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C–H and C–O oxidative addition in reactions of aryl carboxylates with a PNP pincer-ligated Rh(I) fragment†

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Reactions of a series of phenyl esters with a (PNP)Rh fragment have been studied. PhO_2CPh only underwent C–H oxidative addition (OA). PhO_2CCF_3 chiefly underwent acyl–oxygen OA. PhO_2CBu^t and PhO_2CNEt_2 initially underwent OA of an *ortho*-C–H bond of the phenyl group but continued thermolysis led to the phenyl–oxygen OA products.

Catalytic transformations of aryl halides that rely on the oxidative addition (OA) of a C_{Aryl}–halogen bond to a Ni(0) or Pd(0) center are among the most explored, useful, and celebrated reactions in chemistry.[1–3] The ability to perform similar reactions using ArO_2CR (O_2CR = carboxylate, carbamate, carbonate) instead of Ar–Hal is an attractive expansion because Ar–O_2CR substrates are easily prepared from phenols (Ar–OH). In addition, Ar–O_2CR groups may provide avenues for directing functionalization of the arene ring that are not accessible with aryl halides.[4]

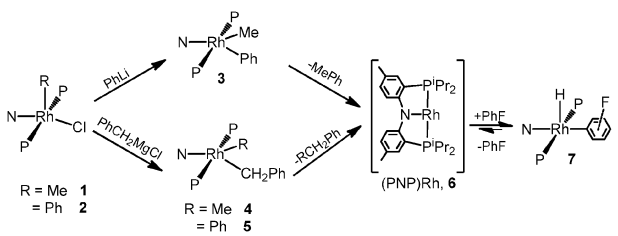
Coupling reactions of Ar–O_2CR and even other Ar–OR′ electrophiles have been successfully explored with Ni catalysts.[5–7] The interest in the use of Ar–O_2CR has increased significantly in the last few years, with reports on Suzuki–Miyaura coupling by Garg *et al.*,[8] Nakamura *et al.*,[9] Shi *et al.*,[10] and Snieckus *et al.*[11] and on aromatic amination by Chatani *et al.*[12] using aryl pivalates and carbamates. There is sound evidence indicating that C_{Aryl}–O_2CR OA is part of the catalytic cycle in these reactions,[8–13] however, authentic, well defined C_{Aryl}–O_2CR OA as an individual reaction has not been studied experimentally.[14]

Our group has been exploring[15] oxidative addition reactions of aryl halides with the T-shaped d^8 (PNP)Rh species **6** (Scheme 1) wherein the Rh center is locked into a rigid PNP pincer ligand framework (PNP = (4-Me-2-^{i}Pr$_2$P-C$_6$H$_3$)$_2$N).[16] The (PNP)Rh fragment **6** participates in reactions similar to those of L_nM^0 (M = Pd, Ni), despite possessing a different geometry and a different d-electron configuration. Recently, we have also explored catalysis of the arylation of aryl halides with a closely related (P^OC^OP)Rh fragment.[17] We became interested in whether such an Rh fragment can also undergo C_{Aryl}–O_2CR OA and here we disclose our results showing that it is indeed possible with (PNP)Rh.

The key fragment **6** cannot be isolated or observed because of its high reactivity.[15] We have devised two ways to access it in solution: (a) either by irreversible C–C reductive elimination (RE) or (b) by reversible dissociation from a placeholder ligand.[15] For (a), RE from **3**,[15c] **4** or **5** can be used to access **6** (Scheme 1), with **5** being conveniently isolable.

For (b), the weakest practical adduct of (PNP)Rh would be the one with a typical solvent. Thermolysis of **3** in fluorobenzene resulted in the formation of a product with an empirical formula of "(PNP)Rh(PhF)" (**7**, Scheme 1). In solution at ambient temperature, **7** is only stable in PhF as a solvent. It gave rise to a single ^{31}P NMR resonance at 20 °C at 52.4 ppm (d, J_{P-Rh} = 113 Hz) while no identifiable ^{19}F NMR or upfield hydride ^{1}H NMR resonance could be detected for **7**. However, upon cooling to −34 °C, a few ^{19}F NMR resonances in the −50 to −95 ppm range and a few broad ^{1}H NMR resonances in the −25 to −41 ppm range were detected.[18] It seems most likely that a rapid equilibrium between various isomers (including rotamers) of (PNP)Rh(H)(C$_6$H$_4$F) takes place, perhaps also involving a π complex of PhF. Caulton *et al.* reported that the ground state of (^{Si}PNP)Rh (where ^{Si}PNP = (^{t}Bu$_2$PCH$_2$SiMe$_2$)$_2$N) is an intramolecular C–H OA product that exists in equilibrium with a phenyl/hydrido "adduct" in benzene solution.[19] The X-ray structural determination on a crystal of **7** (see ESI†) revealed a fluorophenyl/hydride structure. No C–F OA was observed after thermolysis at 95 °C for 18 h in neat PhF.

We selected several Ar–O_2CR substrates for our study and monitored their reaction with **5** (Scheme 2) under mild thermolysis (60 °C, 2–3 h) by NMR spectroscopy *in situ*. These thermolytic conditions were needed to complete the C–C reductive elimination in **5**; the reaction of the presumed **6** so generated with the substrate was much faster as no intermediates were observed.



Scheme 1 Synthesis of various precursors to (PNP)Rh (**6**).

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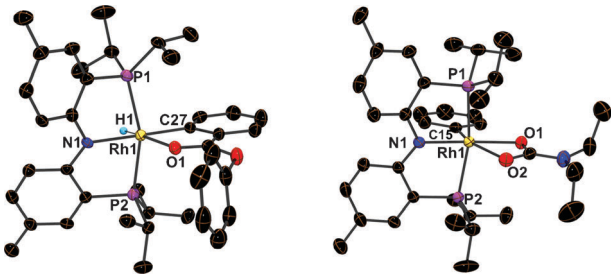
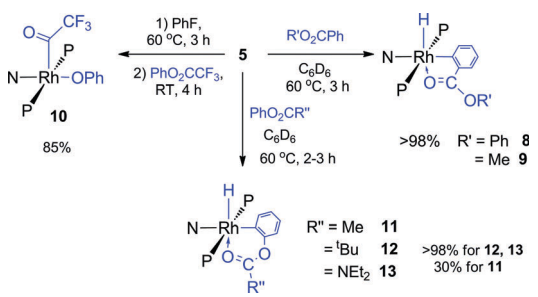


Fig. 1 ORTEP drawings of **8** (left, 50% thermal ellipsoids), and **15** (right, 30% thermal ellipsoids) showing selected atom labeling. Hydrogen atoms (except Rh–H) are omitted for clarity. Selected bond distances (Å) and angles (deg) for **8**: Rh1–P1, 2.301(4); Rh1–P2, 2.291(4); Rh1–N1, 2.128(5); Rh1–C27, 2.017(5); Rh1–O1, 2.264(4); Rh1–H1, 1.46 (5); P1–Rh1–P2, 160.40(7). **15**: Rh1–P1, 2.3061(13); Rh1–P2, 2.3215(12); Rh1–N1, 2.044(2); Rh1–C15, 2.016(3); Rh1–O1, 2.107(2); Rh1–O2, 2.279 (2); P1–Rh1–P2, 165.87(3).

The consumption of **5** in all reactions in Scheme 2 was complete. Compounds **8**, **10**, **12**, and **13** were also isolated in the pure solid form in 42–55% unoptimized yields. We were able to use (PNP)Rh precursors other than **5** for these syntheses (see ESI†).

The reaction of **5** with phenyl benzoate and, for comparison also with methyl benzoate, resulted in complete conversion to the C–H OA products **8** and **9**, respectively. The C–H OA took place exclusively at the *ortho*-position of the benzoate Ph ring, presumably favored by the coordination of the carbonyl oxygen.[21,22] Harsher thermolysis (100 °C, 18 h) of **8** or **9** did not result in any further transformations. We recently described[15a] analogous *ortho*-C–H OA taking place in nitroarenes and arenecarboxylic acid esters. The *ortho*-O chelated C–H OA products share common diagnostic spectroscopic features. For example, **8** gave rise to an ^{1}H NMR hydride resonance at δ −19.9 ppm as well as a $^{13}C\{^{1}H\}$ resonance at 181.0 ppm for the Rh-bound carbon, both of which manifested themselves as doublets of triplets (J_{H-Rh} = 35 Hz, J_{H-P} = 14 Hz; J_{C-Rh} = 28 Hz, J_{C-P} = 10 Hz). A single crystal X-ray diffraction study confirmed the structure of **8** (Fig. 1).[20] As expected, the carbonyl oxygen is coordinated to Rh, completing the d^6 Rh(III) octahedral coordination sphere.

We wondered if phenyl trifluoroacetate might be the most "aryl halide-like" in OA reactivity. However, the reaction of *in situ* generated **7** with it resulted in the acyl–oxygen OA main product **10**,[14] with no evidence for either aryl–oxygen OA or C–H OA (Scheme 2). The diagnostic ^{13}C NMR resonance for the Rh-bound acyl carbon at 191.9 ppm was observed as a doublet of triplets in the $^{13}C\{^{19}F,^{1}H\}$ NMR spectrum with



Scheme 2 Reactions of **5** with various esters.

J_{C-Rh} = 44 Hz and J_{C-P} = 9 Hz. IR spectroscopic analysis revealed a carbonyl stretching band at 1701 cm^{-1}.[23] These data are similar to those of other examples of trifluoroacetyl complexes of Rh as well as Pd/Pt/Ir.[24–26] Extended thermolysis of **10** led to a mixture of products that included (PNP)Rh(CF$_3$)(CO)(OPh)[27] and (PNP)Rh(CO),[28] indicating CO deinsertion as the major pathway of reaction for **10**, typical for late metal trifluoroacetyl compounds.[24,29]

We also tested phenyl acetate in the reaction with **5** (Scheme 2). A mixture of products was obtained, one of which we tentatively identified as **11** based on the solution NMR spectroscopic data. The presence of (PNP)Rh(CO) also indicated that decarbonylation was taking place, likely through intermediates analogous to those in the reactions of PhO_2CCF_3.

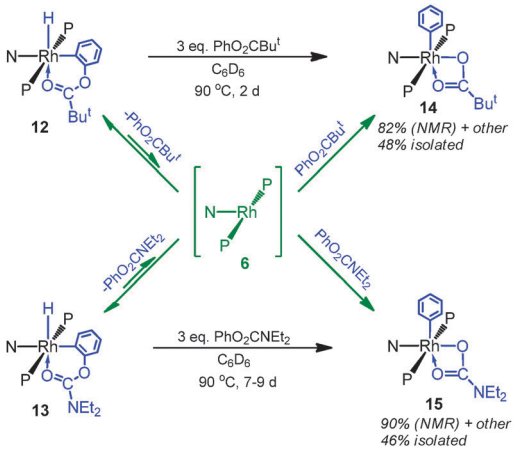
Finally, we turned to PhO_2CBu^t and PhO_2CNEt_2 as substrates, noting that aryl pivalates and carbamates were successfully used in Ni-catalyzed coupling reactions.[8–13] Mild thermolysis of **5** in the presence of PhO_2CBu^t and PhO_2CNEt_2 resulted in the quantitative formation of compounds **12** and **13**, respectively (Scheme 2). The diagnostic NMR spectroscopic features for **12** and **13** were similar to those of **8**/**9**. The immediate coordination environment about Rh is the same for **8**/**9** and **12**/**13**; but the κ^2-*C*,*O* chelate forms a five-membered ring in **8**/**9** and a six-membered ring in **12**/**13**.

We were pleased to find that thermolysis at 90 °C of **12** (2 d) and **13** (9 d) resulted in the conversion to the C$_{Aryl}$–O OA products **14** and **15**, respectively (Scheme 3). Isolation of analytically pure **14** and **15** was accomplished in 46–48% unoptimized yields. Interestingly, it was found (by NMR spectroscopy with an internal integration standard) that the yield of **14**/**15** was only *ca.* 50% if pure samples of **12**/**13** were thermolyzed in C_6D_6 to 100% conversion. The yield of **14**/**15** increased to 82–90% when the thermolysis was carried out in the presence of 3 equiv. of PhO_2CBu^t or PhO_2CNEt_2, respectively. The remainder of the fully consumed **12**/**13** gave rise to a mixture of unidentified products. We hypothesize that the reaction path from **12**/**13** to **14**/**15** involves intermediate liberation of PhO_2CBu^t or PhO_2CNEt_2 by C–H RE and an attack of **6** on the C$_{Aryl}$–O bond in the free substrate. In the absence of added extra substrate, the substrate concentration in solution is low and **6** may undergo unselective and irreversible attack on itself. The notion of intermediate liberation of PhO_2CBu^t or PhO_2CNEt_2 is consistent with the observation of a mixture of **14** and **15** when **12** is thermolyzed in the presence of PhO_2CNEt_2 or **13** in the presence of PhO_2CBu^t.[30]

Concerted RE from a six-coordinate d^6 metal center typically requires prior dissociation of one of the ligands.[22,31] In the case of **12**/**13**, this would necessitate dissociation of the O-donor as the first step. The longer time needed for the conversion of **13** is likely a reflection of the stronger donor power of the carbonyl oxygen in carbamate.

The solid-state structure of **15** was established in a single-crystal X-ray diffraction study (Fig. 1). The environment about Rh is distorted octahedral, with the acute bite angle of the κ^2-carbamate being the major source of deviation.

In summary, the outcome of the reaction of the (PNP)Rh fragment with Ph–O$_2$CR substrates is strongly dependent on the nature of R. It appears that a bulky and/or more electron-donating R group helps block the undesirable C$_{acyl}$–O OA and



Scheme 3 Formation of the aryl–oxygen OA products upon thermolysis at 90 °C. The proposed mechanistic path is shown in green.

channel the reaction towards C_{Aryl}–O OA. The competition between C_{acyl}–O and C_{Aryl}–O OA has been recognized before in the chemistry of Ni/Rh.[8a,13,24b] Our findings here also highlight C–H OA as another potential side reaction and illustrate that pivalate and carbamate may be particularly suitable for pursuing C_{Aryl}–O OA reactions regardless of the metal involved. We hope that the insight from this study with a well-defined (PNP)Rh fragment will help design and understand other systems as well.

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