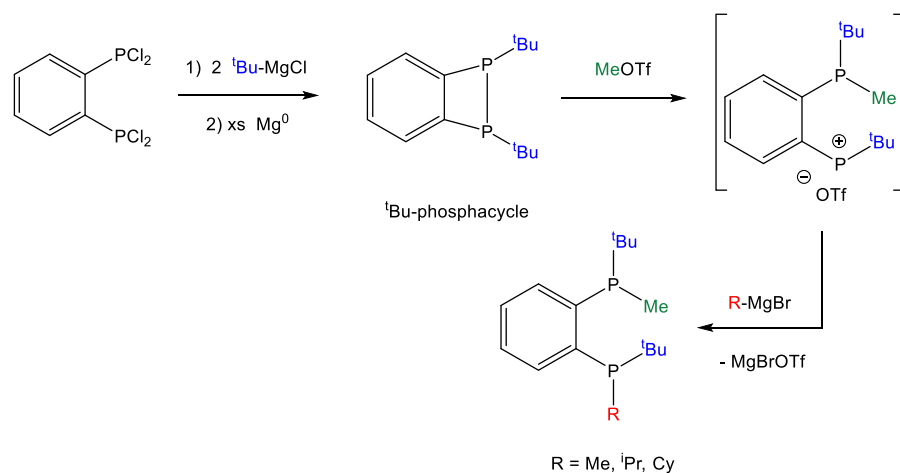

Figure 1. Proposed catalytic cyclic for CO_2−ethylene coupling in the presence of base.

Scheme 1. Synthesis of ᵗBu-phosphacycle and BenzP Derivatives

a. *Synthesis of BenzP ligand derivatives*

ᵗBu-phosphacycle

R = Me, ⁱPr, Cy

b. *Synthesis of Ni(0) complexes*

R = ⁱPr, Cy

R = ⁱPr (ⁱPrBenzP)Ni(COD) (45%)
Cy (CyBenzP)Ni(COD) (85%)
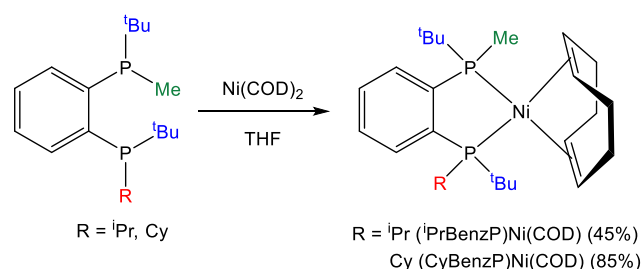
addition of exogenous base was crucial in allowing for the deprotonation of the Ni−lactone intermediate and driving the reaction thermodynamics to produce the more favorable sodium acrylate product (ΔG_{rxn} = −59 kJ mol^{-1}) as opposed to acrylic acid (ΔG_{rxn} = +79 kJ mol^{-1}).[9] Subsequent reports found that the utilization of weaker, less nucleophilic sodium phenoxide bases which react reversibly with CO_2 allowed for a one-pot synthesis to yield sodium acrylate with a TON of approximately 40.[10] This innovation provided a considerable improvement in the operation of the catalytic reaction, and TONs have been further enhanced via the addition of zinc dust, which presumably reduces off-cycle Ni(II) complexes and maintains high concentrations of the catalytically active Ni(0) species.[10] Additionally, advancements in the coupling of CO_2 and ethylene were aided by the discovery that Lewis acids can promote β-hydride elimination from Ni−lactones by destabilizing the nickel−carboxylate interaction. Collectively, all of these studies have led to the employment of three additives— phenoxide base, zinc dust, and Lewis acids—to achieve catalytic turnovers of greater than 400.[11]

Despite these substantial improvements in turnover, increases of many orders of magnitude are still required to become competitive with current industrial methods of acrylate production. A rational approach to this goal in catalyst development necessitates a better understanding of the complex interactions of the three additives with the catalyst. Herein, we report the development of a series of nickel catalysts for the coupling of CO_2 and ethylene to acrylate that are used to gain insight into the structure−reactivity relationships between catalyst architecture and phenoxide substituents.
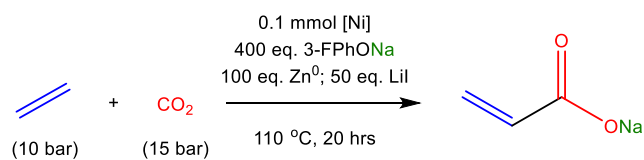
■ RESULTS AND DISCUSSION

To date, there have been relatively few investigations into the relationship between the catalyst or base structure and catalytic efficacy for CO_2−ethylene coupling.[8,10c] The primary focus of earlier investigations has been the empirical optimization of reaction conditions and additives.[8−11] One of the few systematic structure−reactivity studies examined the role of the hydrocarbon bridge on ancillary diphosphine ligands, which suggested that C_2 spacing groups are preferred for CO_2−ethylene coupling. In particular, rigid, nonrotating C_2 bridges, such as ortho-substituted arenes, proved optimal for acrylate formation.[10] The most productive catalyst systems to date are derived from the (R,R)-$(+)$-1,2-bis(*tert*-butylmethylphosphino)benzene (BenzP) ligand, which bears this feature. Additionally, the limited available catalytic data indicate that CO_2−ethylene coupling is best promoted by ligands which bear electron-donating alkyl groups, in lieu of more commonly available aryl phosphino groups. Given this limited prior art, our laboratory targeted a family of alkyl-substituted derivatives of the BenzP ligand in order to elucidate the steric preferences for Ni(0)-catalyzed acrylate formation.

Racemic BenzP ligand and its derivatives were prepared by the addition of methyl triflate to 7,8-diphosphabicyclo[4.2.0]-octa-1,3,5-triene, 7,8-bis(1,1-dimethylethyl) (ᵗBu-phosphacycle).[14] The resulting triflate salt was treated with alkylated Grignard reagent to yield the BenzP derivatives (Scheme 1a). A single isomer was observed in each case, and the relative configuration of the two ᵗBu−P substituents is proposed to be anti in analogy to several closely related species prepared via this method.[12] Attempts were made to further expand the diversity of racemic BenzP ligands by altering the substituents of the phosphacycle precursor. However, these attempts failed

in our hands, as we were unable to isolate any variants of the [t]Bu-phosphacycle. Despite this limitation, new racemic BenzP ligands were successfully prepared featuring isopropyl (1-(*tert*-butylmethylphosphino)-2-(*tert*-butylisopropylphosphino)-benzene ([i]PrBenzP)) and cyclohexyl (1-(*tert*-butylmethylphos-phino)-2-(*tert*-butylcyclohexylphosphino)benzene (Cy-BenzP)) phosphine substituents (Scheme 1a).

Zerovalent Ni complexes featuring the new BenzP derivatives were prepared by dropwise addition of a THF solution of [i]PrBenzP or CyBenzP to a THF solution of bis(1,5-cyclooctadiene)nickel(0) (Ni(COD)$_2$), affording golden colored samples of ([i]PrBenzP)Ni(COD) and (CyBenzP)Ni-(COD) for use in catalytic experiments (Scheme 1b). Both complexes exhibited two doublet signals in the ^{31}P NMR spectrum, as expected for the inequivalent substituents on the P atoms. The effectiveness of ([i]PrBenzP)Ni(COD) and (CyBenzP)Ni(COD) in CO$_2$−ethylene coupling was first benchmarked by comparison with (dicyclohexylphosphino)-ethane (dcpe)- and (dicyclohexylphosphino)propane (dcpp)-ligated catalyst variants. Both dcpe and dcpp ligands have been previously reported in Ni-catalyzed acrylate formation, though interestingly under our conditions the C$_3$-bridged dcpp proved to be slightly more active.[10c] Initial reaction conditions for CO$_2$−ethylene coupling experiments were derived from previously established protocols which include the presence of reducing zinc dust, Lewis acid lithium iodide, and sodium 3-fluorophenoxide (3-FPhONa) base.[11] These conditions and the resulting TONs for acrylate formation using a family of BenzP derivatives as well as dcpe and dcpp are described in Table 1.

Table 1. Comparison of Diphosphine Ni(0) Catalysts for Acrylate Formation[a]

entry	catalyst	TON[b]
1	(BenzP)Ni(COD)	82 ± 7.4
2	(CyBenzP)Ni(COD)	65 ± 7.2
3	([i]PrBenzP)Ni(COD)	60 ± 12.5
4	(dcpp)Ni(COD)	22 ± 5.1
5	([i]Pr$_4$BenzP)Ni(COD)	12 ± 2.8
6	(dcpe)Ni(COD)	6 ± 3.3

[a]Conditions: 0.1 mmol of catalyst, 40 mmol of 3-FPhONa, 10 mmol of zinc, 5 mmol of LiI, 10 bar of C$_2$H$_4$, 15 bar of CO$_2$, 25 mL of THF, 110 °C, 20 h. [b]The TON was determined by ^{1}H NMR analysis in an average of two to four trials.

In accord with prior findings, the (BenzP)Ni(COD) complex was considerably more effective than either (dcpp)-Ni(COD) or (dcpe)Ni(COD) under these reaction conditions, producing acrylate with an average of TON of 82 in comparison to 22 and 6, respectively (Table 1, entries 1, 4, and 6). Likewise, (CyBenzP)Ni(COD) and ([i]PrBenzP)Ni(COD) was more effective than the dcpe- and dcpp-ligated species, affording average TONs of 65 and 60 (entries 2 and 3). Additionally, a tetraisopropyl-substituted ligand variant, 1,2-bis(diisopropylphosphino)benzene ([i]Pr$_4$BenzP), recently reported by our laboratory yielded a TON of 12 (entry 5) under

these conditions. Examination of the data from these comparative catalytic experiments reveals some salient trends between ancillary ligand sterics and TON. Alteration of the top-performing BenzP by replacing one P−Me substituent with a P−Cy substituent in (CyBenzP)Ni(COD) (entries 1 and 2) yielded a small but distinguishable drop in productivity. Similar activity was observed by replacing the P−Me substituent with a P−iPr group, where ([i]PrBenzP)Ni(COD) afforded a TON of 60 (entry 3).

The poor performance of the ([i]Pr$_4$BenzP) ligand (Table 1, entry 5) also offers important insight into the structure−reactivity relationship. The net sterics of having four P−[i]Pr groups on the ligand may be considered similar to having a combination of two P−[t]Bu and two P−Me groups (i.e. BenzP), but the TONs are quite different. One possible explanation is the influence of exhibiting at least one (but preferably two) sterically accessible quadrants created by a P−Me substituent as seen in entries 1−3. These findings hint at a sterically sensitive relationship that underlies BenzP-ligated Ni complexes. Prior studies have also suggested that the rotationally constrained sp^2-linked C$_2$-bridged diphosphines of the BenzP derivatives may be significant to their strong catalytic performance. However, a comparison of entries 4−6 shows any effect from sp^2- versus sp^3-linked diphosphines is likely secondary to steric effects from the phosphine substitutents.[8,10] Overall, the data in hand indicate that preparation of sterically smaller variants of BenzP or diphosphino(ethane) complexes of nickel which maintain two sterically accessible quadrants would be advantageous for acrylate production. Efforts to prepare such species are underway in our laboratory (vide supra).

Multiple prior studies of CO$_2$−ethylene coupling have demonstrated a profound effect from varying the identity of the external base used to drive the catalytic reaction.[10c,11] Limbach et al. demonstrated that switching from NaO[t]Bu to weaker, less nucleophilic sodium phenoxide bases was pivotal in developing batch catalytic processes and improving TONs.[10e] The lower propensity of many sodium phenoxide bases to react with CO$_2$ to produce carbonates was suggested as the origin of the catalytic enhancement. The limited stability of the aryl carbonate species thus prevents complete deactivation of the required base, as was observed with NaO[t]Bu.

Despite indications that phenoxide bases are especially successful in mediating acrylate formation, systematic investigations into the steric and electronic influence of these bases in catalytic acrylate production have been limited.[10,11] To further probe relationships between base identity and acrylate production, a collection of phenoxide bases was employed in comparative catalytic experiments (Table 2). The sterically hindered, strong bases sodium hexamethyldisilazide (NaHMDS) and NaO[t]Bu, which were previously investigated in acrylate formation, were also included to benchmark the results for the phenoxide bases.[8] The pressure conditions used in Table 2 were reoptimized from the diphosphine Ni(0) comparison experiments (Table 1) and modified in order to minimize the mass of base required for each trial. The (BenzP)Ni(COD) catalyst was selected for the base comparison study, owing to its strong performance in Table 1 and its relative ease of synthesis. The change in conditions resulted in a modest increase in TON from 82 to 105 when 3-FPhONa was used (Table 1, entry 1, and Table 2, entry 4). As expected, the strong bases NaHMDS and NaO[t]Bu (entries 7

Table 2. Comparison of Exogenous Bases for Ni-Catalyzed Acrylate Formation[a]
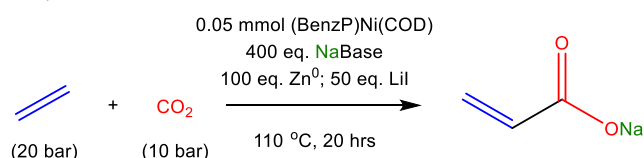
| entry	base	pK_a[b]	TON[c]
1	2,6-(^{i}Pr)$_2$PhONa	11.10	174 ± 9.2
2	2-ClPhONa	8.56	158 ± 9.5
3	2-Cl-6-MePhONa	9.71	111 ± 2.1
4	3-FPhONa	9.29	105 ± 9.9
5	2,6-(^{t}Bu)$_2$-4-MePhONa	12.20	88 ± 8.5
6	2,6-(Cl)$_2$PhONa	6.79	32 ± 9.9
7	NaO^{t}Bu	19.20	7[d]
8	NaHMDS	26	≤1[d]

[a]Conditions: 0.05 mmol of (BenzP)Ni(COD), 20 mmol of base, 5 mmol of zinc, 2.5 mmol of LiI, 20 bar of C_2H_4, 10 bar of CO_2, 25 mL of THF, 110 °C, 20 h. [b]pK_a listed for the conjugate acid.[13] [c]The TON was determined by ^{1}H NMR analysis in an average of two to six trials. [d]Data for a single trial.

and 8) provided only marginal performance in comparison to 3-FPhONa (entry 4), likely due to a deleterious side reaction between these bases and CO_2 (vide infra).

Comparing the monosubstituted phenoxides 3-FPhONa and sodium 2-chlorophenoxide (2-ClPhONa) (Table 2, entries 2 and 4) revealed an improved TON of 158 for the Cl-substituted variant. Further expanding the scope to disubstituted phenoxides (entries 1, 3, 5, and 6) produced a widely varied set of TONs. Table 2 ultimately reveals that there is not a direct relationship between the strength of the phenoxide bases (see the pK_a of conjugate acids; Table 2) and catalytic turnover. Indeed, there appear to be counterbalancing effects with respect to the characteristics of basicity and steric hindrance. A limited tolerance for more basic phenoxides can

be seen in comparing the TON of 32 (entry 6) for sodium 2,6-dichlorophenoxide (2,6-Cl$_2$PhONa) to the TON of 111 (entry 3) for sodium 2-chloro-6-methylphenoxide (2-Cl-6-MePhO-Na). These two phenoxides have relatively similar sterics but show a considerable enhancement for the more basic 2-Cl,6-MePhONa. However, this electronic effect is attenuated by steric influences on comparing the intermediate TON of 88 obtained from the dramatically more basic sodium 2,6-di-*tert*-butyl-4-methylphenoxide (2,6-(^{t}Bu)$_2$-4-MePhONa) (entry 5). We hypothesize that the immense steric protection of the basic O site inhibits the ability of 2,6-(^{t}Bu)$_2$-4-MePhONa to access the nickel complex. A slight reduction of the steric encumbrance in sodium 2,6-diisopropylphenoxide (2,6-(^{i}Pr)$_2$PhONa) (entry 1) provides a marked improvement with a TON of 174. This base appears to have met a preferred balance of being basic enough to deprotonate the Ni−lactone or related intermediate (Figure 1), while providing enough steric protection to limit nucleophilic attack on CO_2, all without obviating access to the nickel complex. Likewise, the high performance of the 2-ClPhONa base (entry 2) could originate from a subtle balance between limiting deactivation via carbonate formation and providing sufficient basicity.

The role of deleterious carbonate formation between phenoxide base and CO_2 was further probed by monitoring the catalytic reaction over several time points. This was particularly illustrative in the 3-FPhONa-mediated reaction, where ^{19}F NMR could be used to confirm the presence of various phenoxide-derived species and the corresponding carbonate is stable at ambient temperature.[10d] The results of this series of catalytic trials are illustrated in Figure 2. The production of acrylate appears to be swift over approximately the first 10 h of the reaction but decreases noticeably after that point. This decrease in catalytic activity over time appears to coincide with the accumulation of carbonate, which would deplete the concentration of base required to complete the reaction. However, it is also possible that the loss in catalytic activity is due to catalyst deactivation that simply allows for
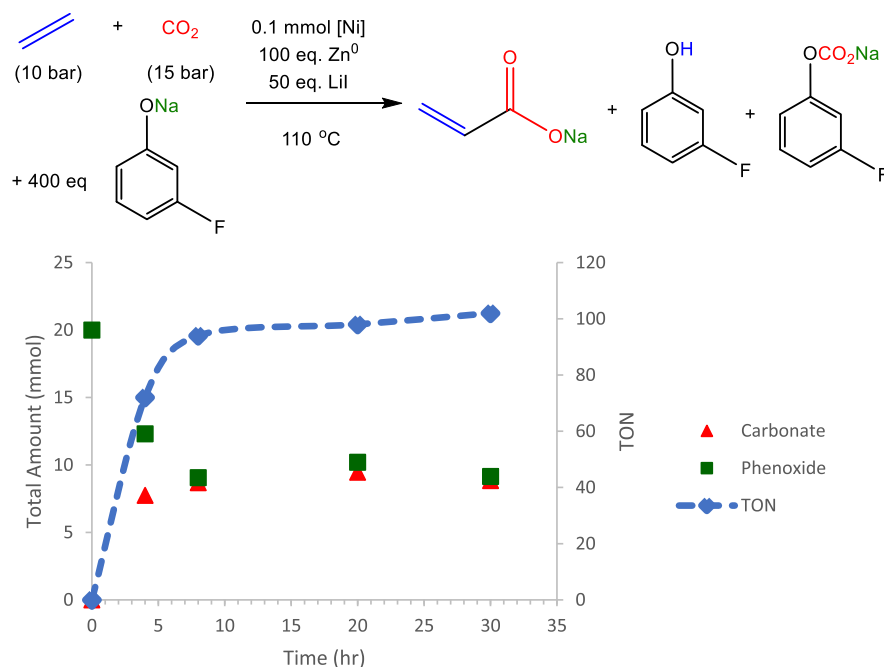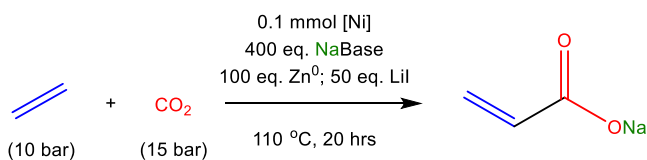

Figure 2. Plot of TON for acrylate production and total moles of 3-fluorophenol and 3-fluorophenylcarbonate vs time during a catalytic trial.

carbonate formation to outcompete acrylate production. To distinguish between these two hypotheses for activity loss, a sequential base addition study was performed using the 2-ClPhONa phenoxide. A reactor was charged with 400 equiv of phenoxide base and allowed to react under the conditions described in Table 2 for 20 h.

The reaction was then paused, and an additional 200 equiv of base was added before the reaction resumed for an additional 20 h. This resulted in a total TON of 245 for acrylate formation. The enhanced turnover (in comparison to 158; Table 2; entry 2) upon addition of a second fraction of base suggests that the nickel catalyst was still active after 20 h. Thus, the loss of acrylate production observed in Figure 2 likely results from base depletion. This is further supported by comparison to a catalytic trial in which all 600 equiv of 2-ClPhONa was added at the outset to afford only 163 turnovers, a conversion indistinguishable from that observed in Table 2.

The catalytic influence of steric and electronic effects from both the nickel catalysts and the phenoxide bases is evident from the results in Tables 1 and 2. However, there appears to be a balancing of these effects, which suggests that conclusions regarding the identity of the most effective phenoxide base for acrylate production may not be universally applied. For example, it is likely that certain "pairings" between catalyst ancillary ligand structure and base could reorder the trends observed in Table 2. To test for this possibility, a small set of comparative catalysis trials were conducted using the sterically and electronically dissimilar bases 2,6-(^{t}Bu)$_2$PhONa and 3-FPhNa, along with (CyBenzP)Ni(COD) and (BenzP)Ni-(COD) (Table 3). When 2,6-(^{t}Bu)$_2$PhONa was used instead

Table 3. Comparison of Stereoelectronic Influences between Base and Catalyst[a]

0.1 mmol [Ni]
400 eq. NaBase
100 eq. Zn^0; 50 eq. LiI
110 °C, 20 hrs

(10 bar) (15 bar)

entry	catalyst	base	TON[b]
1	(BenzP)Ni(COD)	3-FPhONa	82 ± 7.37
2	(CyBenzP)Ni(COD)	3-FPhONa	70 ± 0.71
3	(BenzP)Ni(COD)	2,6-(^{t}Bu)$_2$PhONa	33 ± 3.79
4	(CyBenzP)Ni(COD)	2,6-(^{t}Bu)$_2$PhONa	49 ± 4.24

[a]Conditions: 0.1 mmol of catalyst, 40 mmol of base, 10 mmol of zinc, 5 mmol of LiI, 10 bar of C$_2$H$_4$, 15 bar of CO$_2$, 25 mL of THF, 110 °C, 20 h. [b]The TON was determined by ^{1}H NMR analysis in an average of two to four trials.

of 3-FPhONa, the productivity of both catalysts decreased due to the greater steric limitation of the base. Interestingly though, the modest favorability for using (BenzP)Ni(COD) over (CyBenzP)Ni(COD) in the presence of 3-FPhONa is inverted with 2,6-(^{t}Bu)$_2$PhONa. The precise origins for this inversion in relative activity are not self-evident with the data in hand and may involve participation from the Zn or LiI additives required to achieve high conversion. Still, these observations serve as a caution regarding comparisons of relative catalytic activities when only a single base is used to benchmark the reaction.

■ CONCLUDING REMARKS

The series of diphosphine nickel catalysts prepared and investigated here illustrate the subtle and competing influences of both electronic and steric effects in CO$_2$−ethylene coupling to acrylate. These influences are important in both the ancillary phosphine ligand substituent as well as the substituent of the phenoxide bases typically used to drive the thermodynamics of acrylate production. The interplay of several factors complicates establishment of the broad structure−reactivity relationships required to rationally guide catalyst design. However, several features of a ligand and base selection can be gleaned from the data in hand. As diphosphine-supported nickel complexes are among the most studied promotors of CO$_2$-derived acrylate formation, it is useful to consider the four quadrants of the metal coordination sphere created by the four phosphorus substituents. On the basis of the trends observed here it appears that optimal catalysts maintain a relatively unhindered approach in at least two of the quadrants. Additionally, the activating influence of utilizing a benzene annulated diphosphine structure appears to be secondary to steric effects in comparison to other bulky diphosphine ligands with more flexible two-carbon bridges. Finally, the effect of the phenoxide base substituents should not be undervalued in optimizing reactivity. Optimization experiments must compare varied base electronic and steric effects for each new catalyst structure. Clearly, further efforts to expand the basis set for drawing structure−reactivity relationships are required to strengthen the effect of rational design for this class of catalysts, and such investigations are currently ongoing in our laboratory.

■ EXPERIMENTAL SECTION

General Considerations. All manipulations were carried out using standard glovebox, Schlenk, cannula, or vacuum techniques. Ethylene (dry) and carbon dioxide (laser-grade) were purchased from Airgas and used as received. All other chemicals were purchased from Fischer, Aldrich, Strem, VWR, or Cambridge Isotope Laboratories. Solvents were dried and deoxygenated according to literature procedures.[14] The ligand precursor 7,8-diphosphabicyclo[4.2.0]octa-1,3,5-triene, 7,8-bis(1,1-dimethylethyl) (^{t}Bu-phosphacycle) was prepared as previously described.[12] BenzP was prepared as previously described and obtained as a racemic mixture.[12] Nonvolatile solids were dried under vacuum at 50 °C overnight. ^{1}H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker 300 MHz DRX and 500 MHz DRX spectrometers at ambient temperatures. ^{1}H and ^{13}C chemical shifts were referenced to residual solvent signals; ^{31}P chemical shifts were referenced to an external standard of H$_3$PO$_4$. Probe temperatures were calibrated using ethylene glycol and methanol as previously described.[15] High-pressure catalytic hydrogenation reactions were performed using a Parr 5500 Series compact reactor with a 100 mL glass insert.

Preparation of 1,2-Bis(dialkylphosphino)benzene Complexes. A 20 mL scintillation vial was filled with 757 mg (3.00 mmol) 7,8-diphosphabicyclo[4.2.0]octa-1,3,5-triene, 7,8-bis(1,1-dimethylethyl) (^{t}Bu-phosphacycle), the solids were dissolved in 20 mL of dichloromethane, and the mixture was transferred to a 50 mL sealed glass reaction vessel. The yellow solution was cooled to −196 °C, and 3.30 mmol of methyl triflate was added via vapor-phase gas addition. The resulting light yellow solution was stirred at ambient temperature for 4 h. The solvent was removed under vacuum, leaving behind an oily, yellow residue. A 20−30 mL volume of Et$_2$O was added to the residue and cooled to −35 °C, at which point 3.15 mmol of the appropriate alkyl Grignard reagent was added. The resulting dark yellow solution was stirred at ambient temperature overnight. The solution was filtered through Celite in a Pasteur pipet, and the solvent was removed under vacuum. The resulting yellow solid was

dissolved in pentane and filtered through Celite in a Pasteur pipet. The pentane was removed under vacuum, leaving a thick oil that was pale yellow to colorless and was used without further purification. Isolated yields of ligands: CyBenzP, 68.0%; ^{i}PrBenzP, 74.5%.

Spectral Data for CyBenzP. ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −24.66 (d, J = 152.6 Hz), 1.19 (d, J = 152.6 Hz). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.10 (m, 18 H, P^{t}Bu-CH$_3$), 1.13 (s, 3 H, P-CH$_3$), 1.48 (m, 10 H, Cy-CH$_2$), 2.17 (m, 1H, PCy-CH), 7.13 (m, 2 H, Benz-CH), 7.43 (m, 1 H, Benz-CH), 7.48 (m, 1 H, Benz-CH). ^{13}C{^{1}H} NMR (500 MHz, C$_6$D$_6$): δ 6.19 (P-CH$_3$), 26.77 (PCy-CH$_2$), 27.36 (PCy-CH$_2$), 27.72 (P^{t}Bu-CH$_3$), 29.45 (P^{t}Bu-CH$_3$), 30.72 (P^{t}Bu-C), 30.99 (PCy-CH$_2$), 31.17 (P^{t}Bu-C), 31.43 (PCy-CH$_2$), 31.68 (PCy-CH$_2$), 34.23 (PCy-CH$_2$), 132.02 (Benz-CH), 132.40 (Benz-CH), 145.64 (Benz-C), 146.95 (Benz-C).

Spectral Data for ^{i}PrBenzP. ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ −25.44 (d, J = 151.2 Hz), 7.66 (d, J = 150.8 Hz). ^{1}H NMR (300 MHz, C$_6$D$_6$): δ 0.96 (dd, J = 6.9, 13.1 Hz, 3 H, P^{i}Pr-CH$_3$), 1.11 (m, 18 H, P^{t}Bu-CH$_3$), 1.17 (m, 3 H, P-CH$_3$), 1.27 (dd, J = 6.7, 13.9 Hz, 3 H, P^{i}Pr-CH$_3$), 2,25 (m, 1 H, P^{i}Pr-CH), 7.12 (m, 2 H, Benz-CH), 7.39 (m, 2 H, Benz-CH). ^{13}C{^{1}H} NMR (500 MHz, C$_6$D$_6$) δ 6.11 (P-CH$_3$), 21.85 (P^{i}Pr-CH$_3$), 22.02 (P^{i}Pr-CH$_3$), 22.78 (P^{i}Pr-CH$_3$), 27.67 (P^{t}Bu-CH$_3$), 29.17 (P^{t}Bu-CH$_3$), 31.00 (P^{t}Bu-C), 132.23 (Benz-CH), 146.08 (Benz-C), 146.70 (Benz-C).

Preparation of [1,2-bis(dialkylphosphino)benzene]Ni(COD) Complexes. A 20 mL scintillation vial was filled with 196 mg (0.71 mmol) of Ni(COD)$_2$, the solid was dissolved in 10 mL of THF, and the mixture was stirred for 10 min in order to fully dissolve the solid. In a separate vial, 0.71 mmol of 1,2-bis(dialkylphosphino)benzene ligand was dissolved in 5 mL of THF and added dropwise to the stirred nickel solution. The resulting dark brown solution was transferred to a 50 mL sealed glass reaction vessel and stirred at 50 °C overnight. The THF solvent was then removed under vacuum, and the resulting dark brown oil was dissolved in pentane and filtered through Celite in a Pasteur pipet. The filtrate was dried under vacuum, and the resulting dark golden brown solid was recrystallized in diethyl ether at −35 °C to afford the catalyst complex as a dark golden brown solid. Isolated yields of catalysts: (CyBenzP)Ni(COD), 85%; (^{i}PrBenzP)Ni(COD), 45%.

Spectral Data for (CyBenzP)Ni(COD). ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ 50.97 (d, J = 25.4 Hz), 71.81 (d, J = 25.4 Hz). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 1.01 (m, 18 H, P^{t}Bu- CH$_3$), 1.24 (m, 7 H, PCy-CH$_2$), 1.42 (d, J = 4.5 Hz, 3 H, P-CH$_3$), 1.53 (d, J = 11.0 Hz, 1 H, PCy-CH$_2$), 1.61 (d, J = 9.5 Hz, 1 H, PCy-CH$_2$), 1.85 (d, J = 13.0 Hz, 1 H, PCy-CH$_2$), 2.01 (apparent qt, J = 4.0, 12.8 Hz, 1 H, COD-CH$_2$), 2.16 (m, 1 H, COD-CH$_2$), 2.39 (m, 2 H, COD-CH$_2$), 2.56 (apparent qt, J = 3.8, 11.5 Hz, 1 H, PCy-CH), 2.81 (m, 2 H, COD-CH$_2$), 2.90 (td, J = 8.0, 4.0 Hz, 1 H, COD-CH$_2$), 3.13 (m, 1 H, COD-CH$_2$), 4.29 (m, 1 H, COD-CH), 4.52 (m, 2 H, COD-CH), 4.93 (apparent quintet, 1 H, COD-CH), 7.09 (m, 2 H, Benz-CH), 7.52 (m, 2 H, Benz-CH). ^{13}C{^{1}H} NMR (500 MHz, C$_6$D$_6$): δ 8.78 (P-CH$_3$), 26.69 (PCy-CH$_2$), 27.66 (P^{t}Bu-CH$_3$), 27. 52 (PCy-CH$_2$), 27.85 (PCy-CH$_2$), 28.07 (COD-CH$_2$), 29.03 (P^{t}Bu-CH$_3$), 29.31 (COD-CH$_2$), 30.06 (PCy-CH$_2$), 33.24 (P^{t}Bu-C), 36.86 (COD-CH$_2$), 37.59 (COD-CH$_2$), 38.24 (PCy-CH), 78.98 (COD-CH), 79.73 (COD-CH), 85.20 (COD-CH), 86.15 (COD-CH), 127.37 (Benz-CH), 127.84 (Benz-CH), 129.78 (Benz-CH), 130.66 (Benz-CH), 147.43 (Benz-C), 148.24 (Benz-C).

Spectral Data for (^{i}PrBenzP)Ni(COD). ^{31}P{^{1}H} NMR (300 MHz, C$_6$D$_6$): δ 50.87 (d, J = 25.3 Hz), 77.66 (d, J = 25.3 Hz). ^{1}H NMR (500 MHz, C$_6$D$_6$): δ 0.83 (dd, J = 7.1, 14.2 Hz, 3 H, P^{i}Pr-CH$_3$), 1.00 (m, 18 H, P^{t}Bu-CH$_3$), 1.41 (d, J = 4.8 Hz, 3 H, P-CH$_3$), 1.48 (dd, J = 7.0, 13.0 Hz, 3 H, P^{i}Pr-CH$_3$), 2.14 (m, 2 H, COD-CH$_2$), 2.39 (m, 2 H, COD-CH$_2$), 2.67 (apparent ddt, J = 7.0, 11.5, 14.0 Hz, 1 H, P^{i}Pr-CH), 2.79 (m, 2H, COD-CH$_2$), 2.86 (apparent td, J = 8.0, 15.5 Hz, 1 H, COD-CH$_2$), 3.09 (m, 1 H, COD-CH$_2$), 4.28 (m, 1 H, COD-CH), 4.50 (m, 2 H, COD-CH), 4.83 (apparent quintet, 1 H, COD-CH), 7.08 (m, 2H, Benz-CH), 7.42 (m, 1H, Benz-CH), 7.50 (m, 1H, Benz-CH). ^{13}C{^{1}H} NMR (500 MHz, C$_6$D$_6$): δ 8.76 (P-CH$_3$), 20.10 (P^{i}Pr-CH$_3$), 21.53 (P^{i}Pr-CH$_3$), 26.58 (P^{t}Bu-CH$_3$), 27.62 (COD-CH$_2$), 28.06 (P^{i}Pr-CH), 28.73 (COD-CH$_2$), 33.24 (P^{t}Bu-C), 36.82 (COD-

CH$_2$), 37.46 (COD-CH$_2$), 78.32 (COD-CH), 79.51 (COD-CH), 85.05 (COD-CH), 85.95 (COD-CH), 129.94 (Benz-CH), 130.05 (Benz-CH), 130.50 (Benz-CH), 130.60 (Benz-CH), 147.18 (Benz-C), 148.30 (Benz-C).

Preparation of Sodium Phenoxide Bases. A 20 mL scintillation vial was filled with 3.60 g (150 mmol, 1 mol equiv) of NaH and then quantitatively transferred to a 250 mL Schlenk flask via a THF slurry (40 mL). In a separate vial, 158 mmol (1.05 mol equiv) of freshly distilled liquid phenol was weighed out and then taken up into a 20 mL syringe. In the case of solid 2,6-^{t}Bu$_2$PhOH, the phenol was first dissolved in 50 mL of THF prior to being taken up in the syringe. The sodium hydride solution was cooled to 0 °C and the phenol added dropwise under a positive flow of argon. The solution was stirred overnight at ambient temperature, and then the solvent was removed under vacuum and the resulting oily solid triturated with 20−40 mL off Et$_2$O to remove residual THF. The solid product was dissolved in Et$_2$O and filtered through Celite. The Et$_2$O was removed under vacuum, and the solid was washed with cold pentane on a frit. The remaining bases were then recrystallized in Et$_2$O (with the exception of 2,6-^{i}Pr$_2$PhONa, which was recrystallized in THF layered with pentane).

General Procedure for Catalytic Acrylate Production Experiments. A stainless-steel autoclave reactor fitted with a glass insert was loaded with the appropriate amount of catalyst (0.1 or 0.05 mmol; 1 mol equiv), sodium phenoxide base (400 mol equiv), zinc dust (100 mol equiv), lithium iodide (50 mol equiv), and 25 mL of THF. The reactor was sealed under an inert atmosphere and removed from the glovebox. The contents of the reactor were stirred while the reactor was pressurized with ethylene followed by carbon dioxide. The reactor was heated to 110 °C for 20 h. Following the reaction period, the vessel was removed from the heating element, cooled in an ice−water bath for 30 min, and slowly vented to ambient pressure. The reaction residue was extracted with D$_2$O, and an internal standard of sodium sorbate was added. The organic-soluble species were removed by washing with Et$_2$O. Production of the acrylate salt was quantified by integration of the ^{1}H NMR spectrum.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.9b00708.

Selected NMR spectra, complete catalytic trial data, and additional experiment descriptions (PDF)

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Notes

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