Oxidative Addition of C–Cl Bonds to a Rh(PONOP) Pincer Complex

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ABSTRACT: Straightforward procedures for the generation of rhodium(I) κCl− chlorocarbon complexes of the form [Rh(PONOP−tBu)(κCl−CIR)][BArF_6] [R = CH_3Cl, Ar; Ph, 1; Cy, 2; tBu, 3; PONOP−tBu = 2,6-di-tert-butylphosphinophenitino]-pyridine; A = 3,5-bis(trifluoromethyl)phenyl] in solution are described, enabling isolation of analytically pure A and crystallographic characterization of the new complexes 1 and 2. Complex 1 was found to be stable at ambient temperature, but prolonged heating in chlorobenzene at 125 °C resulted in formation of [Rh(PONOP−tBu)(Ph)Cl][BArF_6] 4 with experimental and literature evidence pointing toward a concerted C(sp^3)−Cl bond oxidative addition mechanism. C(sp^3)−Cl bond activation of dichloromethane, chlorocyclohexane, and 2-chloro-2-methylpropane by the rhodium(I) pincer occurred under considerably milder conditions, and radical mechanisms that commence with chloride atom abstraction and involve generation of the rhodium(II) metalloradical [Rh(PONOP−tBu)(H)Cl][BArF_6] 6 are instead proposed. For dichloromethane, [Rh(PONOP−tBu)(CH_2Cl)Cl][BArF_6] 5 was formed in the dark, but facile photo-induced reductive elimination occurred when exposed to light. Net dehydrochlorination affording [Rh(PONOP−tBu)(H)Cl][BArF_6] 7 and an alkene byproduct resulted for chlorocyclohexane and 2-chloro-2-methylpropane, consistent with hydrogen atom abstraction from the corresponding alkyl radicals by 6. This suggestion is supported by dynamic hydrogen atom transfer between 6 and 7 on the ^1H NMR time scale at 298 K in the presence of TEMPO.

1. INTRODUCTION

The activation of organohalides by C−X bond oxidative addition to late transition metal complexes is a keystone organometallic transformation with diverse applications in catalysis.1 Despite economic and environmental imperatives for the use of chlorocarbons as substrates, the robust nature of C−Cl bonds remains a significant practical impediment, conferring attenuated or divergent reactivity compared to heavier halide counterparts.1,2 With respect to well-defined rhodium complexes, only a limited number of examples of C−Cl bond activation can be found in the literature, but the use of rigid mer-tridentate “pincer” ligands is an emerging trend (Scheme 1).3−5,8 These versatile ancillary ligands are evidently well-suited to supporting the reactive rhodium centers required to bring about cleavage of a C−Cl bond.13

The activation of aryl chlorides by rhodium(I) pincers is of particular interest for applications in catalysis14 and typically associated with transient three-coordinate rhodium(I) derivatives, for which concerted oxidative addition mechanisms that proceed with high selectivity over C−H bond activation have been substantiated by computational studies.15,16 A wider range of mechanisms have been proposed for the activation of alkyl chlorides, but classification is obfuscated by more facile entry into nucleophilic and radical oxidative addition manifolds. Indeed, most documented examples are based on reactions of square planar rhodium(I) chlorocarbon complexes (X = Cl in Scheme 1), where the stereochemistry of the oxidative addition can be masked in the product.5,6 As part of their work with rhodium(I) xantphos complexes, Estebueas and co-workers have examined the activation of a range of chlorocarbons by neutral square planar derivatives.5,7 In most cases, direct concerted oxidative addition was invoked, including aryl chlorides. Competitive nucleophilic oxidative addition was, however, suggested for dichloromethane to reconcile the formation of cis- and trans-rhodium(III) dichloride products. This S_n2 pathway has been proposed for the oxidative addition of dichloromethane to phosphate-based complexes of the form [Rh(PNP)Cl] by comparison to reactions with methyl iodide and studying the effect of the phosphate substituents on the reaction rate (Ph > iPr > tBu > Mes).8 Evidence for single-electron reactivity has also emerged for reactions of alkyl chlorides with rhodium(I) pincer complexes. For instance, a cascade of chloride abstraction and single-electron transfer steps is advocated by Hulley and co-workers to account for the formation of the methylene complex [Rh(POP−Bu)(CH_2)Cl] from the reaction between [Rh(POP−Bu)Cl] and K[B(C_3F_7)_4] in dichloromethane {POP−Bu = 4,6-di-tert-butylphosphinophenito}dibenz[o][b,d]furan.9

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Scheme 1. Oxidative Addition of C–Cl Bonds to Rhodium(I) Pincer Complexes

Scheme 2. Synthesis and Reactivity of 1a

Chart 1. Target rhodium(I) κCl-chlorobenzene complexes.

Analytically pure material of 1 was subsequently isolated in good yield (74%) after two consecutive recrystallizations from chlorobenzene/hexane, to perturb the equilibrium toward the desired product through removal of cyclooctadiene, and fully characterized (Figure 1).

Structural analysis of 1 in the solid state confirmed κCl-coordination of chlorobenzene (Figure 1). The metal adopts a pseudo square planar geometry, with the dative bound chloride atom associated with a distinctly non-linear N20Cl bond. Prolonged heating of 1 in chlorobenzene at room temperature unless otherwise stated, [Rh] = [Rh(PONOP- tBu)[POP-ArCl].

Facile ligand exchange (vide infra) limited analysis of 1 by NMR spectroscopy to data acquired using chlorobenzene as the solvent. Nevertheless, observation of time-averaged C2v symmetry indicates a highly fluxional structure and was found to be otherwise stable for extended periods of time in chlorobenzene at room temperature (no change after 3 days, light/dark). Prolonged heating of 1 (20 mM) in chlorobenzene at 125 °C did, however, result in smooth conversion into the rhodium(III) derivative [Rh(PONOP-tBu)(PhCl)][POP-Ar]2, which was obtained in a quantitative spectroscopic yield after 4 days. The reaction was unaffected by the addition of TEMPO as a radical scavenger. Complex 4 was subsequently isolated in 60% yield and fully characterized in solution and the solid state. In line with structurally related Rh(pincer) precedents,3,4 we propose that 4 is the product of a concerted—three-center-two-electron—oxidative addition of the C(sp3)−Cl bond (BDE = 400 kJ mol−1).29 Mechanistic work on the activation of aryl halides by Ozerov and co-workers points toward an early transition state for concerted insertion into the C(sp3)−Cl bond, and explicit isolation of the κCl-coordinated chlorobenzene adduct 1 supports this conclusion.
A square pyramidal metal geometry is observed for 4 in the solid state, with the aryl ligand in the apical position [Rh1-C2 = 2.029(5) Å] (Figure 1). In line with formation of a covalent bond and the increased oxidation state, the Rh1−C1 bond length [2.3158(13) Å] is contracted relative to 1 [2.3451(9) Å]. Complex 4 is stable in dichloromethane solution, with no onward reactivity detected after 24 h at room temperature (light/dark/presence of TEMPO). C2 symmetry is retained in CD2Cl2 solution, with a downfield doublet of triplet aryl 13C resonance at δ 141.9 (JRF = 34 Hz, JFC = 8 Hz) and the reduction of the JRF coupling constant from 136 to 103 Hz fully consistent with the assigned structure.21

Going forward, 1 proved to be the precursor of choice for synthesis of the other κ3Cl−chlorocarbon targets through ligand substitution. Notably, given the forcing conditions required to bring about the formation of 4, the chlorobenzene byproduct generated in this procedure is unlikely to participate in any further metal-based reactivity. Turning to the activation of homolytically weaker C(sp3)−Cl bonds, we next chose to re-examine the synthesis and reactivity of 4, first prepared by Weller and co-workers.10 Gratifyingly, dissolution of 1 (20 mM) in dichloromethane resulted in quantitative conversion into A upon mixing at room temperature (Scheme 3). Spectroscopic data agree with the literature (time averaged C2, symmetry; δ31P 204.5, 1JHPB = 136 Hz) and, in our hands, analytically pure material could be obtained by recrystallization from dichloromethane/hexane in 86% isolated yield. Samples of A prepared from CH2Cl2 are instantaneously converted into the d4-isotopologue upon dissolution in CD2Cl2 (20 mM) with concomitant liberation of CH2Cl. Otherwise, no appreciable onward reactivity was detected by 1H and 31P NMR spectroscopy when left to stand at room temperature in the light for 24 h. In the absence of light, however, 3% conversion to a new species characterized by a doublet 31P resonance at δ 182.0 with an appreciably reduced 1JHPB coupling constant of 104 Hz was observed under otherwise equivalent conditions. A follow-up experiment involving heating a 20 mM CD2Cl2 solution of A at 50 °C in the dark confirmed this onward reactivity, which was found to proceed with pseudo-first-order kinetics (τ1/2 = 14 h, Figure S32) and resulted in complete consumption of the rhodium(I) starting material within 96 h. Analysis of the resulting reaction mixture by 1H and 31P NMR spectroscopy indicated formation of an 8:2 mixture of organometallic species, which we ultimately identified as the rhodium(III) complex [Rh(PONOP-tBu)(CD2Cl)Cl][BARF6] d2-5 and the rhodium(II) metalloradical [Rh(PONOP-tBu)-Cl][BARF6] 6 (Scheme 3 and Figure 2).

Complex 5 is the PONOP pincer homologue of B (Scheme 1) and was isolated in highest purity by heating a 50 mM CH2Cl2 solution of A at 50 °C in the dark for 96 h (9:1 ratio of 5:6), followed by recrystallization from CH2Cl2/hexane at −30 °C in the dark (co-crystallization of 5:6 in a 9:1 ratio).22 This sample was sufficiently enriched in 5 to permit structural elucidation in CD2Cl2 solution by 1H, 13C, and 31P NMR spectroscopy (in the dark) despite contamination by paramagnetic 6. Complex 5 is characterized by C2 symmetry, with the coordination of the chloroalkyl ligand confirmed by a 2H triplet of doublet resonance at δ 5.65 (1JHH = 6.8, 2JHH = 3.4 Hz) and doublet of triplets 13C resonance at δ 48.1 (1JHC = 30, 2JCC = 5 Hz).23 Additionally, the 31P NMR signature (δ31P 181.9, 1JHPB = 104 Hz) is strikingly similar to 4 (δ31P 182.8, 1JHPB = 103 Hz). The proposed structure of 5 is further borne by crystallographic analysis of the co-crystalline mixture.

Scheme 3. Synthesis and Reactivity of A+4

Reactions in CH2Cl2/CD2Cl2 at room temperature unless otherwise stated, [Rh] = [Rh(PONOP-tBu)][BARF6].

Figure 1. Solid-state structures of 1 (left) and 4 (right) with thermal ellipsoids at 30% probability. Minor disordered components (Ph in 1) and anions omitted. Selected bond lengths (Å) and angles (°): 1, Rh1−Cl1, 2.3451(9); Rh1−Cl1−C2/C2A, 118.3(3)/117.8(4); Rh1−N20, 2.006(2); Rh1−P2, 2.2690(8); Rh1−P3, 2.2985(9); P2−Rh1−P3, 161.45(3); 4, Rh1−Cl1, 2.3158(13); Rh1−C2, 2.029(5); Rh1−C2−Cl1, 101.97(16); Rh1−N20, 2.020(4); N20−Rh1−Cl1, 168.21(13); Rh1−P2, 2.3386(12); Rh1−P3, 2.3338(13); P2−Rh1−P3, 161.92(5).
As for B, the solid-state structure of 5 is notable for the adoption of a square pyramidal metal geometry, with the chloroalkyl ligand in the apical position [Rh1−C2 = 2.079(4) Å] and the chloride projected over the pyridine donor [Cl1−Rh1−C2−Cl2 dihedral angle of 172.0(2)°]. Co-crystallization of B and 5 with structurally related [Rh(PNP-tBu)(H)Cl][BArF4] and 6, respectively, prevents meaningful analysis of their metrics and comparison to 4: an unusual and slightly disturbing coincidence.

Assignment of 6 as a metalloradical was informed by the detection of a very broad ¹H resonance at δ 25 during in situ analysis of the reaction of A with dichloromethane, the aforementioned work by Hulley and co-workers, and isolation of the PNP homologue [Rh(PNP-tBu)Cl][BArF4] C by Milstein and co-workers 15 years ago. Independent synthesis of purple 6 by one-electron oxidation of [Rh(PONOP-tBu)Cl] with Fe[BArF4] (E1/2 = −0.01 V vs Fe/Fe⁰, 48% yield; Fe = ferrocene) corroborates this assignment and enabled full characterization in solution and the solid state. No ³¹P resonance could be located for 6 between δ −600 and 600, but paramagnetically shifted tBu (δ 24.6), 3-py (δ 1.5), and 4-py (δ −17.3) resonances are evident in the ¹H NMR spectrum.

The crystal structure shows 6 with a square planar metal geometry and a Rh1−Cl1 bond length of 2.2956(6) Å that is considerably shorter than that observed in both the rhodium(I) precursor [2.3562(7) Å] and rhodium(III) aryl 4 [2.3158(13) Å, Figure 1]. This metric may help reconcile the short ensemble value for the Rh1−Cl1 bond in the co-crystalline sample of 5 and 6 [2.3032(9) Å] compared to that in 4 [2.3158(13) Å]. A less pronounced rhodium(I/II) contraction was observed for C [2.381(1)/2.332(1) Å] and attributed to enhanced chloride-to-rhodium π-donation.

Magnetic susceptibility measurements were performed to investigate the spin state of 6. Figure 3a shows the temperature dependence of dc magnetic susceptibility, χₐₙₐ(T), and the inverse dc magnetic susceptibility vs temperature, χ₋¹(T) for 6. The data were collected while cooling in an applied field, H, of 1 kOe. The solid line shows a fit using a Curie–Weiss law [χ₋¹(T) = C/(T − θ₀) + Χ₀] between 2 and 20 K. (b) Magnetization vs applied field for 6 at 5 K. The inset shows single quadrant M(H) curves at 1.8 [●], 3.5 [■], 5 [▲], and 10 K [●].

Figure 2. Solid-state structures of 5 (left) and 6 (right) with thermal ellipsoids at 30% probability. The former was established using a 9:1 co-crystalline sample of 5 and 6. CHCl₃ solvate (6) and anions omitted. Selected bond lengths (Å) and angles (°): 5, Rh1−Cl1, 2.3032(9); Rh1−C2, 2.079(4); C2−Rh1−Cl1, 88.72(12); Rh1−N20, 2.035(3); N20−Rh1−Cl1, 175.41(10); Rh1−P2, 2.3370(10); Rh1−P3, 2.3518(9); P2−Rh1−P3, 160.53(3); 6, Rh1−Cl1, 2.2956(6); Rh1−N20, 2.023(2); N20−Rh1−Cl1, 178.11(5); Rh1−P2, 2.3008(5); Rh1−P3, 2.3049(6); P2−Rh1−P3, 162.40(2).

Figure 3. (a) Temperature dependence of the dc magnetic susceptibility χₐₙₐ(T) [●] and the inverse dc magnetic susceptibility vs temperature χ₋¹(T) [○] for 6. The data were collected while cooling in an applied field, H, of 1 kOe. The solid line shows a fit using a Curie–Weiss law [χ₋¹(T) = C/(T − θ₀) + Χ₀] between 2 and 20 K. (b) Magnetization vs applied field for 6 at 5 K. The inset shows single quadrant M(H) curves at 1.8 [●], 3.5 [■], 5 [▲], and 10 K [●].

a spin S = 1/2 ion. Similar values have been reported for rhodium(II) in a square planar environment, including C. A Weiss temperature, θ₀, of +0.007(5) K is also consistent with the absence of magnetic order. Magnetization measure-
ments are linear in magnetic fields below 10 kOe with no hysteresis. Figure 3b shows a four quadrant $M(H)$ curve collected at 5 K. At higher fields, the magnetization tends to saturate. The inset of Figure 3b shows that 6 has a saturation moment of approximately 1.10(5) $\mu_B$ at 1.8 K, which is consistent with $S = 1/2$.

Mixtures of 5 and 6 (9:1 ratio, [Rh] = 20 mM) in CD$_2$Cl$_2$ remained unchanged (with no H/D scrambling of the methylene group) over 48 h at room temperature in the dark, indicating that the rhodium(III) complex is thermodynamically stable in solution. Upon exposure of the solution to light, however, complete reversion of 5 into A was observed within 4 h at room temperature (Scheme 3). This photoinduced reductive elimination process reconciles the apparent lack of reactivity of A when exposed to light in solution and suggests that the rhodium(I)–dichloromethane complex should be viewed as a photo-stationary rather than a thermodynamic ground state. To interrogate the mechanism associated with reversion of 5 to A, the experiment was repeated in the presence of TEMPO as a radical trapping agent. No reaction was apparent in the dark, but exposure to light resulted in complete conversion of 5 into 6 within 4 h at room temperature with contaminant generation of a species assigned as TEMPO–CH$_2$Cl. Control experiments involving heating isolated 6 in CD$_2$Cl$_2$ at 50 °C for 24 h in the presence or absence of light were conducted, but no onward reactivity of the metalloradical was detected. Based on these observations and recognizing that oxidative addition and reductive elimination processes follow the same pathway, we propose that 5 is the product of non-chain radical oxidative addition of the C(sp$^2$)–Cl bond (BDE = 338 kJmol$^{-1}$). Interpreted this way, the formation of 6 during the reaction is ascribed to incomplete recombination with the CHCl$_2^*$ radical. While it is currently unclear what organic byproduct is formed alongside 6, we note that thermolysis of A in the solid state (110 °C for 18 h) also gives a mixture of 5 and 6.

Moving on to examination of other alkyl chlorides, dissolution of 1 (20 mM) in chlorocyclohexane resulted in quantitative spectroscopic conversion into the corresponding rhodium(1) κ$_5$-bound complex 2 (time averaged C$_{2v}$ symmetry, $\delta_{31P}$ = 204.5, $J_{31P}$ = 138 Hz) upon mixing at room temperature (Scheme 4). Complex 2 is sufficiently stable at standing in chlorocyclohexane solution at room temperature for 24 h, partial conversion of 2 into the new rhodium(III) hydride [Rh(PONOP-Ph)(H)Cl][BAR$_2^+$] 7 (C$_s$ symmetry; $\delta_{31P}$ = 197.1, $J_{31P}$ = 100 Hz; $\delta_{\text{tol}}$ = -26.12, $J_{\text{tol}}$ = 42.3; $J_{\text{H}}$ = 10.6 Hz) was observed (ca. 10% conversion). Quantitative spectroscopic conversion into 7 and 1 equiv of cyclohexene was subsequently achieved within 24 h by heating 4 (20 mM) in chlorocyclohexane at 50 °C (Scheme 4). The dehydrochlorination was unaffected by the presence of light.

A considerably faster dehydrochlorination resulted when 1 (20 mM) was dissolved in 2-chloro-2-methylpropane. The putative κ$_5$-chlorocarbon complex 3 could not be detected and instead complete conversion into 7 and isobutene was observed upon mixing at room temperature (Scheme 5). This proved to be our method of choice for the preparation of 7, which was isolated as an analytically pure material in 87% yield following removal of volatiles and recrystallization from CH$_2$Cl$_2$/hexane. Crystals grown in this way were suitable for X-ray diffraction and the solid-state structure is fully consistent with our assignment (Figure 4). In particular, while requiring tight restraints, the hydride ligand was located off the Fourier difference map during the refinement. The component Rh–Cl bond length [2.3049(8) Å] is notably shorter than that in rhodium(III) aryl 4 [2.3158(13) Å] and approaching that observed in the rhodium(II) metalloradical 6 [2.2956(6) Å]. Indeed, we cannot exclude the possibility that the single crystal analyzed was free of co-crystallized 6.

Extrapolating from our mechanistic work with A, we propose that activation of chlorocyclohexene and 2-chloro-2-methylpropane involves homolytic cleavage of the C(sp$^3$)–Cl bonds (BDE = 356 and 352 kJmol$^{-1}$, respectively) through chlorine atom abstraction by the latent [Rh(PONOP)]$^+$ fragment, generating 6 and an alkyl radical. Compared to methyl chloride, the cyclohexyl and tert-butyl radicals are more thermodynamically stable (ΔH$^0$ = +117, +75, and +48 kJmol$^{-1}$, respectively) and characterized by considerably weaker C–H bonds (BDE = 427, 138, and 153 kJmol$^{-1}$, respectively). Informed by these data, we suggest that formation of 7 and alkene occurs by hydrogen atom abstraction from the alkyl radical, rather than direct C-radical recombinaction with 6 and β-H elimination. Supporting this hypothesis, addition of 0.5–2.0 equiv of TEMPO to 7 (20 mM) in CD$_2$Cl$_2$ resulted in hydrogen atom abstraction [BDE(O–H) = 292 kJmol$^{-1}$] and establishment of a dynamic equilibrium involving hydrogen atom transfer between 6 and 7 on the $^1$H NMR time scale at 298 K (400 MHz; Scheme 6). The latter is most notably evidenced by the presence of a broad 36H resonance at $\delta$ 13.2 (≈ equally weighted average of the tBu signals of 6 and 7), which was sharper with higher concentrations of added TEMPO (Figure S70). No hydrogen atom shuttling was observed when a 1:1 mixture of 6 and 7 in CD$_2$Cl$_2$ was prepared in the absence of TEMPO, confirming that the aminoxyl radical is required to mediate the process. Moreover, 40% conversion of 6 into 7 was observed after heating with 0.9 equiv of dihydroanthracene in CD$_2$Cl$_2$ at 50 °C for 2 weeks.

3. CONCLUSIONS

As a platform for investigating C–Cl bond activation reactions, we have developed operationally simple procedures for the generation of low-valent rhodium κ$_5$–chlorocarbon complexes of the form [Rh(PONOP-Ph)(κ$_5$-Cl)][BAR$_2^+$] (R = CH$_2$Cl, A; Ph, I; Cy, 2; tBu, 3) in solution. Notably, the

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**Scheme 4. Synthesis and Reactivity of 2**

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<th>[Rh]</th>
<th>CIPh</th>
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Reactions in CyCl at room temperature unless otherwise stated, [Rh] = [Rh(PONOP-Ph-Bu)][BAR$_2^+$].

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chlorobenzene derivative 1 was isolated by displacement of
cyclooctadiene from \([\text{Rh}(\text{PONOP-tBu})][\text{BAr}^4]_2\)
and serves as a well-defined precursor for the other
\(\kappa_{1,2}^1\)-chlorocarbon complexes through facile ligand substitution,
with only innocuous chlorobenzene as a byproduct. In this
way, the first rhodium(I) \(\kappa_{1,2}^1\)-complexes of chlorobenzene and
chlorocyclohexane have been isolated and structurally
characterized in the solid state by single-crystal X-ray
diffraction.

Complex 1 is stable under ambient conditions, but onward
C–Cl bond oxidative addition of chlorobenzene to the
rhodium(I) pincer affording \([\text{Rh}(\text{PONOP-tBu})(\text{Ph})\text{Cl}][\text{BAr}^4]_2\)
4 could be induced by prolonged heating in the
neat chlorocarbon at 125 °C (Scheme 7). This reaction
proceeded in one step and was unaffected by addition of
TEMPO. Informed by these reaction characteristics, literature
precedents, and the robust nature of the C(sp\(^2\))–Cl bond, we
propose that formation of 4 occurs by a concerted oxidative
addition mechanism. Consistent with their homolytically
weaker C(sp\(^3\))–Cl bonds, activation of dichloromethane (96
h at 50 °C in the dark), chlorocyclohexane (24 h at 50 °C),
and 2-chloro-2-methylpropane (<5 min at RT) by the
rhodium(I) pincer occurred under considerably milder
conditions and were rationalized by radical mechanisms that
commence with chloride atom abstraction and involve
formation of the rhodium(III) product \([\text{Rh}(\text{PONOP-tBu})\text{Cl}][\text{BAr}^4]_2\)
(Scheme 7). For dichloromethane, subsequent recombination of 6 with the\(\text{ICl}_2\) radical and
formation of the rhodium(III) product \([\text{Rh}(\text{PONOP-tBu})\text{Cl}][\text{BAr}^4]_2\) 5 is
masked by rapid photo-induced reductive elimination when the
reaction is conducted in the
light. The metalloradical 6 was directly observed as a minor
reaction component in the dark. Net dehydrochlorination
affording \([\text{Rh}(\text{PONOP-tBu})(\text{H})\text{Cl}][\text{BAr}^4]_2\) 7 and an alkene
byproduct resulted when 1 was dissolved in chlorocyclohexane
and 2-chloro-2-methylpropane. With these substrates, we
believe that hydrogen atom abstraction from the corresponding
alkyl radicals is considerably faster than C-radical
recombination with 6. This suggestion is supported by the
observation of dynamic hydrogen atom transfer between 6
and 7 on the \(^1\text{H}\) NMR time scale at 298 K in the presence of
TEMPO (Scheme 6).

4. EXPERIMENTAL SECTION

4.1. General Methods. All manipulations were performed in the
light under an atmosphere of argon using Schlenk and glovebox
techniques unless otherwise stated. Glassware was oven-dried at 150
°C overnight and flame-dried under vacuum prior to use. Molecular
sieves were activated by heating at 300 °C in vacuo overnight.
Anhydrous \(\text{CH}_2\text{Cl}_2\) and hexane were purchased from commercial
suppliers, freeze–pump–thaw degassed, and stored over activated 3 Å
molecular sieves. Chlorobenzene, chlorocyclohexane, 2-chloro-2-
methylpropane, and \(\text{CDCl}_3\) were freeze–pump–thaw degassed and
stored over activated 3 Å molecular sieves. 1,2-Difluorobenzene
was stirred over neutral aluminum oxide, filtered, dried over CaH\(_2\),
vacuum distilled, freeze–pump–thaw degassed, and then stored over
activated 3 Å molecular sieves.

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Organometallics XXXX, XXX, XXX–XXX
COD)\[BAr^F\]], was prepared from [Rh(COD)]\[BAr^F\] and PONOP-tBu\[Cl\] in 1,2-difluorobenzene using a procedure developed by our group.\(^7\) [Rh(PONOP-tBu)\[Cl\]] and Fc[BAr^F] were prepared using literature protocols. All other reagents are commercial products and were used as received. NMR spectra were recorded on Bruker spectrometers under argon at 298 K unless otherwise stated. Chemical shifts are quoted in parts per million, and coupling constants are given in hertz. Virtual coupling constants are reported as the separation between the first and third lines.\(^7\) NMR spectra in non-deuterated solvents were recorded using an internal capillary of C\(_6\)D\(_6\). High-resolution electrospray ionization mass spectrometry (HR-ESI-MS) spectra were recorded on a Bruker MaXis mass spectrometer. Microanalyses were performed by Elemental Microanalysis Ltd. Measurements of dc magnetization were performed using a Quantum Design MPMS-5S SQUID (superconducting quantum interference device) magnetometer. The powdered sample was immobilized in a small quantity of C\(_6\)D\(_6\) and was subjected to high-resolution NMR spectroscopy. Measurements of dc magnetic susceptibility, \(\chi_{\text{dc}}\) versus temperature, \(T\), were performed between 2 and 300 K in zero-field-cooled warming (ZFCW) and field-cooled cooling (FCC) modes in applied fields, \(H\), between 50 0e and 5 kOe. Magnetization versus field measurements were performed at fixed temperatures in magnetic fields between \(-50\) and 50 kOe.

4.2. NMR Scale Reaction of [(Rh(PONOP-tBu)]\[μ-η^2-η^2-COD)]\[BAr^F\]] with PhCl. To a J. Young’s valve NMR tube charged with [Rh(PONOP-tBu)]\[μ-η^2-η^2-COD)]\[BAr^F\]] (141.4 mg, 5.0 \(\mu\)mol) was added PhCl (0.5 mL). The resulting orange homogeneous solution was analyzed in situ using \(^1\)H and \(^31\)P NMR spectroscopy, with constant mixing at room temperature when not in the spectrometer. Liberation of COD and formation of [Rh(PONOP)]\(κ^3-Ciph)]\[BAr^F\]] [\(δ_{\text{1H}} \text{Ph} = 203.0\) (d, \(J_{\text{Ph}} = 136\))] were observed, with a 4:1 equilibrium mixture of 1 and [Rh(PONOP)\(κ^3-COD)]\[BAr^F\]] [\(δ_{\text{1H}} \text{Ph} = 202.3\) (d, \(J_{\text{Ph}} = 135\))] obtained after 6 h.

4.3. Preparation of [(Rh(PONOP-tBu)]\(κ^3-Ciph)]\[BAr^F\]]. To a flask charged with [(Rh(PONOP-tBu)]\(κ^3-η^5-η^5-COD)]\[BAr^F\]] (100.7 mg, 35.5 \(\mu\)mol) was added PhCl (10 mL) with vigorous stirring. The resulting orange solution was left to stand for 18 h at room temperature, and the analytically pure material obtained as orange crystals after two consecutive crystallizations from C\(_6\)H\(_6\)/hexane at room temperature. Yield: 77.4 mg (52.4 \(\mu\)mol, 74%). Crystals grown in this way were suitable for analysis by X-ray diffraction.

\(^1\)H NMR (400 MHz, PhCl; selected data): \(δ\) 8.04–8.10 (m, 8H, Ar\(^2\)), 7.43 (br, 4H, Ar\(^2\)), 6.12 (d, \(J_{\text{HH}} = 8.1\), 2H, 3-py), 0.91 (v, \(J_{\text{HH}} = 14.7\), 36H, tBu). No paramagnetic signals observed in the range \(-50\) to \(+50\) ppm.

\(^31\)P\(^1\)H NMR (162 MHz, PhCl): \(δ\) 203.0 (d, \(J_{\text{Ph}} = 138\)).
\( J_{\text{PB}} = 16.5, 18 \text{H}, \text{Bu}) \). No paramagnetic signals were observed in the range -50 to +50 ppm.

4.7. Preparation of [Rh(PONOP-Bu)(C\(_2\)H\(_5\)Cl)][BAR\(_2\)F\(_2\) A]
To a flask charged with [Rh(PONOP-Bu)](κ\(_3\)-C\(_3\)Ph)][BAR\(_2\)F\(_2\) (134.8 mg, 23.5 \text{\mu}mol) was added CH\(_2\)Cl\(_2\) (1 mL). The resulting orange solution was left to stand for 5 min at room temperature, and then the solution was exposed to light for 24 h.

4.8. Stability at 50 \(^\circ\text{C} \) in CD\(_2\)Cl\(_2\): A 20 mM solution of d\(_2\)-A (14.5 mg, 10.0 \text{\mu}mol) in CD\(_2\)Cl\(_2\) (0.5 mL) was prepared within a J. Young’s valve NMR tube in the dark at 50 \(^\circ\text{C} \) in the dark and monitored in situ using \(^{1}H \text{ and } ^{31}P \text{ NMR spectroscopy}. No significant onward reaction of d\(_2\)-A was apparent upon standing at room temperature for 24 h in the dark and periodically monitored in situ using \(^{1}H \text{ and } ^{31}P \text{ NMR spectroscopy}. The same outcome was observed when the solution was subsequently exposed to light for 24 h.

4.8.2. Stability at 50 \(^\circ\text{C} \) in CD\(_2\)Cl\(_2\): A 20 mM solution of d\(_3\)-A (14.5 mg, 10.0 \text{\mu}mol) in CD\(_2\)Cl\(_2\) (0.5 mL) was prepared within a J. Young’s valve NMR tube in the dark, heated at 50 \(^\circ\text{C} \) in the dark and monitored in situ using \(^{1}H \text{ and } ^{31}P \text{ NMR spectroscopy}. No significant onward reaction of d\(_3\)-A was apparent upon standing at room temperature for 24 h in the dark (orange solution).
4.10.2. Stability in the Presence of TEMPO in CD$_2$Cl$_2$. To a J. Young’s valve NMR tube charged with 9:1 mixture of RhH$_2$Cl$_2$ and TEMPO (1.6 mg, 10.2 μmol) was added CD$_2$Cl$_2$ (0.5 mL) at room temperature in the dark. The resulting solution was left to stand at room temperature for 24 h in the dark. No onward reaction was apparent from analysis in situ using $^1$H and $^{31}$P NMR spectroscopy. The solution was exposed to light, resulting in a gradual change in color from orange to deep red. Generation of a species assigned as TEMPO-CH$_2$-Cl ($\delta_{1H} = 6.6$ (s, OCH$_2$Cl), $\delta_{13}$C = 23.96 (vbr, fwhm = 600 Hz, tBu)) was observed within 4 h by $^1$H NMR spectroscopy.

4.11. NMR Scale Reactions of [Rh(PONOP-tBu)[Cl][BAR$_4$]]$_2$. 4.11.1. Stability at 50 °C in CD$_2$Cl$_2$. A 2:1 mM solution of 6 (14.5 mg, 10.3 μmol) in CD$_2$Cl$_2$ (0.5 mL) was prepared within J. Young’s valve NMR tube in the dark, heated at 50 °C in the dark, and periodically monitored in situ using $^1$H and $^{31}$P NMR spectroscopy at room temperature in the dark. No onward reaction was apparent after heating for 24 h (purple solution). The same outcome was observed when repeated in the presence of light.

4.11.2. Reaction with Dihydroanthracene. A solution of 6 (140 mg, 10.0 μmol) and 9,10-dihydroanthracene (1.6 mg, 8.9 μmol) in CD$_2$Cl$_2$ (0.5 mL) within a J. Young’s valve NMR tube was heated for 2 weeks at 50 °C. Partial conversion (40%) of 6 into [Rh(PONOP-tBu)[Cl][BAR$_4$]]$_2$ ($\delta_{1H} = 26.23 (d, J_{tBu} = 41.9, J_{RhH} = 9.9, J_{RhH} = 197.8 (d, J_{tBu} = 102))$, with concomitant generation of anthracene ($\delta_{1H} = 8.47 (s, 2H); red/purple solution) was observed.

4.12. Preparation of [Rh(PONOP-tBu)(Cl)$_2$(Cly)][BAR$_4$]$_2$. To a flask charged with [Rh(PONOP-tBu)(Cl)$_2$(Cly)][BAR$_4$]$_2$ (1.84 mg, 12.5 μmol) was added CyCl (0.5 mL). The resulting orange solution was left to stand at room temperature for 5 min before the volatiles were removed in vacuo to afford the analytically pure product as a yellow powder. Yield: 14.6 mg (9.8 μmol, 79%). Crystals suitable for analysis by X-ray diffraction were grown from CyCl/hexane at room temperature.

4.13. NMR Scale Reactions of [Rh(PONOP-tBu)(Cl)$_2$(Cly)][BAR$_4$]$_2$. 2. Reactions were performed within J. Young’s valve NMR tubes using 20 mM solutions of 2 (14.8 mg, 10.0 μmol) in CyCl (0.5 mL) and monitored in situ using $^1$H and $^{31}$P NMR spectroscopy.

4.14. Preparation of [Rh(PONOP-tBu)[Cl][BAR$_4$]]$_2$. 7. To a flask charged with [Rh(PONOP-tBu)[Cl][BAR$_4$]]$_2$ (1 (29.6 mg, 20.0 μmol) was added BuCl (1 mL) in the dark. The solution was left to stand at room temperature for 5 min before volatiles were removed in vacuo. Recrystallization from CH$_2$Cl$_2$/hexane at room temperature in the dark afforded the analytically pure product as yellow crystals. Yield: 24.3 mg (17.3 μmol, 87%). Crystals grown in this way were suitable for analysis by X-ray diffraction.

$^1$H NMR (500 MHz, CD$_2$Cl$_2$): $\delta$ 7.96 (t, $J_{1H} = 8.2, 1H, 4$-py), 7.68–7.74 (m, 8H, Ar$^*$), 7.55 (br, 4H, Ar$^*$), 7.01 (d, $J_{1H} = 8.3, 7H, 3$-py), 1.50 (s, $J_{tBu} = 16.3, 18H, tBu$), 1.46 (vbr, $J_{tBu} = 16.8, 18H, tBu$), $-26.25 (d, J_{tBu} = 41.9, J_{RhH} = 10.1, 1H, RhH$).

$^{13}$C($^1$H) NMR (126 MHz, CD$_2$Cl$_2$): $\delta$ 165.0 (v, $J_{1H} = 4, 2$-py), 162.3 (q, $J_{1H} = 50, Ar^*$), 147.3 (s, 4-py), 135.3 (s, Ar$^*$), 129.4 (qq, $J_{1H} = 32, J_{1H} = 3, Ar^*$), 125.1 (q, $J_{1H} = 272, Ar^*$), 118.0 (sept, $J_{1H} = 4, Ar^*$), 105.7 (v, $J_{tBu} = 4, py$), 43.1 (v, $J_{tBu} = 12, tBu(C)$), 41.0 (vtd, $J_{tBu} = 14, J_{tBu} = 2, tBu(C)$), 27.33 (v, $J_{tBu} = 6, tBu(CH$_2$)$), 27.31 (v, $J_{tBu} = 6, tBu(CH$_2$)$).

$^{31}$P($^1$H) NMR (162 MHz, CD$_2$Cl$_2$): $\delta$ 197.7 (d, $J_{tBu} = 100$).

HR-ESI-MS (positive ion, 4 kV): not sufficiently stable under the analysis conditions employed.

NMR and ESI-MS spectra of new compounds and selected reactions, cyclic voltammograms for the oxidation of [Rh(PONOP-tBu)Cl], and ac magnetic susceptibility measurements for 6 (PDF)

Accession Codes
CCDC 2195204–2195209 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/data_request/cif, or by

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**ASSOCIATED CONTENT**

**Supporting Information**

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organometallics.0c00400. NMR and ESI-MS spectra of new compounds and selected reactions, cyclic voltammograms for the oxidation of [Rh(PONOP-tBu)Cl], and ac magnetic susceptibility measurements for 6 (PDF)
emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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NOTES

The authors declare no competing financial interest.

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REFERENCES


16. There are < 40 (non-chelated) platinum group examples deposited in total.


22. Corroborated by crystallographic refinement, combustion analysis and \(^1\)H NMR spectroscopy.

23. The equivalent \(^1\)H and \(^13\)C NMR data for B are not available to enable direct comparison.


29. Whilst no significant decomposition of 7 was observed upon standing in CD\(_2\)Cl\(_2\) at room temperature in the dark, exposure of the solution to light resulted in ca. 2% conversation into 6 over 72 h.
