Rh(III)-Catalyzed Coupling of N-Chloroimines with α-Diazo-α-Phosphonoacetates for Skeleton-Oriented Synthesis of 2H-Isoindoles

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A major hurdle for realizing the full potential of transition metal-catalyzed, directed C-H functionalization synthesis of heterocycles is the blocking of ability for designated structural elaboration by the reactivity-assisting group derived, unintended appendages. We communicate herein Rh(III)-catalyzed coupling of N-chloroimines with α-diazo-α-phosphonoacetates for skeleton-oriented synthesis (SOS) of 2H-Isoindoles. Comprehensive mechanistic studies with rhodacycle intermediates support an associative covalent relay mechanism for this first reported N-chloroimine-directed C-H functionalization reaction. The initial dechlorination/dephosphonation under Rh(III) catalysis and subsequent deesterification under Ni(II) catalysis allow the complete elimination of unintended appendages and full exposure of reactivity for C3 and N2 ring atoms. The proof of concept utility has been demonstrated with electrophilic substitution at the C3 site (formylation, azo derivatization) and nucleophilic reaction (methylation) at the N2 site, showcasing the enormous synthetic potential of SOS for attaching structurally unrelated appendages and enabling entry to distinct chemical space.

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Rh(III)-Catalyzed Coupling of $N$-Chloroimines with $\alpha$-Diazoo-$\alpha$-Phosphonoacetates for Skeleton-Oriented Synthesis of 2$H$-Isoindoles

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Abstract: A major hurdle for realizing the full potential of transition metal-catalyzed, directed C-H functionalization synthesis of heterocycles is the blocking of ability for designated structural elaboration by the reactivity-assisting group-derived, unintended appendages. We communicate herein Rh(III)-catalyzed coupling of N-chloroimines with α-diazo-α-phosphonoacetates for skeleton-oriented synthesis (SOS) of 2H-isoindoles. Comprehensive mechanistic studies with rhodacycle intermediates support an associative covalent relay mechanism for this first reported N-chloroimine-directed C-H functionalization reaction. The initial dechlorination/dephosphonation under Rh(III) catalysis and subsequent deesterification under Ni(II) catalysis allow the complete elimination of unintended appendages and full exposure of reactivity for C3 and N2 ring atoms. The proof-of-concept utility has been demonstrated with electrophilic substitution at the C3 site (formylation, azo derivatization) and nucleophilic reaction (methylation) at the N2 site, showcasing the enormous synthetic potential of SOS for attaching structurally unrelated appendages and enabling entry to distinct chemical space.
A central theme of organic synthesis is to provide well defined chemical space for the discovery of novel properties (e.g., for drug development). The chemical space can be accessed through either target-oriented synthesis (TOS) or diversity-oriented synthesis (DOS). TOS and DOS rely on efficient retro- and forward-synthetic planning, respectively, for achieving desired combination of molecular skeletons and appendages. In this regard, innovations in synthetic methodologies provide the key to the successful implementation of TOS and DOS. For reaction development, the creation of polarity and reactivity for a coupling site typically needs assistance from the neighboring groups. However, these groups, when installed in the product as unintended appendages, can be a major hurdle for further planning of structural functionalization and diversification, thus impeding the achievement of both TOS and DOS.

Transition metal-catalyzed directed C-H functionalization has recently emerged as a promising step-economic strategy for the synthesis of diverse range of structures. Heterocycles have been the center of focus in this nascent field for their role as privileged pharmaceutical scaffolds. Forward reactivity analysis, a process of streamlining multi-step reaction steps/pathways in silico based on projected matching of reactivity between directing groups and coupling partners, can instill an element of rationality into reaction design. However, this level of reasoning has not been routinely practiced in the context of appendage planning. Appendage planning should be an important guiding principle for reaction development as without this, the synthetic utility of painstakingly established protocols can be seriously compromised. Indeed, unintended appendages from the directing groups and/or coupling partners have been frequently stuck in the heterocyclic skeletons: they not only are relatively inert to designated transformations but also can completely block the inherent high reactivity of ring atoms. Considering the thoroughly demonstrated enormous synthetic power from the heterocyclic ring atoms, a synthetically useful approach to reaction
development is skeleton-oriented synthesis (SOS): SOS refers to a traceless appendage planning synthetic strategy for fabricating molecular skeletons without unintended appendages from the reactivity-assisting groups and using, subsequently, the reactivity of exposed ring atoms for attaching intended appendages.

We envisioned that Rh(III)-catalyzed coupling of N-chloroimines (N-chloroimine group is used herein for the first time for directed C-H activation) with α-diazo-α-phosphonoacetates would allow the achievement of SOS (Fig. 1): 1) the labile N(δ+)-Cl(δ-) bond from N-chloroimines could react intramolecularly with C(δ-)-P(δ+) bond in a regiochemically allowed, polarity-matched fashion, leading to the simultaneous formation of 2H-isoindoles and elimination of part of unwanted, reactivity-assisting appendages (Cl and phosphonate ester groups); 2) the remnant reactivity-assisting appendage carboxylate ester group could be facilely removed through metal-mediated decarbonylative protocols. Reaction development supports our conjecture and described herein is a SOS strategy for the construction of 2H-isoindoles based on initial Rh(III)-catalyzed dechlorinative/dephosphonative coupling of N-chloroimines with α-diazo-α-phosphonoacetates under NaOAc condition and subsequent Ni(II)-catalyzed deesterification processes. The 2H-isoindoles acquired thereof can be further elaborated, through exploitation of the reactivity of C3 site (electrophilic substitution: dimethylaminomethylidene derivatization and formylation; azo derivatization) and N2 site (nucleophilic reaction: methylation), for incorporating structurally distinct appendages and therefore accessing distinct chemical space.
Fig. 1 The SOS strategy for access to 2H-isooindoles.

Isoindoles are important structural moieties in biologically active molecules. For example, lenalidomide has been approved as a drug against multiple myeloma by the U.S. Food and Drug Administration (FDA) in 2004. Although various methods have been developed for the synthesis of isoindoles (e.g., reductive amination of phthalaldehydes, Diels-Alder reactions, retro-Diels-Alder reactions, intramolecular cyclization reactions), drawbacks are apparent, including complicated synthetic procedures, harsh reaction conditions, and limited substrate scope, etc. Rh(III)- and Ru(II)-catalyzed C-H activation has been recently explored as an alternative strategy to address these issues. Despite the effectiveness, all these protocols employ acrylates for either migratory insertion- or aza-Michael addition-enabled ring closure, thus inevitably leaving one or two unintended, recalcitrant carboxylate ester groups in isoindoles; due to extra carbon atoms between isoindole skeleton and ester groups, it is extremely challenging, if not impossible, to completely remove these appendages.

Results

Reaction development. We initiated the reaction development by screening experimental conditions for the coupling of N-chloro-1-phenylethan-1-imine (1a) with ethyl 2-diazo-2-(diethoxyphosphoryl)acetate (2a). Initial examination of the reaction in dichloroethane (DCE) at 80 °C under the catalysis of [RhCp*Cl2]2 (2

elimination of reactivity-assisting groups and unintended appendages

reactivity of ring atoms: attachment of intended appendages

Fig. 1 The SOS strategy for access to 2H-isooindoles.
mol %)/AgSbF$_6$ (8 mol %) and additional participation of 1 equiv. of either HOAc, AgOAc, LiOAc, NaOAc, KOAc, or CsOAc shows that basic condition is crucial and NaOAc is the best additive for transformation into expected dechlorinative/dephosphonative product, ethyl 3-methyl-2$H$-isoindole-1-carboxylate (3aa, 64% yield after 12 h). Virtually no conversion can be observed in the absence of either AgSbF$_6$ or NaOAc. A decrease or increase of the NaOAc quantity to 0.5 or 2 equiv. substantially retards the reaction. A switching of the solvent to either MeOH, trifluoroethanol (TFE), MeCN, 1,4-dioxane, or THF is not beneficial. The generation of a cationic Rh(III) catalyst is essential for the transformation; the reaction does not occur under [RhCp*(OAc)$_2$]$_2$ (2 mol %) but proceeds to the 79% 3aa yield under [RhCp*(MeCN)$_3$]$(SbF$_6$)$_2$ (4 mol %). The replacement of AgSbF$_6$ with either AgO$_2$CCF$_3$ or AgBF$_4$ identifies AgBF$_4$ as an even better halide abstraction reagent (84% 3aa yield). A negative control experiment under AgBF$_4$/NaOAc testifies the critical role played by [RhCp*Cl$_2$]$_2$. Further optimization of the [RhCp*Cl$_2$]/AgBF$_4$ quantity indicates that 1 mol %/4 mol % gives the best 3aa yield (91%).

**Substrate scope.** Under afore optimized reaction conditions, we then undertook an extensive survey of the substrate scope (Fig. 2). By fixing 2a as the coupling partner, the substrate scope of $N$-chloroimines was first investigated. The reaction proceeds well for $N$-chloroimines bearing both electron-donating (Me, 1b; Et, 1c; $^\text{‘}Am$, 1d; Ph, 1e; OMe, 1f) and electron-withdrawing (F, 1g; Cl, 1h; Br, 1i; I, 1j; CF$_3$, 1k; CN, 1l) groups at the para position of phenyl ring. The yields of 3ba, 3ea, and 3ga reach the impressive 98%, 95%, and 95%, respectively. A single-crystal X-ray diffraction of 3ga$^{34}$ unambiguously confirms the 2$H$-isoindole structure. **Meta** substitution, irrespective of its electronic character (Me, 1m; OMe, 1n; F, 1o; Cl, 1p; Br, 1q; CF$_3$, 1r), can be tolerated in general. Regiospecific coupling is observed for sterically more demanding substituents (1m, 1p, 1q, 1r) whereas regioisomers are identified for sterically less bulky ones (1n, 1o). **Ortho** substitution is also
synthetically compatible (F, 1s), albeit with a slightly lower yield compared to the *para* and *meta* counterparts. Di-substitution (1t) further hinders the reactivity. The alteration of imino C-Me group to either C-Et (1u), C-^n^Pr (1v), or C-Ph (1w) group results in a diminished yield, suggestive of a steric effect. The steric effect is more pronounced for a fused ring system (1x). Preliminary examination of the substrate scope for α-diazo-α-phosphonoacetates shows largely preserved reactivity for different acetate substituents (Me, 2b; tBu, 2c; Ph, 2d). With Ph as both imino C-substituent (1w) and acetate substituent (2d), the reaction proceeds to a comparable extent to that with either 1w and 2a or 1a and 2d as the reactants.

**Fig. 2** Substrate scope for the synthesis of 2H-isoindoles.  

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| 3aa | R1 = H, 91% |
| 3ba | R1 = Me, 98% |
| 3ca | R1 = Et, 52% |
| 3da | R1 = nAm, 83% |
| 3ea | R1 = Ph, 95% |
| 3fa | R1 = OMe, 56% |
| 3ga | R1 = F, 95% |
| 3ha | R1 = Cl, 84% |
| 3ia | R1 = Br, 87% |
| 3ja | R1 = I, 86% |
| 3ka | R1 = CF3, 76% |
| 3la | R1 = CN, 68% |
| 3pa | R1 = Cl, 51% |
| 3qa | R1 = Br, 78% |
| 3ra | R1 = CF3, 28% |

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*Conditions: N-chloroimine (0.2 mmol), α-diazo-α-phosphonoacetate (0.3 mmol), DCE (2 mL).*  
Yield of isolated product. *[^1]RhCp^*^Cl2^0 (1 mol %), AgBF4 (4 mol %).*  
[^2]AgSbF6 instead of AgBF4.

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Mechanistic studies and proposed catalytic pathway. With the substrate scope inspected, we then performed a comprehensive set of experiments to establish the reaction mechanism. A H/D scrambling experiment on 1a under standard catalytic conditions and with the extra addition of D source shows 14% D labeling at the ortho position of N-chloroimine group, supporting a directed C-H activation process (Supplementary Information). An intermolecular competition experiment on reaction between either 1b/1g or 1f/1g and 2a reveals no significant electronic preference for either electron-rich 1b and 1f or electron-poor 1g (product quantity ratio: 3ba/3ga = 1.4, 3fa/3ga = 1.4), providing evidence for a concerted metalation-deprotonation (CMD) C-H activation pathway. A kinetic isotope effect (KIE) experiment on reaction between 1a/1a-d5 and 2a furnishes a kH/kD value of 3.0, consistent with a turnover-limiting C-H activation step.

We further sought to delineate the reaction pathway by examining the reactivity of five-membered rhodacycles. A reaction between [RhCp*(MeCN)3](SbF6)2 and 1g under NaOAc in DCE, dichloromethane (DCM), or CHCl3 at room temperature (rt) affords the rhodacycle 1g-Rh-Cl35 (Fig. 3). In this case, rhodacycle-stabilizing ligand Cl- comes from DCE, DCM, or CHCl3. A switching of the solvent to either MeOH or THF mandates the addition of Cl- (e.g., from NaCl) for acquiring 1g-Rh-Cl. Further comprehensive experiments offer the following observations: 1) initial attempt at the stoichiometric reaction between 1g-Rh-Cl and 2a fails to deliver 3ga (eq. 1); 2) neither HOAc nor 1g is capable of changing the reaction outcome for 1g-Rh-Cl and 2a when added at the post-reaction stage (eqs. 2 and 3); 3) the reaction between 1g-Rh-Cl and 2a can proceed to the 3ga stage with the additional participation of 1g (eq. 4); 4) a reaction for 1g-Rh-Cl, 1a, and 2a gives a mixture of 3ga and 3aa (eq. 5); 5) although 1-phenylethan-1-one oxime (1y) does not react with 2a, it can effect the reaction between 1g-Rh-Cl and 2a (eq. 6); 6) 1g-Rh-Cl can efficiently
catalyze the reaction between 1g and 2a as well as between 1a and 2a (eqs. 7 and 8); 7) neither the stoichiometric reaction nor the catalytic reaction involving 1g-Rh-Cl (as well as 2a and 1g) can proceed without NaOAc (eqs. 9 and 10); 8) the rhodacycle 1h'-Rh-Cl (synthesized from [RhCp*Cl2]2 and 1h under NaOAc in DCE at 45 °C) (Fig. 4), with Cl portion of the N-chloroimine group removed, neither exhibits reactivity toward 2a (without or with the additional participation of 1h) (eqs. 15 and 16) nor catalyzes the reaction between 1h and 2a (eq. 17), which advocates the importance of Cl moiety of N-chloroimine group at the early stage of reaction pathway and is consistent with the proposal of P-Cl bond formation as a late-stage event; and 9) adventitious H2O is excluded as a necessary component for cleaving the C-P bond based on its negative effect on the transformation (eq. 11). Taken together, these observations are consistent with the following associative covalent relay mechanism (with 1a and 2a as the illustrative reactants) (Fig. 5): the reaction between 1a, [RhCp*Cl2], AgBF4, and NaOAc produces C-H-activated intermediate I; coordination of I with 2a furnishes Rh(III) carbene species II; OAc− coordination and 1,1-migratory insertion provides III; further coordination of III with 1a results in the formation of coordination site-exchanged species IV; C-H activation of coordinated 1a under the assistance of OAc− delivers V and HOAc; proto-demetalation of V with HOAc releases I and OAc−, and simultaneously initiates C-P/N-Cl bond cleavage and C-N/P-Cl bond formation/ring closure for the generation of 3aa (via tautomerization). In perspective, associative relay might be a prevalent operating mechanism in transition metal catalysis, especially for directed C-H functionalization reactions. It is speculated that many directing groups, along with the coupling partners, can trap transition metals in the non-reacting chelating states (e.g., III in Fig. 5); only via competitive binding from directing group of the next catalytic cycle, the final turnover steps can occur.
Fig. 3 Mechanistic studies involving 1g-Rh-Cl.
Mechanistic studies involving $\text{1h'}$-$\text{Rh}$-$\text{Cl}$.

**Fig. 4**

Proposed reaction mechanism.

**Fig. 5**
Reaction under acidic condition. An interesting finding for 1h'-Rh-Cl is its conversion, when reacting with 2a, to an isoquinolin-3(2H)-one derivative (3ha'), under HOAc (eq. 18). The same type of isoquinolin-3(2H)-one derivative (3ga') can be acquired starting from 1g-Rh-Cl (with 2a) (eq. 12). Reexamination of the reaction between either 1h and 2a or 1g and 2a shows the Rh(III)-catalyzed transformation to respective target product (3ha' or 3ga') under HOAc (eqs. 19 and 20). In addition, 1h'-Rh-Cl also allows catalytic access to 3ha' from 1h and 2a only under HOAc (eq. 21). Essentially, the NaOAc and HOAc processes are in direct competition with each other (eqs. 13 and 14): basic condition favors a late-stage N-Cl cleavage pathway, whereas acidic condition biases the reaction for an early stage N-Cl cleavage pathway.

Structural elaboration of 2H-isoindole skeleton. The goal of SOS is to construct molecular skeletons without undesired appendages from the reactivity-assisting groups and exploit the reactivity of ring atoms for further structural elaboration (Fig. 6). To this end, the ester groups on the C3 site of 2H-isoindoles should therefore be eliminated first. For proof-of-concept demonstration, 3wd was selected and subjected to deesterification reaction. The ester group can be removed to afford SOS target product 4 under Ni(OAc)₂/dcype/Ph₃SiH catalysis.³⁷ Unlike 3wd, 4 exhibits high reactivity at the C3 site, which also renders itself an unstable molecule against chromatography.³⁸ However, electrophilic substitution can proceed on 4 without purification. For example, reaction between the crude product of 4 and Vilsmeier reagent affords a C3-dimethylaminomethylidene derivative 5.³⁹ Hydrolysis of 5 in NaOH generates C3-formyl derivative 6.³⁹ 6 can be deprotonated at the N2 site with NaH and undergo further nucleophilic methylation with CH₃I to produce 7. Collectively, these transformations have allowed the complete erasure of any trace of original reactivity-assisting groups and installation of structurally completely unrelated appendages, thus offering an enabling tool for accessing distinct chemical space. As a second illustrative
example, 4 can also undergo initial azo derivatization at the C3 site and subsequent methylation at the N2 site, affording 8 and 9, respectively.

![Chemical structure](image)

**Fig. 6** Illustrative demonstration of SOS.

**Discussion**

In summary, we have developed herein a SOS strategy for 2H-isoindoles based on Rh(III)-catalyzed coupling of N-chloroimines with α-diazo-α-phosphonoacetates. The initial dechlorination/dephosphonation from the directing group-installed group and subsequent deesterification allow the full removal of unwanted appendages from the 2H-isoindole skeleton. The tremendous synthetic potential of SOS is exemplified by the ability to achieve electrophilic substitution and nucleophilic reaction at the C3 and N2 ring atoms for the installation of structurally distinct appendages. Given the generally high reactivity of ring atoms for heterocycles, SOS is expected to become an important guiding concept in future development of synthetically useful reactions for TOS and DOS applications.

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