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# Direct Evidence for Competitive C−H Activation by a Well-Defined Silver XPhos Complex in Palladium-Catalyzed C−H Functionalization

Gayathri Athavan, Theo F. N. Tanner, Adrian C. Whitwood, Ian J. S. Fairlamb,* and Robin N. Perutz*

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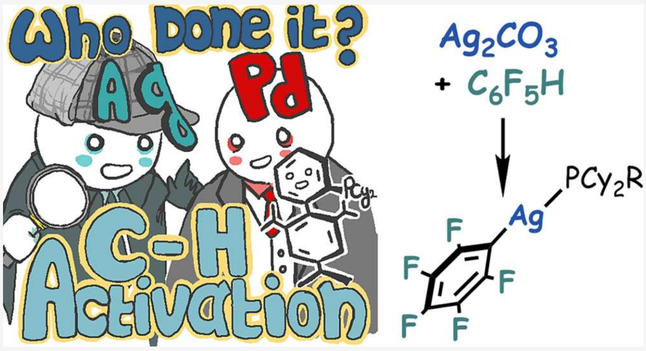
**ABSTRACT:** Increasing evidence indicates that silver salts can play a role in the C−H activation step of palladium-catalyzed C−H functionalization. Here we isolate a silver(I) complex by C−H bond activation and demonstrate its catalytic competence for C−H functionalization. We demonstrate how silver carbonate, a common but highly insoluble additive, reacts with pentafluorobenzene in the presence of a bulky phosphine, XPhos, to form the C−H bond activation product Ag($C_6F_5$)(XPhos). By isolating and fully characterizing this complex and the related carbonate and iodide complexes, $[Ag(XPhos)]_2(\mu\text{-}\kappa^2,\kappa^2\text{-}CO_3)$ and $[AgI(XPhos)]_2$, we show how well-defined Ag(I) complexes can operate in conjunction with palladium complexes to achieve C−H functionalization even at ambient temperature. Reactions are tested against the standard cross-coupling of $C_6F_5H$ with 4-iodotoluene, catalyzed by palladium acetate at 60 °C in the presence of silver carbonate and Xphos. Key observations are that (a) PdI($C_6H_5$)(XPhos) reacts stoichiometrically with Ag($C_6F_5$)(XPhos) to form Ph−$C_6F_5$ instantly at room temperature; (b) catalytic cross coupling can be achieved using 5% Ag($C_6F_5$)(XPhos) as the sole silver source; and (c) palladium acetate (typical precatalyst) can be replaced for catalytic cross coupling by the expected oxidative addition compound PdI($C_6H_5$)(XPhos). These investigations lead to a catalytic cycle in which Ag(I) plays the C−H bond activation role and palladium plays the coupling role. Moreover, we show how the phosphine can be exchanged between silver complexes, ensuring that it is recycled even though silver carbonate is consumed during catalytic cross-coupling.



## INTRODUCTION

The functionalization of C−H bonds of low reactivity has emerged as a powerful and selective strategy for the installation of a plethora of organic motifs, increasing structural complexity and diversity in applied chemical synthesis.[1−3] A variety of transition metals can be used to activate a C−H bond, from precious metals through to earth-abundant metals, each with their individual merits in terms of practical synthetic procedures.[4,5] There has been significant interest in palladium salts,[6,7] which catalyze the functionalization of a myriad of (hetero)arenes, with varying electronic and steric differences. Of interest are the electron-deficient fluorinated arenes,[8−11] which undergo reaction with iodoarenes in the presence of phosphines and bases such as carbonates and acetates. Extensive mechanistic studies have led to a consensus that C−H bond activation occurs by the concerted metalation deprotonation (CMD) mechanism,[9,12−15] alternatively described as ambiphilic metal−ligand assistance (AMLA-6).[16,17] Typically, these reactions are thought to involve mononuclear Pd species, operating homogeneously, with the caveat that there is some experimental evidence implicating hybrid homogeneous−heterogeneous behavior and higher order Pd species.[18−21] In early work, Fagnou et al. demonstrated the coupling of pentafluorobenzene to iodotoluene and studied its mechanism; we also select this as an exemplar reaction. Fagnou et al. employed potassium carbonate as the base with $P^tBu_2Me$ as the ligand,[9] but later a variety of other bases were used, often including silver carbonate. Bulky phosphines continue to be employed, but even $PPh_3$ is active.[22] In the past few years, Ag(I) has been demonstrated to play an active role in the critical C−H bond activation step in several reactions, starting with independent discoveries in 2016 by Lee and Hartwig[23] and by Larrosa et al.[24] Silver(I) can form several dinuclear complexes with triphenylphosphine with bridging carbonate or bicarbonate,[25] and silver(phosphine)halide complexes with bulky phosphines have been known since 1978. Notably, these silver complexes behave as neutral molecular species in dichloromethane solution.[26] In NMR spectra, they are characterized by large $^{107}Ag-^{31}P$ and $^{109}Ag-^{31}P$ coupling

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constants that decrease as the coordination number of Ag increases.[27−30]

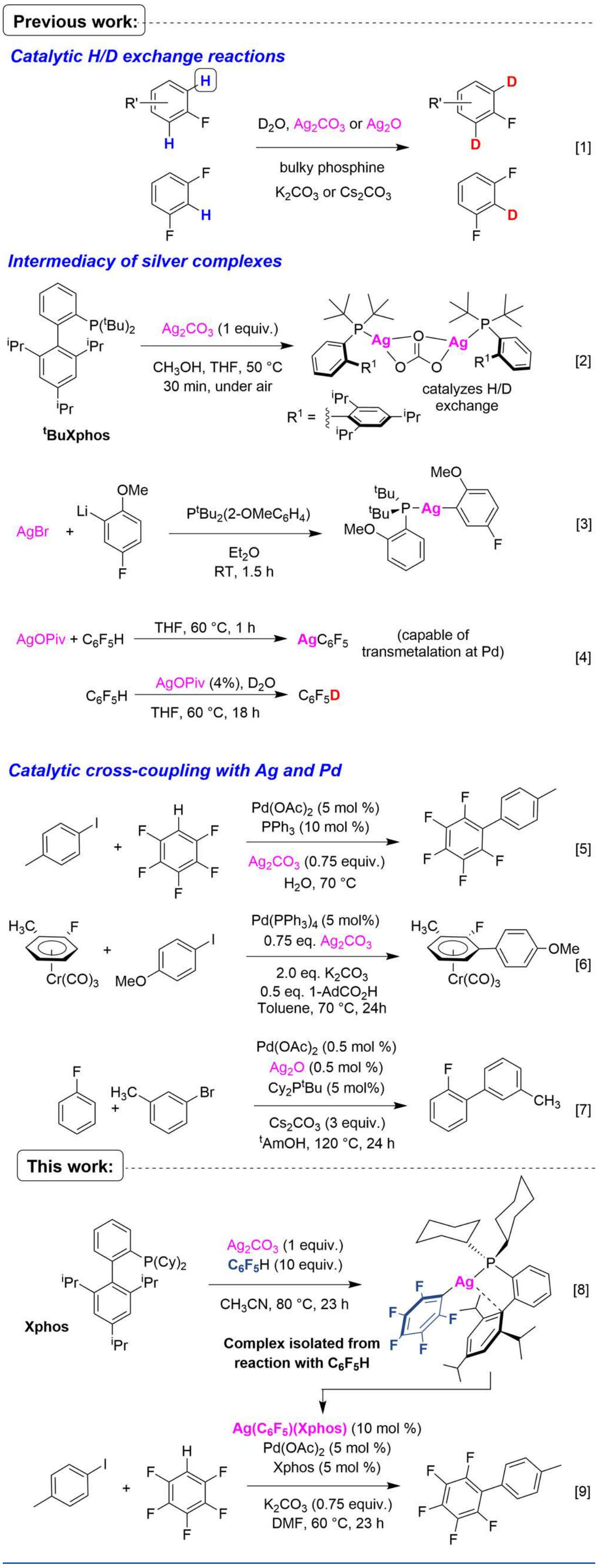
A series of papers implicated silver salts in the C−H bond activation of fluoroarenes, several of which are summarized in reviews.[7,31−33] We first consider the evidence in the absence of palladium. Simple silver salts have been shown to effect H/D exchange in pentafluorobenzene (or heptafluorotoluene) with $D_2O$ + AgOPiv (Piv = pivalate).[34−36] H/D exchange with $D_2O$ in the position ortho to the fluorine of a fluoroarene (or a metal complex of fluoroarene) was also reported, employing $Ag_2CO_3$ (or $Ag_2O$) and a bulky phosphine (Scheme 1, eq 1).[37−39] Similar studies including DFT calculations have been reported with AgOC(O)Ad + $PPh_3$ (Ad = adamantyl).[24]

Such H/D exchange implicates the occurrence of a C−H bond activation process between a silver salt, a phosphine, and a substrate. Identification of such intermediates is important in understanding the catalytic exchange. A recent paper (published while our work was in progress) demonstrated that selective catalytic H/D exchange occurs between $CH_3OD$ and numerous heteroarenes in the presence of silver carbonate and certain bulky phosphines. Moreover, silver carbonate reacts with $^t$BuXPhos to form a dinuclear silver phosphine carbonate complex which catalyzes H/D exchange of thiophene with $CH_3OD$ (Scheme 1, eq 2).[40] Thus, this complex is a likely intermediate in catalysis.

We now consider reactions in the presence of both silver and palladium. In the initial 2016 work, it was shown that a silver phosphine fluoroaryl complex reacts stoichiometrically with a palladium allyl complex to form the corresponding allyl arene. Notably, this silver complex was formed, not by reaction with the neutral arene but via lithium salt (Scheme 1, eq 3).[23] Nevertheless, this complex is again a plausible intermediate in catalysis. A further study focused on the reaction of palladium complexes with pentafluorobenzene in the presence of various silver salts, revealing the formation of $Ag(C_6F_5)$ identified by its $^{19}F$ ortho-fluorine resonance. The same species could be formed by reaction of Ag(OPiv) (Piv = pivalate) with $C_6F_5H$ in the absence of palladium complex. Silver pentafluorophenyl was shown to be capable of transmetalation at palladium and catalytic H/D exchange (Scheme 1, eq 4).[34] Ag(OPiv) has also been employed in the catalytic carboxylation of thiophene.[41]

We now turn to mechanisms of cross-coupling involving silver salts and palladium precatalysts. Such reactions are exemplified by the coupling of $C_6F_5H$ and iodotoluene in the presence of $Ag_2CO_3$, $PPh_3$, and $Pd(OAc)_2$ (Scheme 1, eq 5).[22] In one approach, supported by computational studies, there is direct formation of heterobimetallic Ag−Pd complexes;[42] although Ag−Pd clusters are known,[43] their role in C−H functionalization has not been established experimentally. In a second approach of more relevance here, silver(I) effects C−H bond activation as implicated by the ortho-selective H/D exchange mentioned above[44] and is followed by transmetalation. Several key observations support participation of silver in the second type of pathway. In addition to the evidence already cited (Scheme 1, eq 1−4), there is strong evidence from reaction kinetics, including kinetic isotope effects and rates dependent on concentrations of silver complex (Scheme 1, eq 6 and eq 7).[33,39,24,23,45,46] These studies are also supported by H/D exchange in the presence of both silver salts and palladium salts.

### Scheme 1. Involvement of Ag Salts in C−H Functionalization Chemistry



Notably, the catalytic cycles proposed in these papers address the use of alkyl carboxylic acids or acidic alcohols to displace the aryl group from silver, but the mechanism of action of the silver carbonate was not clarified until 2021.[40] The cycles also implicate a requirement for sufficient phosphine for coordination to both palladium and silver. In at least one proposed cycle, there is no mention that AgI may act as a sink for phosphine with potential implications for productive catalysis.[24] Furthermore, dynamic behavior involving phosphine ligand at both silver and palladium has not been explored, although it may have an important role in the reaction mechanism.

In this paper, we report the isolation of silver aryl and silver carbonate complexes derived directly from reaction of silver carbonate with a sterically hindered and commonly used phosphine, XPhos, and pentafluorobenzene (Scheme 1, eq 8). The aryl derivative can be formed directly or via isolation of the carbonate complex and is competent to form a cross-coupled product by reaction with a matching palladium phosphine complex. We also exemplify cross-coupling in the presence of catalytic quantities of the silver aryl complex without another silver source (Scheme 1, eq 9). These silver complexes undergo dynamic exchange with free phosphine. These studies lead to a proposal for a catalytic cycle in which the key steps have been verified stoichiometrically.

## ■ RESULTS AND DISCUSSION

An initial survey of reactions of silver carbonate with pentafluorobenzene in acetonitrile or DMF in the presence of different phosphines at 60 °C was conducted to test for C−H bond activation. With $PPh_3$ and $P(4\text{-OMeC}_6H_4)_3$, the $^{19}F$ NMR spectrum showed evidence of a new peak around $\delta$ −100 consistent with the ortho fluorine of an $Ag(C_6F_5)$ complex,[47] but the $^{31}P\{^1H\}$ NMR spectrum showed a singlet with no evidence for coupling to $^{107}Ag$ or $^{109}Ag$ at room temperature. Upon cooling to −100 °C, the sample with $PPh_3$ showed the presence of numerous species, each observed as a pair of concentric doublets with Ag−P coupling (Figure 1a). A more electron-withdrawing phosphine, $P(furyl)_3$, did not react at all. The results show that use of $PPh_3$ as a ligand in C−H functionalization chemistry involving Ag may be complicated by the presence of multiple $Ag{-}PPh_3$ species. In contrast, the corresponding reaction with the strongly electron-donating and sterically hindered phosphine Xphos (Figure 1b) revealed a pair of doublets of triplets in the $^{31}P\{^1H\}$ NMR spectrum at room temperature characteristic of a product **1** containing an $Ag(C_6F_5)(Xphos)$ unit. We therefore selected this reaction for more detailed study. Without Xphos, only traces of an $Ag(C_6F_5)$ product were formed.

Reaction of $Ag_2CO_3$ with Xphos (2 equiv) and $C_6F_5H$ (10 equiv) at 80 °C yielded **1** with 66% yield which crystallized on cooling (Scheme 2). The $^{31}P\{^1H\}$ NMR spectrum recorded in $CD_2Cl_2$ exhibited a pair of doublets of triplets at $\delta$ 13.0 ($^1J_{^{107}Ag^{31}P} = 444$, $^1J_{^{109}Ag^{31}P} = 512$, and $^3J_{PF} = 3.0$ Hz; Figure 1b). The $^{19}F$ NMR spectrum showed three resonances at $\delta$ −107.0 (m, 2F), − 61.5 (t, $J_{FF} = 19.8$ Hz, 1F), − 163.3 (m, 2F). The $^{31}P\text{-}^{109}Ag$ HMQC spectrum revealed the $^{109}Ag$ chemical shift as $\delta$ 713. The LIFDI mass spectrum showed a parent radical cation at $m/z = 752.251$ ($^{107}Ag$ isotopologue) with an isotope pattern consistent with monomeric $Ag(C_6F_5)(Xphos)$.

The molecular structure of **1** determined by single-crystal X-ray crystallography confirmed that $Ag(C_6F_5)(Xphos)$ is monomeric with Ag−C and Ag−P distances of 2.124(2) and 2.380(6) Å, respectively (Figure 2a). The coordination at Ag(I) is close to linear [C−Ag−P 168.86(6)°]. The distal ring of the biphenyl shows an approach between the ipso carbon C(7) and Ag [3.062(2) Å]. Such interactions are longer and hence weaker in our Ag complexes containing the Xphos ligand than in related Pd(II) complexes [C(ipso)-Pd interactions ca. 2.45 Å].[48] The $C_6F_5$ ring exhibits $\pi$-stacking with the adjacent molecule, with a centroid-to-centroid distance of 3.336(2) Å. Other $Ag(C_6F_5)L$ (L = EtCN) complexes are known but have polymeric structures.[49] Hartwig et al. have isolated a monomeric silver fluoroaryl phosphine, $Ag\{C_6H_3(2\text{-OMe})(4\text{-F})\}\{P(o\text{-anisyl})_3\}$, with a similar structure to **1**.[23] Notably, their complex was not synthesized by a C−H bond activation process but by reaction of AgBr with the corresponding lithiated arene and phosphine.

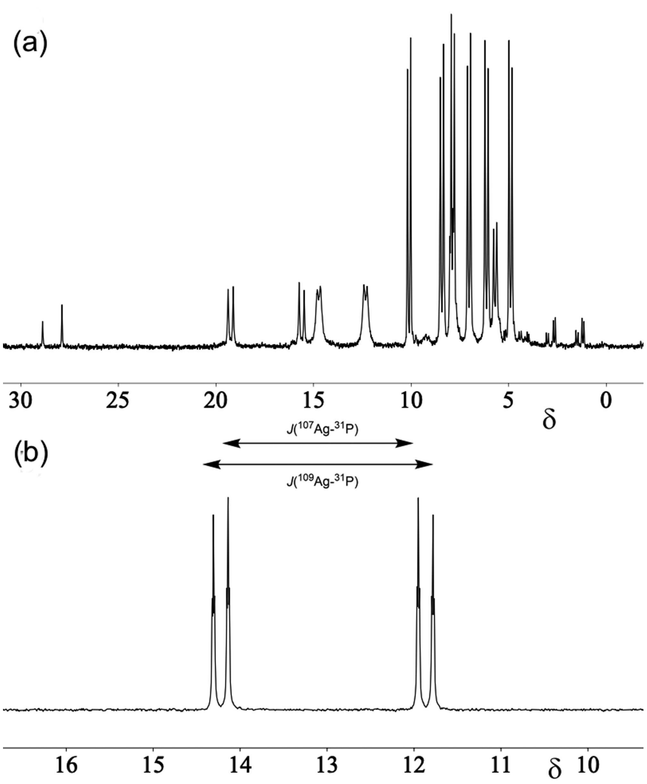
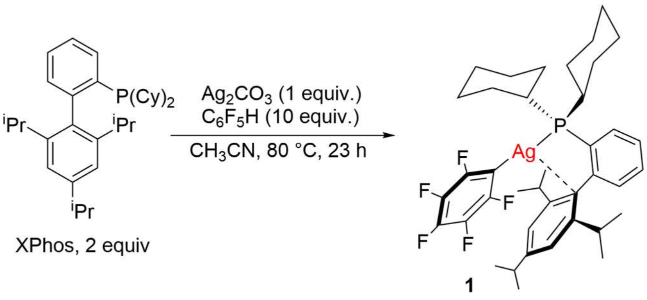


**Figure 1.** (a) $^{31}P\{^1H\}$ NMR spectrum (202.5 MHz) at −100 °C in toluene-$d_8$: $CD_2Cl_2$ (20:80), following reaction of $Ag_2CO_3$ with pentafluorobenzene in the presence of $PPh_3$; (b) $^{31}P\{^1H\}$ NMR spectrum at room temperature of **1** in $CD_2Cl_2$ obtained by reaction of $Ag_2CO_3$ with pentafluorobenzene in the presence of Xphos. (Cooling to −70 °C caused slight broadening but no new species were observed.)

**Scheme 2. Synthesis of $Ag(C_6F_5)(Xphos)$ 1**



The synthesis of **1** demonstrated that silver carbonate is capable of C−H bond activation with pentafluorobenzene. We now wanted to test whether this product was competent for cross-coupling under stoichiometric conditions. Employing a literature procedure,[50] we prepared the Pd(II) complex

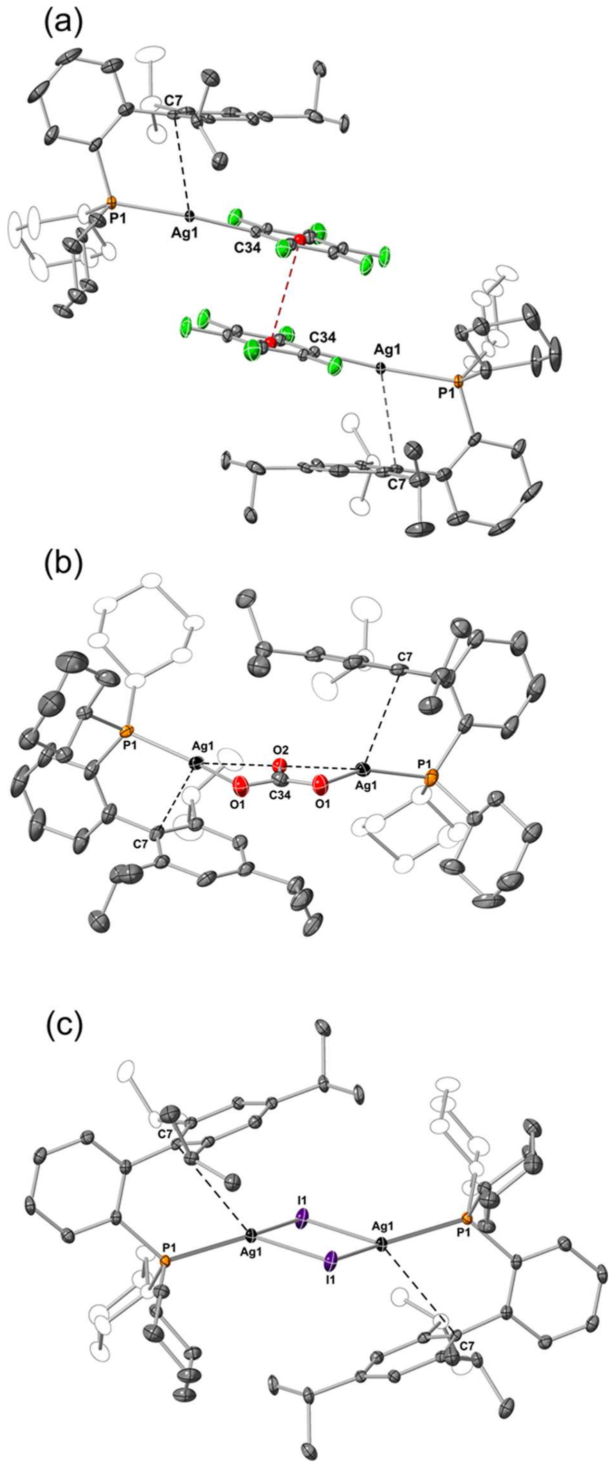
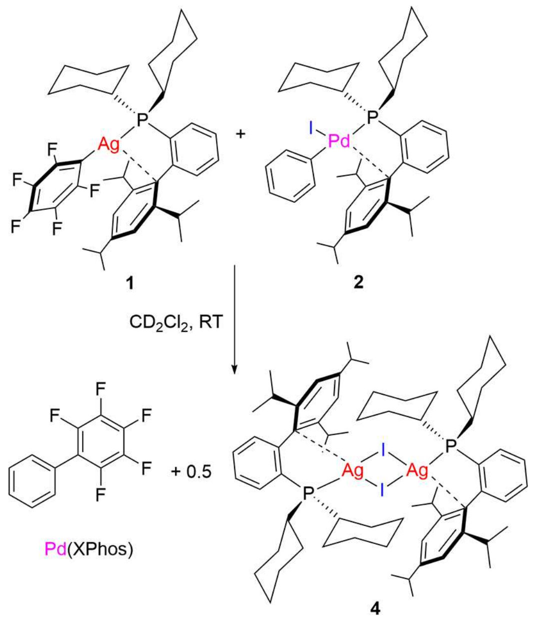


**Figure 2.** Molecular structures of (a) Ag($C_6F_5$)(Xphos), **1**, (b) [Ag(Xphos)]$_2$($\mu$-$\kappa^2$-$CO_3$), **3**, (c) [Ag(Xphos)]$_2$($\mu$-I)$_2$, **4**. Hydrogen atoms are omitted; thermal ellipsoids are shown at the 50% level. Principal bond lengths and angles (Å/deg): **1** Ag(1)−P(1) 2.3801(5), Ag(1)−C(34) 2.124(2), Ag(1)−C(7) 3.062(2), C(34)−Ag(1)−P(1) 168.86(6); **3** Ag(1)−P(1) 2.3328(9), Ag(1)−O(1) 2.249(2), Ag(1)−O(2) 2.3572(2), Ag(1)−C(34) 2.678(2), C(34)−O(1) 1.281(3), C(34)−O(2) 1.303(5), Ag(1)−C(7) 3.071(3), P(1)−Ag(1)−C(34) 167.29(3), P(1)−Ag(1)−O(1) 150.85(7), C(34)−Ag(1)−O(1) 28.48(10), O(1)−Ag(1)−O(2) 57.56(8), Ag(1)−O(2)−Ag(1′) 178.444(13); **4** Ag(1)−I(1) 2.8357(3), Ag(1)−P(1) 2.4255(7), Ag(1)−C(7) 3.277(3), I(1)−Ag(1)−I(1′) 100.057(8), P(1)−Ag(1)−I(1) 128.803(18), P(1)−Ag−I(1)−I(1′) 151.26(3).

PdI($C_6H_5$)(Xphos) **2** analogous to PdI($C_6H_4$4-F)(Xphos) described previously [synthesized from (COD)Pd($CH_2SiMe_3$)$_2$)][51] and reacted it stoichiometrically with Ag($C_6F_5$)(Xphos) in $CD_2Cl_2$ at room temperature. Complete conversion to Ph−$C_6F_5$, as determined by NMR, occurred immediately (Scheme 3) with concomitant formation of [AgI(Xphos)]$_2$ (see below).

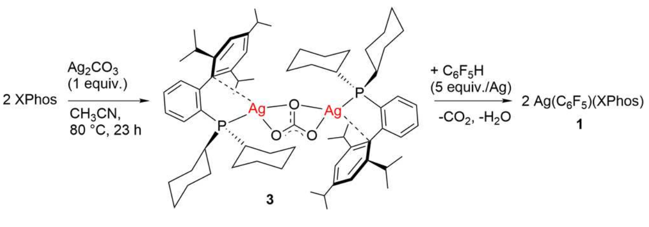
**Scheme 3. Stoichiometric Reaction of 1 and 2**



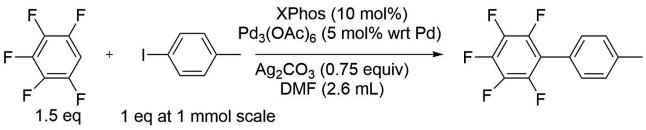
Furthermore, a mixture of **1** and **2** was prepared at −70 °C in $CD_2Cl_2$ and analyzed by NMR spectroscopy at −70, − 50, and −30 °C. Formation of Ph−$C_6F_5$ was observed from −30 °C, but no transmetalation product was detected. For comparison, Hartwig et al. reacted Ag{$C_6H_3$(2-OMe)(4-F)}{P(o-anisyl)$_3$} with Pd($\eta^3$-allyl-Ph)(Opiv){P(o-anisyl)$_3$} at room temperature to obtain the cross-coupling product.[23] As a control, we attempted cross-coupling of **1** with iodotoluene but found no reaction up to 130 °C showing the requirement for Pd.[52] A further control reaction of $C_6F_5H$ (10 equiv) with **2** without silver complexes or base showed no reaction at room temperature.

Since silver carbonate is highly insoluble in acetonitrile, we anticipated that the first step in the reaction with pentafluorobenzene and Xphos may be formation of a silver Xphos carbonate complex. Reaction of $Ag_2CO_3$ with 2 equiv Xphos at 80 °C in MeCN yielded an amber solution from which brown crystals formed (yield 24%, Scheme 4). The product was identified as [Ag(Xphos)]$_2$($\mu$-$\kappa^2$,$\kappa^2$-$CO_3$) **3** by

**Scheme 4. Synthesis and Reactivity of [Ag(Xphos)]$_2$($\mu$-$\kappa^2$-$CO_3$) 3**



### Table 1. Catalytic Reactions



| entry | variation of reaction conditions from standard above: base or Ag source | ligand | Pd catalyst | temp (°C) | time (h) | NMR yield (isolated yield[a])/% |
|---|---|---|---|---|---|---|
| 1 | standard | standard | standard | 60 | 3 | 96 (84) |
| 2 | standard | standard | standard | 20 | 23 | 75 |
| 3 | standard | standard | no $Pd(OAc)_2$ | 60 | 3 | 0 |
| 4 | $Ag_2CO_3$ (10 mol %) | standard | standard | 60 | 3 | 21 |
| 5 | $Ag_2CO_3$ (10 mol %) | standard | standard | 60 | 23 | 23 |
| 6 | $Ag_2CO_3$ (10 mol %) + $K_2CO_3$ (0.75 equiv) | standard | standard | 60 | 23 | 65 |
| 7 | **1** (5 mol %) + $K_2CO_3$ (0.75 equiv) | XPhos (5 mol %) | standard | 60 | 23 | 57 |
| 8 | $Cs_2CO_3$ | standard | standard | 60 | 3 | <10 |
| 9 | AgOAc | standard | standard | 60 | 3 | <10 |
| 10 | standard | standard | intermediate Pd complex **2** (5 mol %) | 20 | 23 | 63 |
| 11 | standard | standard | intermediate Pd complex **2** (5 mol %) | 60 | 3 | 86 |

[a] For methods of determining NMR yields, see the Supporting Information; yield of isolated product obtained following chromatography on silica-gel.

NMR, CHN analysis, and X-ray crystallography.[53] The $^{31}P\{^1H\}$ NMR spectrum recorded in $C_6D_6$ showed a pair of doublets at $\delta$ 15.9 ($^1J_{^{107}Ag^{31}P}$ 634, $^1J_{^{109}Ag^{31}P}$ 731 Hz). The molecular structure of **3** (Figure 2b) shows a $C_2$-symmetric complex with an Ag($\mu$-$CO_3$)Ag unit that is almost planar with one oxygen bridging the two silver atoms [Ag(1)−O(2)−Ag(1)′ = 178.444(13)°] and the O(1) oxygens bonded to one silver each. The Ag−O(2) distances [2.3572(2) Å] are longer than the Ag−O(1) distances [2.249(2) Å]. The C(34)−O(1) and C(34)−O(2) distances are 1.281(3) and 1.303(5) Å, respectively. The sum of the angles around C(34) is 360.0(5), indicating trigonal planar coordination. The coordination at Ag is Y-shaped with O(1)−Ag−O(2) = 57.56(8)°. The ipso carbon on the distal benzene ring C(7) lies in close contact [3.071(3) Å] with the silver atom bearing the corresponding phosphorus. The CHN analysis shows one acetonitrile of crystallization per Ag, in agreement with the crystal structure. During the course of our work, Tlahuext-Aca and Hartwig reported two direct analogues of **3**, one with a P$^t$BuXPhos ligand which was characterized crystallographically and one with a Johnphos ligand. Their $^{31}$P−Ag coupling constants and metrics are similar to those of **3**.[40] The $M_2(\mu$-$\kappa^2,\kappa^2$-$CO_3)$ motif is quite common among first row transition metal carbonates from Mn to Zn and has also been observed for both Pd as well as Ag.[54−61]

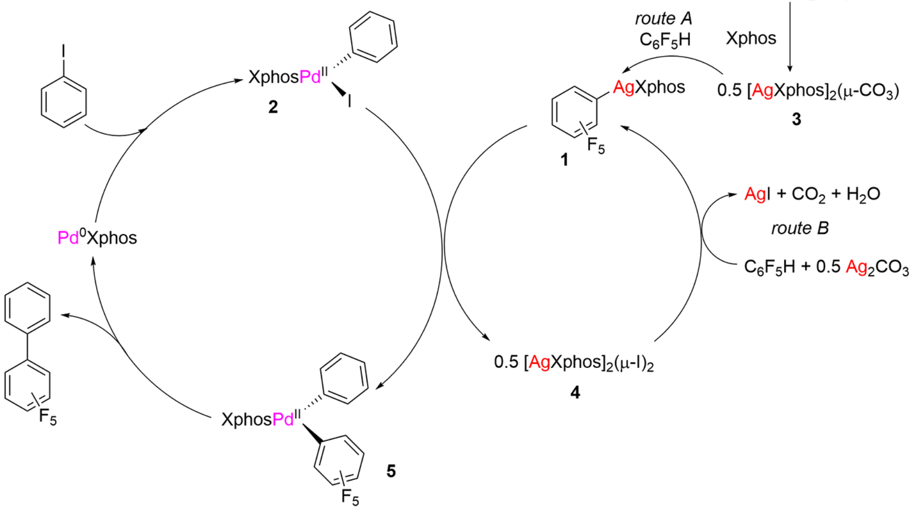
Complex **3** reacts with pentafluorobenzene (5 equiv wrt Ag) in $C_6D_6$ at room temperature to form **1** as the sole product containing the Ag(Xphos) moiety (Scheme 4). Benzene was used as the solvent since mass spectra show that **3** reacts with chlorine sources such as chloroform or dichloromethane to form $[Ag(Xphos)]_2(\mu$-$Cl)_2$.

At this stage, we needed to establish Xphos as a suitable phosphine for catalytic C−H bond arylation. Pentafluorobenzene (1.5 equiv) was reacted with iodotoluene (1 equiv) with palladium(II) acetate (5 mol % wrt Pd, nitrite free $Pd_3(OAc)_6$),[62] Xphos (10 mol %), and $Ag_2CO_3$ (0.75 equiv) in DMF at 60 °C for 3 h resulting in 96% conversion (measured by both $^1$H and $^{19}$F NMR) to 4-$MeC_6H_4$−$C_6F_5$ (Table 1, entry 1). Repetition of the reaction at room temperature resulted in 72% ($^1$H) and 77% ($^{19}$F) conversion after 23 h (entry 2). A fully worked-up reaction gave 84% isolated yield after 3 h reaction at 60 °C and separation by column chromatography on silica gel (entry 1), whereas a control reaction without palladium(II) acetate at 60 °C gave no product (entry 3). When the quantity of $Ag_2CO_3$ was reduced to 0.1 equiv, the yield after 3 h was still 21%, but it barely increased after 23 h indicating that carbonate became limiting (entries 4 and 5). Use of a reduced quantity of $Ag_2CO_3$ (10 mol %) with $K_2CO_3$ (0.75 equiv) at 60 °C (23 h) restored the conversion to 65% ($^1$H NMR, entry 6). When a similar experiment was performed with **1** (5 mol %) as the sole source of Ag(I) and $K_2CO_3$ (0.75 equiv) at 60 °C (23 h), the conversion was 57% (entry 7). Replacement of $Ag_2CO_3$ by either $Cs_2CO_3$ or AgOAc gave conversions under 10% (entries 8 and 9).

These studies demonstrated that XPhos is active in catalytic cross-coupling as is **1**. Moreover, catalytic quantities of silver carbonate or **1** are sufficient in the presence of potassium carbonate. For comparison, Fagnou performed his C−H arylation reactions of pentafluorobenzene with P*t*$Bu_2$Me and $K_2CO_3$ in DMA at 120 °C,[9] while Zhang et al. used $PPh_3$ and $Ag_2CO_3$ in water at 70 °C for 16 h.[22] As mentioned above, Hartwig et al. demonstrated that their silver complex Ag{$C_6H_3$(2-OMe)(4-F)}{P(o-anisyl)$_3$} is competent for cross-coupling in a stoichiometric reaction, but we did not find mention of its use in catalysis.[23]

The reaction of **1** with **2** yielded a silver iodide complex as a byproduct identified in the $^{31}P\{^1H\}$ NMR ($CD_2Cl_2$) spectrum by a pair of concentric doublets. The same product $[Ag(XPhos)(\mu$-$I)]_2$ **4** was formed by reaction of AgI with XPhos in $CD_2Cl_2$ at room temperature for 24 h ($^{31}P\{^1H\}$ NMR $\delta$ 16.89, pair of d, $^1J_{^{107}Ag^{31}P}$ = 542 Hz, $^1J_{^{109}Ag^{31}P}$ = 627 Hz, $^{109}$Ag NMR $\delta$ 590) (Scheme 3). The LIFDI mass spectrum of **4** dissolved in dichloromethane shows $m/z$ = 1295.459 (100%)

(a) Cycle with Ag performing C-H bond activation



(b) Ag base-assisted Concerted Metallation Deprotonation (CMD) Pathway

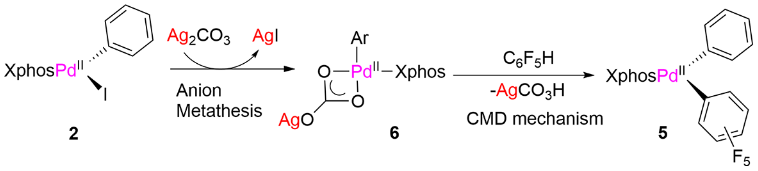


**Figure 3.** Proposed catalytic mechanisms. (a) Catalytic cycle with C−H bond activation by silver. (b) Silver carbonate acting as a base in the CMD mechanism. Note that **1** may be generated by reaction of $C_6F_5H$ with **3** (route A) or by reaction with **4** (route B).

with isotope pattern consistent with two silver atoms (quoted for $^{107}Ag^{109}Ag$) and a much smaller peak at $m/z$ = 710.183 (12%) for the monomer (quoted for $^{107}Ag$). This spectrum suggests that this complex exists as a dimer in solution or as an equilibrium between monomer and dimer. The molecular structure determined crystallographically reveals a $C_2$-symmetric dimer with bridging iodides. The central $Ag_2(\mu\text{-}I_2)$ unit is planar, but the phosphorus atoms lie out of that plane with a P(1)−Ag−I(1)−I(1′) torsional angle of 151.26(3)°. Similar interactions between the distal benzene ring C(7) and the Ag atom [3.277(3) Å] are found to those in complexes **1** and **3** (Figure 2c).

Reaction of **4** with excess $Ag_2CO_3$ (10 equiv) and a large excess of pentafluorobenzene (100 equiv) generates **1** and precipitates silver iodide (eq 1). As controls, we attempted to react $C_6F_5H$ with **4** but found no reaction in either DMF at 60 °C or $CH_2Cl_2$ at room temperature. We also showed that **4** does not react with $Ag_2CO_3$ in DMF at 60 °C.

In addition, we investigated the acetate complex, Ag(OAc)(XPhos) **5**, formed by reaction of XPhos with AgOAc in $CH_3CN$ at 80 °C. Complex **5** exhibits a characteristic $^{31}P\{^1H\}$ NMR resonance $\delta$ 16.55 (pair of d, $^1J_{^{107}Ag^{31}P}$ = 643.9 Hz, $^1J_{^{109}Ag^{31}P}$ = 743.2 Hz). The crystal structure of this complex revealed a monomer with $\kappa^1$-coordination of the acetate ligand (see the Supporting Information). In contrast to the behavior of **3**, the reaction of AgOAc in the presence of Xphos (1 equiv) and $C_6F_5H$ (10 equiv) did not produce any **1** (none detected by $^{31}P\{^1H\}$ or $^{19}F\{^1H\}$ NMR spectroscopy) but generated **5** instead.

Further information was obtained from kinetic isotope effects measured both for the stoichiometric and for the catalytic reaction. For the stoichiometric reaction of **3** with $C_6F_5H$ ($C_6F_5D$), we employed a low temperature in order to ensure a reasonable number of data points for the reaction with $C_6F_5H$ which was monitored in situ by NMR. A temperature of −40 °C in toluene proved optimal, but, under these conditions, the reaction did not proceed to completion. A fast process lasting ca. 20 min was recorded, followed by a much slower process with KIEs were determined as 3.7 ± 0.3 and 0.91 ± 0.01, respectively, for the fast and slow processes. The KIE for the fast process is consistent with rate-determining C−H bond breaking in this reaction of this silver−carbonate complex. The product of reaction was 4-$MeC_6H_4$−$C_6F_5$ as usual, but nature of the slow process has not been determined.

In separate experiments, catalytic reactions were conducted under the standard conditions (see Table 1) at 60 °C, and the products were analyzed by NMR at different reaction times. The KIE for the catalytic reaction was determined from the initial rates of reaction as 4.5 ± 0.8.

The recycling of XPhos was clarified by synthesizing $Ag(C_6F_5)$ independently.[49] With the authentic sample of $Ag(C_6F_5)$, we confirmed that this species is formed in low yield (ca. 10%) upon reaction of $Ag_2CO_3$ with pentafluorobenzene in the absence of XPhos. Additionally, as expected, $Ag(C_6F_5)$ reacts rapidly with XPhos at room temperature to form **1**. Of particular interest is the observation that $Ag(C_6F_5)$ reacts with **4** to form **1** and a precipitate of AgI (eq 2). The reactions of eq 1 and eq 2 provide opportunities to recycle phosphine in the catalytic reactions and explain how AgI may be formed as a final product. The reactions of $Ag(C_6F_5)$ in $CD_3CN$ and **1** in $CD_2Cl_2$ with $D_2O$ at room temperature both give $C_6F_5D$; however, the reaction of **1** takes several days.

$$[\mathrm{Ag(XPhos)}(\mu-\mathrm{I})]_2 + \text{excess } \mathrm{C_6F_5H} + \mathrm{Ag_2CO_3} \rightarrow \mathrm{AgI}\downarrow + 2\mathrm{Ag(C_6F_5)(XPhos)} \quad (1)$$

$$[\mathrm{Ag(XPhos)}(\mu-\mathrm{I})]_2 + 2\mathrm{Ag}(\mathrm{C_6F_5}) \rightarrow \mathrm{AgI}\downarrow + 2\mathrm{Ag}(\mathrm{C_6F_5})(\mathrm{XPhos}) \quad (2)$$

The observations described above lead us to postulate the catalytic cycle in Figure 3a in which Ag performs C−H bond activation and Pd effects cross-coupling.[63] According to this cycle, PdI($C_6H_5$)(XPhos) (**2**, 5 mol %) should act as a catalyst for the coupling of 4-iodotoluene with pentafluorobenzene in the presence of 5 mol % XPhos and $Ag_2CO_3$ (0.75 equiv). On testing this hypothesis at room temperature, we obtained yields of tol−$C_6F_5$ after 3 and 23 h of 6% and 63%, respectively; at 60 °C, they increase to 86% and 100%, respectively (Table 1, entries 10, 11). As expected, Ph−$C_6F_5$ was also formed with yield 5% wrt tol−$C_6F_5$. This cycle is also supported by the catalytic reaction with 5 mol % **1** as the source of Ag(I) (entry 7). All the steps in the catalytic cycle have been verified stoichiometrically other than the formation and reaction of a Pd(0) species which is not expected to be detectable under our conditions (oxidative addition being fast). The cycle shows two alternative routes from $Ag_2CO_3$ to form **1** reflecting the experiments described above. The experiments with reduced $Ag_2CO_3$ with and without $K_2CO_3$ confirm that carbonate is required for the C−H bond activation acting as the Brønsted base. The postulated alternative mechanism invoking Ag(I) as a base and Pd as involved in a CMD process is expected to involve Ag−carbonato−Pd **6** as an intermediate (Figure 3b).

A further group of experiments illuminates the ability of XPhos to undergo exchange, thereby ensuring that its supply is not exhausted prematurely. To test the lability of the silver complexes, **1**, **3**, and **4**, we reacted each of them with $^t$BuXPhos, in which the isopropyl groups are replaced by *t*butyl groups. Addition of $^t$BuXPhos (1 equiv) to **1** resulted in immediate formation of a new silver phosphine species at room temperature ($^{31}$P NMR $\delta$ 38.5, pair of dt, $^1J_{^{107}\mathrm{Ag}^{31}\mathrm{P}}$ = 448 Hz, $^1J_{^{109}\mathrm{Ag}^{31}\mathrm{P}}$ = 516 Hz, and $J_{\mathrm{PF}}$ = 2.7 Hz, compared to free ligand at $\delta$ 21.4) in 50% conversion consistent with exchange of the phosphine to form the $^t$BuXPhos analogue Ag($C_6F_5$)($^t$BuXPhos) **1′**. Assuming this is an equilibrium reaction, we deduce an equilibrium constant of 1.03 ± 0.05 for formation of **1′** (see eq 3). Similar behavior was observed for **3** and **4** (eqs 4 and 5).[64]

$$\mathbf{1} + t\text{-BuXPhos} \xrightleftharpoons{K_{\mathrm{eq}}=1.03} \mathbf{1'} + \text{XPhos} \quad (3)$$

$$\mathbf{3} + 2t\text{-BuXPhos} \xrightleftharpoons{K_{\mathrm{eq}}=0.49} \mathbf{3'} + 2\text{XPhos} \quad (4)$$

$$\mathbf{4} + t\text{-BuXPhos} \xrightleftharpoons{K_{\mathrm{eq}}=0.80} \mathbf{4'} + \text{XPhos} \quad (5)$$

**4** and **4′** assumed to be monomers in solution for calcn of $K_{\mathrm{eq}}$

The experiments with *t*BuXPhos encouraged us to test for exchange between Ag(XPhos) complexes and free XPhos. A $^{31}$P−$^{31}$P EXSY spectrum of a sample of **1** in the presence of XPhos (5 equiv, mixing time 2 s) revealed cross peaks consistent with intermolecular exchange between **1** and XPhos on the time scale of seconds. Since there is exchange between two sites only, 1D-EXSY[65] is suitable and is more economical in instrument time. 1D-EXSY experiments on **1** in the presence of a range of concentrations of free XPhos were conducted in $CD_2Cl_2$ yielding evidence that the rate of exchange $V_{\mathrm{ex}}$ depends linearly on [XPhos] (where $V_{\mathrm{ex}} = k_{\mathrm{obs}}[\mathrm{XPhos}][\mathbf{1}]/([\mathrm{XPhos}] + [\mathbf{1}])$ and $k_{\mathrm{obs}}$ is derived from the variation of fractional integration of [XPhos] with mixing time $\tau_{\mathrm{m}}$ on selective excitation of **1**).[66,67] Variable temperature 1D-EXSY experiments with excess XPhos (5 equiv) were performed in $C_6D_6$ in order to access a suitable temperature range to determine of activation parameters yielding $\Delta H^{\ddagger}$ = 40.0 ± 1.2 kJ/mol and $\Delta S^{\ddagger}$ = −162 ± 4 J/K mol, providing clear evidence for associative exchange.

## ■ CONCLUSION

In conclusion, silver carbonate is capable of C−H bond activation of pentafluorobenzene in the presence of XPhos yielding discrete and well-defined Ag($C_6F_5$)(XPhos) **1**. This reaction can also be carried out stepwise yielding first the carbonate complex $[\mathrm{Ag(XPhos)}]_2(\mu\text{-}\kappa^2,\kappa^2\text{-}\mathrm{CO_3})$ **3** and then **1**. A third silver complex has been isolated by reaction of AgI with XPhos, $[\mathrm{Ag(XPhos)}(\mu\text{-I})]_2$ **4**. All three silver complexes have been characterized in solution and crystallographically. They are all labile with respect to associative exchange with free XPhos or with *t*BuXPhos and all participate in cross-coupling. The viability of **1** for cross-coupling has been demonstrated stoichiometrically by reaction of **1** with PdI($C_6H_5$)(XPhos) **2** yielding **4** as a byproduct; this reaction even occurs at −30 °C. Catalytic cross-coupling of 4-iodotoluene to pentafluorobenzene may be achieved in the presence of palladium(II) acetate, XPhos, and silver carbonate at 60 °C or at room temperature. Catalytic cross-coupling also occurs with **2** as the catalyst in the presence of $Ag_2CO_3$ and a reduced quantity of XPhos. Catalytic quantities of silver in the form of $Ag_2CO_3$ or **1** are active in conjunction with potassium carbonate as the stoichiometric base. A catalytic cycle involving C−H bond activation at silver has been proposed consistent with the set of tested stoichiometric reactions. It is now clear how the phosphine solubilizes silver carbonate and silver iodide; however, the phosphine is labile enough to allow precipitation of silver iodide as the final byproduct of catalysis. We stress that the study does not exclude competing C−H bond activation steps at palladium or a role for higher-order catalyst species. Nevertheless, the evidence for the C−H bond activation abilities of silver carbonate in the presence of a suitable phosphine is now conclusive and is shown to involve well-defined, soluble, mononuclear, and dinuclear silver phosphine complexes that are active in cross-coupling reactions with palladium complexes.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.2c00063.

> Synthetic procedures, catalytic reactions, stoichiometric reactions, phosphine-exchange experiments, EXSY experiments, kinetic isotope effect experiments, crystallographic data, characterization data including NMR spectra (PDF)

### Accession Codes

CCDC 2110192− 2110194 and 2160367 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by 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.

## AUTHOR INFORMATION

### Corresponding Authors

**Ian J. S. Fairlamb** − *Department of Chemistry, University of York, York YO10 5DD, U.K.;* orcid.org/0000-0002-7555-2761; Email: ian.fairlamb@york.ac.uk

**Robin N. Perutz** − *Department of Chemistry, University of York, York YO10 5DD, U.K.;* orcid.org/0000-0001-6286-0282; Email: robin.perutz@york.ac.uk

### Authors

**Gayathri Athavan** − *Department of Chemistry, University of York, York YO10 5DD, U.K.*

**Theo F. N. Tanner** − *Department of Chemistry, University of York, York YO10 5DD, U.K.;* orcid.org/0000-0001-7563-9325

**Adrian C. Whitwood** − *Department of Chemistry, University of York, York YO10 5DD, U.K.;* orcid.org/0000-0002-5132-5468

Complete contact information is available at:
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### Notes

The authors declare no competing financial interest.

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## DEDICATION

We dedicate this paper to Professor Maurice Brookhart in admiration for his achievements in organometallic chemistry.

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