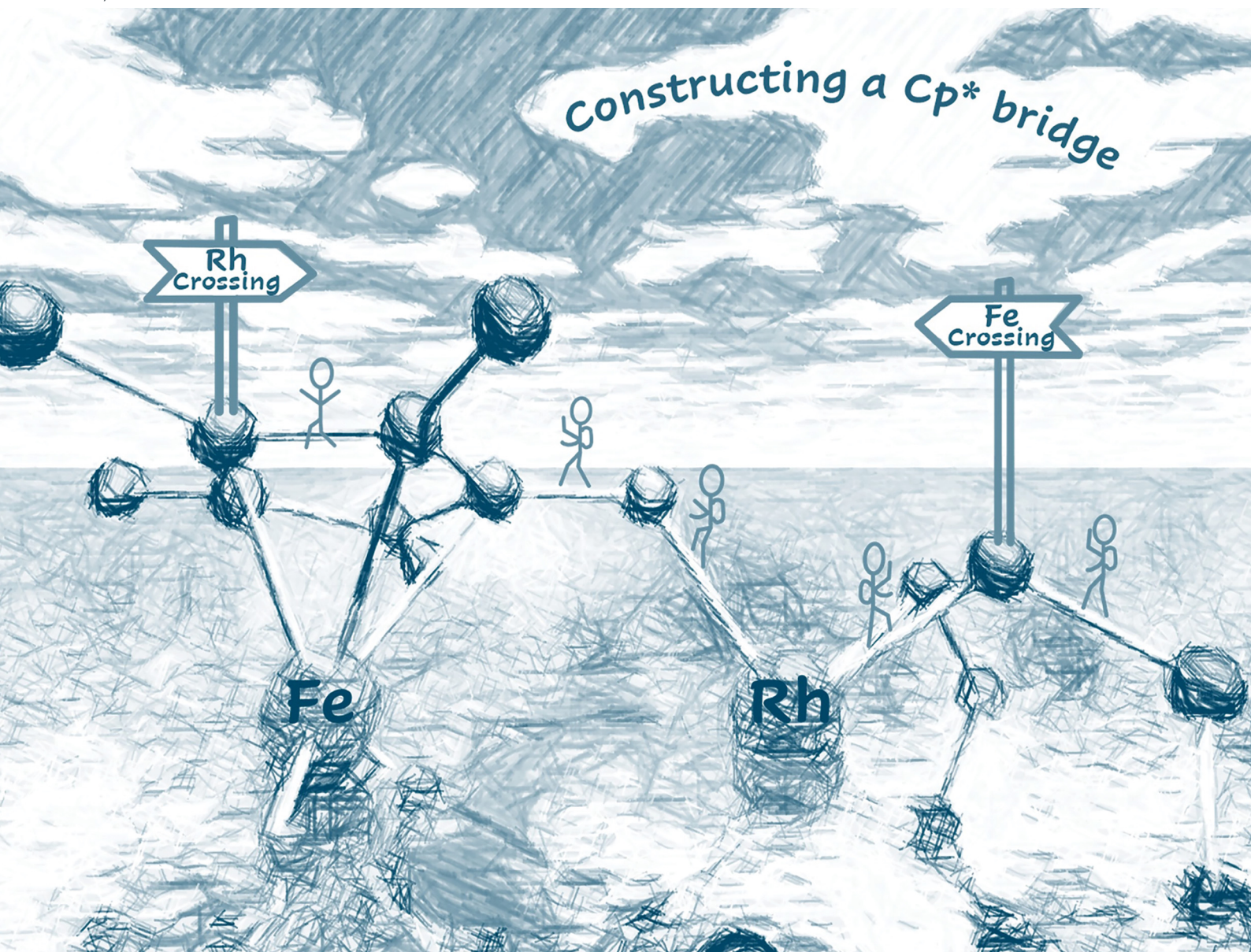


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**Studies that independently investigate [M]–C transmetalation reactions using two different metals are uncommon and yet understanding this reactivity is important to unlocking new synthetic approaches and product classes. Here, we show that the strained [Fe]–C complex,  $[(\eta^6\text{-C}_5\text{Me}_4\text{-CH}_2)\text{Fe}(\text{diphosphine})]$  undergoes transmetalation with rhodium(i) and iridium(i) diolefin salts, leading to rapid Fe–C(sp<sup>3</sup>) bond cleavage and M–C(sp<sup>3</sup>) (M = Rh or Ir) bond generation.**

Carbon-element (C–E) bond forming reactions are key to accessing synthetic diversity.<sup>1–4</sup> Contributions to the selective generation of C–C bonds, for example, were acknowledged with the 2010 Nobel prize in chemistry.<sup>5</sup> These metal-mediated transformations have had a measurable impact on the fields of drug development and discovery. The Suzuki–Miyaura coupling reaction, for example, is one of the most utilized across medicinal chemistry.<sup>6</sup> Such reactions proceed in the presence of a transition metal often *via* stepwise oxidative addition, transmetalation, and reductive elimination.<sup>7</sup>

Transmetalation can be used to forge reactive metal–carbon ([M]–C) bonds that can be later transferred or coupled *via* reductive elimination.<sup>8,9</sup> Of steps associated with cross-coupling, a detailed mechanistic understanding of transmetalation is comparatively lagging and has consequently been the subject of numerous studies.<sup>10–15</sup> Intimate knowledge surrounding preferred [M]–C generation routes helps to provide a general landscape for reaction optimization.<sup>16</sup> Electronegativity trends and by-products can sometimes be used to predict transfer propensity and the reaction outcome.

As an example of a strained [Fe]–C bond, we recently reported the preparation of an Fe(II) tucked-in complex,

## Ring strain governs transmetalation behaviour at a tucked-in iron complex†

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and Marcus W. Drover<sup>‡</sup>

$[(\eta^6\text{-C}_5\text{Me}_4\text{-CH}_2)\text{Fe}(\text{dnppe})]$  (dnppe = 1,2-bis(di-*n*-propylphosphino)ethane) (**1**).<sup>17,18</sup> Despite the prevalence of related sandwich complexes,  $[(\text{Cp}/\text{Cp}^*)_2\text{M}]$ ; Cp = C<sub>5</sub>H<sub>5</sub><sup>−</sup>; Cp\* = C<sub>5</sub>Me<sub>5</sub><sup>−</sup>, the reactivity of tucked-in compounds, especially those with late 3d elements, remains underexplored due to a size mismatch between the metal and L<sub>2</sub>X<sub>2</sub>–Cp\* ring donor (compared to group 4 metals, for example).<sup>19,20</sup> With **1** in hand, we wondered whether reaction with suitable metal sources would result in transmetalation, affording a programmable route towards heterometallic Cp\*{Fe,M} compounds. This transformation would simultaneously enable a detailed study of Fe–C(sp<sup>3</sup>) bond cleavage and M–C(sp<sup>3</sup>) bond generation between two model organometallic molecules, helping to determine how ring strain impacts carbon-transfer chemistry, whilst informing the use of {[Fe]–C} compounds as transmetalation partners.

Herein, we investigate the transmetalation behaviour of **1** with Rh(I) and Ir(I) halides – metals known for application in a wide variety of carbon-element bond-forming cycles (Scheme 1). This reaction leads to rapid Fe–C(sp<sup>3</sup>) bond cleavage and the formation of new M–C(sp<sup>3</sup>) (M = Rh or Ir) bonds. This behavior is reversible: the addition of a diphosphine prompts regeneration of complex **1** and produces Cl–M(diphosphine). Intermolecular control reactions between [Cp\*Fe(CH<sub>3</sub>)(diphosphine)] and Cl–ML<sub>*n*</sub> (L<sub>*n*</sub> = diolefin or diphosphine) provide a differential outcome, resulting in clean formation of Fe–Cl and M–C species, pointing toward a heterometallic effect. These findings provide a clear example of Fe-to-Rh or – Ir hydrocarbyl transfer – and its reverse, differentiating inter-*versus* intramolecular transmetalation.

To begin, red C<sub>6</sub>D<sub>6</sub> solutions of **1**<sup>17</sup> were reacted with 0.5 equiv. of [Rh(nbd)Cl]<sub>2</sub> (nbd = bicyclo[2.2.1]hepta-2,5-diene) or [M(COD)Cl]<sub>2</sub> (M = Rh or Ir, COD = 1,5-cyclooctadiene), affording ring-opened μ-Cl heterometallic complexes  $[(\eta^5\text{-C}_5\text{Me}_4\text{-CH}_2\text{-}\{\text{M}(\text{L}_n)\})\text{Fe}^{\text{II}}(\text{dnppe})(\mu\text{-Cl})]$  **2**, **3**, and **4**, respectively (Scheme 2). These reactions proceeded similarly, with a notable colour change occurring immediately upon addition – yellow brown for **2/3** and burgundy for **4**. The generation of **2–4** requires

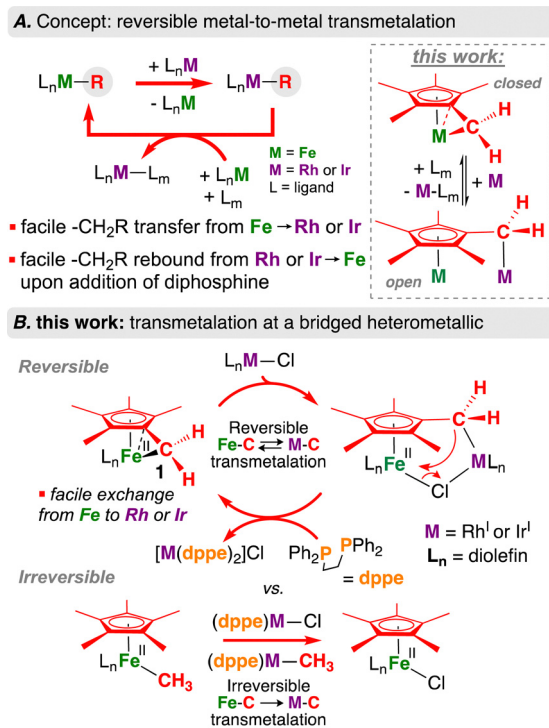
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† Electronic supplementary information (ESI) available: Experimental details, spectroscopic data, and computational methods. CCDC 2380939–2380943. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc06176d>

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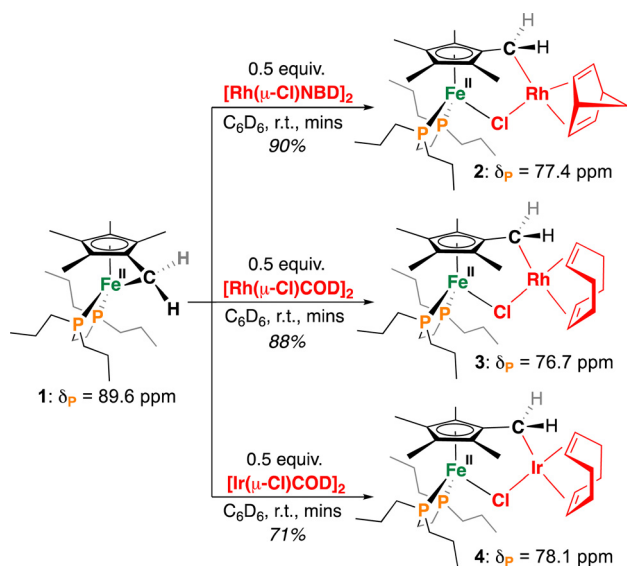




Scheme 1 (A) Concept: reversible metal-to-metal transmetalation; (B) present work: transmetalation at a bridged heterometallic.

tucked-in ring-opening, giving new M-C(sp<sup>3</sup>) bonds *via* Fe-to-M alkyl transmetalation.

The formation of these products is evidenced by a shift in their <sup>31</sup>P{<sup>1</sup>H} NMR spectrum, from  $\delta_{\text{p}} = 89.6$  ppm (for **1**)<sup>17</sup> to 77.4, 76.7, and 78.1 ppm, for **2–4** respectively. These chemical shifts are similar to mononuclear [Cp\*Fe(dnppe)Cl] ( $\delta_{\text{p}} = 79.4$  ppm)<sup>21</sup> and suggest the formation of a dative Fe-Cl bond. Additionally



Scheme 2 Reactions of **1** with M(I) (M = Rh, Ir) precursors to generate heterobimetallic complexes **2–4**.

supporting a  $\mu$ -Cl bridge between Fe and Rh, the <sup>31</sup>P{<sup>1</sup>H} NMR signature for **2** and **3** appears as a Rh-coupled doublet with  $J_{\text{P-Rh}} = 3.1$  and 2.7 Hz, respectively.

By <sup>1</sup>H NMR spectroscopy, desymmetrization of the Cp\*-Me protons proximal (2, 5-) and distal (3, 4-) to the [M]-CH<sub>2</sub> (M = Rh or Ir) bond can be used as an additional means to support a Cp\*-bound heterometallic with  $\Delta\delta \sim 1.40$  ppm. We suggest that shielding of the proximal (2, 5-) methyl sites results from adjacent metalation of an electron-rich Rh or Ir center. This shielding effect is additionally observed in the Cp\*-CH<sub>2</sub>-M(L<sub>n</sub>) group, which shifts from  $\delta_{\text{H}} = 2.74$  ppm in **1** to 1.13 ppm in **2**. Metalation of the Cp\*-CH<sub>2</sub>-M(L<sub>n</sub>) is further cemented by <sup>13</sup>C{<sup>1</sup>H} and <sup>1</sup>H-<sup>13</sup>C{<sup>1</sup>H} HSQC NMR spectroscopy, which for **2**, displays a Rh-coupled doublet at  $\delta_{\text{C}} = 27.5$  ppm ( $^1J_{\text{C-Rh}} = 27.2$  Hz).<sup>22</sup> To the best of our knowledge, compounds **2–4** represent the only known Fe(II)/Rh(I) or Ir(I) complexes merged from a single Cp\*-derived ligand scaffold.<sup>23</sup> More broadly, this represents the first programmable route towards such heterometallics using a single tucked-in precursor, providing a vast space for future design.

The structures of **2–4** were confirmed by single-crystal X-ray diffraction analysis (Fig. 1). Each of the three compounds comprises a five-membered Fe-C-C-M-Cl (M = Rh or Ir) ring system having an envelope-type conformation, with the  $\mu$ -Cl group occupying the *endo*-position. Across the series, the Fe-M distance increases from 3.816(1) Å (**2**) to 3.863(2) Å (**3**) to 3.875(1) Å (**4**) with most other inter-ring distances staying within *ca.* 0.02 Å of one another. This can be rationalized by the larger diolefin ligand (COD vs. nbd) for Rh(I) and the greater atomic radius of Ir *cf.*, Rh on going from **3** to **4**.

Given the inherent lability of metal-bound diolefin groups, we next became interested in the onwards functionalization chemistry of **2–4** with neutral L-type donor ligands, settling on diphosphines due to a strong drive for M-P bond formation and ease of monitoring by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy (Scheme 3A). Using the nbd precursor, **2**, treatment with 1,2-bis(diphenylphosphino)ethane (dppe) at  $-78$  °C immediately resulted in the formation of three new resonances by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy at  $\delta_{\text{p}} = 79.2$  for Fe-dnppe as well as 72.9 (dd,  $^1J_{\text{Rh-P}} = 234.7$  Hz,  $^2J_{\text{P-P}} = 26.7$  Hz) and 47.0 (dd,  $^1J_{\text{Rh-P}} = 126.6$  Hz,  $^2J_{\text{P-P}} = 26.7$  Hz) for the Rh-dppe component, attributed to the product **5**, [( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>-{Rh(dppe)})Fe<sup>II</sup>(dnppe)( $\mu$ -Cl)] (Scheme 3). A *trans*-influence of the bound Cp\*CH<sub>2</sub> group is borne out in a marked decrease in  $^1J_{\text{Rh-P}}$  coupling value from 234.7 (*trans*-Cl) to 126.6 Hz (*trans*-Cp\*CH<sub>2</sub>).

Single crystals of **5** suitable for analysis by X-ray diffraction confirm a  $\mu$ -Cl Fe-Cl-Rh(dppe) complex (Scheme 3B). Complex **5** maintains the longest distance between Fe and Rh (3.924(1) Å), lengthened by nearly 0.11 Å when compared to its nbd precursor **2**. Of the heterobimetallic species generated, compound **5** has the shortest Fe-C2 (2.116(3) Å) and Fe-Cl (2.346(1) Å) bond lengths, suggesting the greatest “dissociation” from Rh. This point is further supported by a lengthened Rh-C1 bond of 2.142(3) for **5** vs. 2.088(2) Å for **2**, ascribed to a *trans*-influence of the newly installed phosphorus donor.

Solutions of **5** were found to be unstable at room-temperature, cleanly returning tucked-in complex **1** and mixtures of



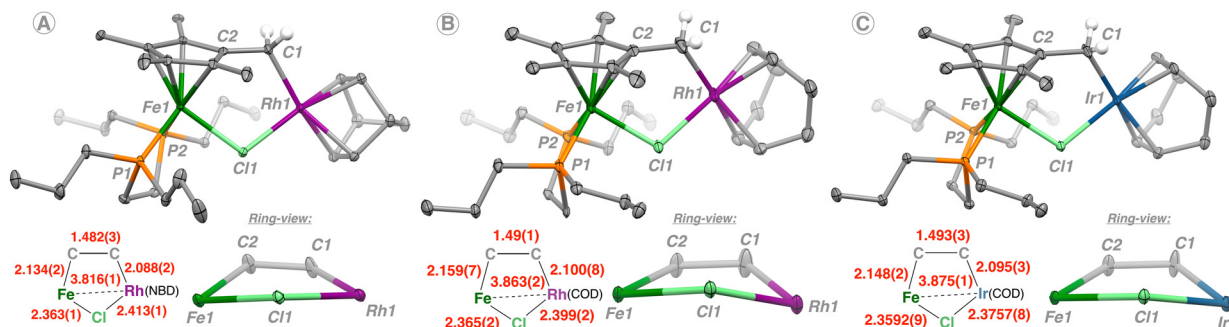
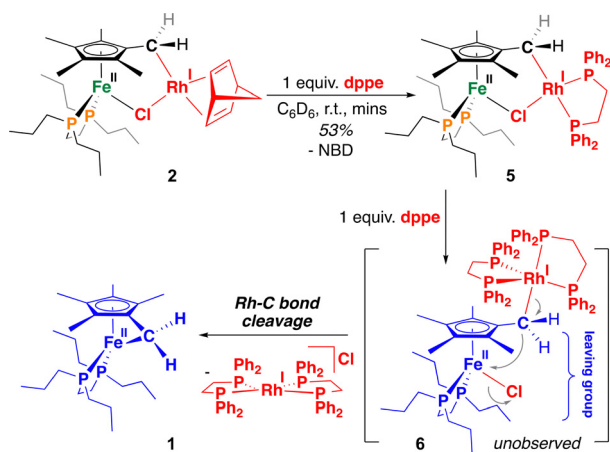
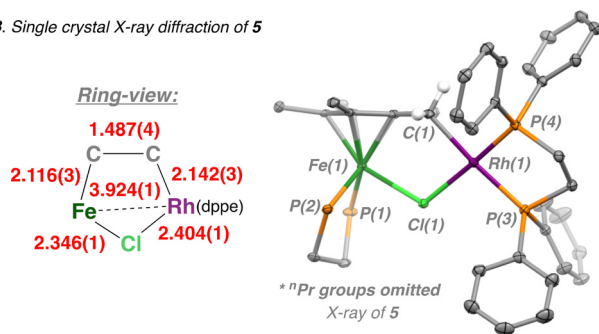


Fig. 1 Molecular structures of (A) **2**, (B) **3**, and (C) **4** with ellipsoids drawn at 40% probability. Hydrogen atoms except for those on C(1) are omitted for clarity.

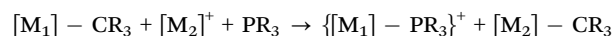


B. Single crystal X-ray diffraction of **5**



Scheme 3 (A) Generation of complex **5** and onwards Rh-to-Fe–C(sp<sup>3</sup>) bond exchange; (B) the molecular structure of **5** with ellipsoids drawn at 40% probability. Hydrogen atoms are omitted except for those on C(1).

[Rh(dppe)(μ-Cl)]<sub>2</sub> and [Rh(dppe)<sub>2</sub>]Cl (Scheme 3A).<sup>24</sup> Given the preparative route used to access **2**: reaction of **1** with 0.5 equiv. [Rh(nbd)(μ-Cl)]<sub>2</sub>, one might conclude that ring-opening or -closing (to return **1**) is apparently dictated by group 9 metal ligand type *i.e.*, Rh(diolefin) vs. Rh(diphosphine). This reaction is accelerated by the addition of excess dppe causing the formation of tucked-in complex **1** and [Rh(dppe)<sub>2</sub>]Cl, which precipitates from solution (Scheme 3A) – possibly *via* the unobserved intermediacy of five-coordinate complex **6**. Examples of this elementary transformation, donor-induced transmetalation, where M = metal:



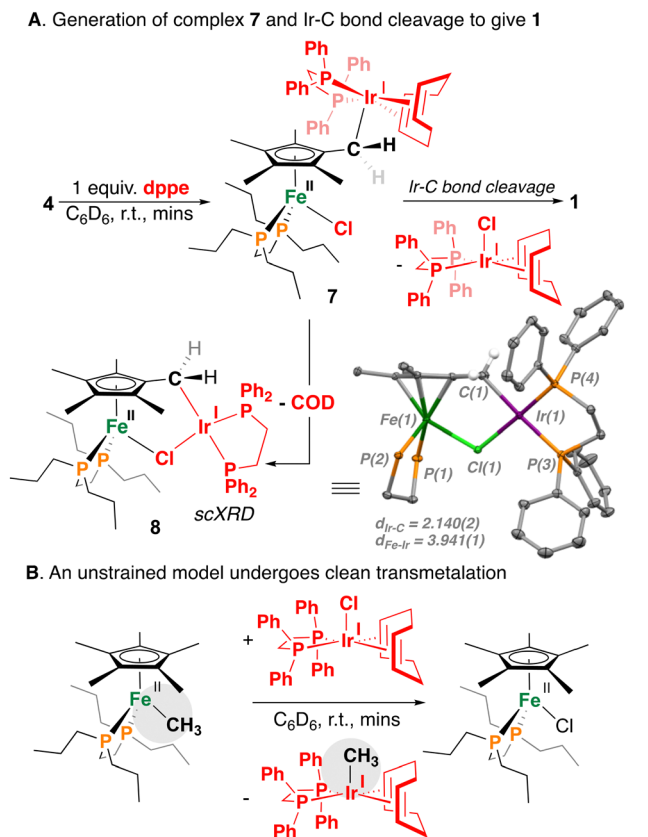
are unusual with the present case benefiting from the leaving group propensity of **1**.

To assess the favourability of this reaction the dissociation of **5** was modelled computationally. This reaction was found to be roughly thermoneutral ( $\Delta G^\circ = -0.3 \text{ kcal mol}^{-1}$ ) having a positive value of  $\Delta H^\circ = 16.8 \text{ kcal mol}^{-1}$  (see ESI†).

To explore the relationship between Fe–C bond strain and transmetalation outcome, the reactivity of the unstrained model, [Cp\*Fe<sup>II</sup>(dnppe)(CH<sub>3</sub>)] with [Rh(μ-Cl)(nbd)]<sub>2</sub> was also tested. In this case, Fe–C(sp<sup>3</sup>) bond cleavage results to give [Cp\*Fe<sup>II</sup>(dnppe)(Cl)] by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. By <sup>1</sup>H NMR spectroscopy, the related Rh(i)–CH<sub>3</sub> compound [Rh(nbd)(μ-CH<sub>3</sub>)<sub>2</sub>] is not observed. However, the observation of CH<sub>4</sub> is consistent with its implied intermediacy. Indeed, related reactions of [Rh(diolefin)(μ-Cl)]<sub>2</sub> and CH<sub>3</sub>Li, to generate bridging alkyl Rh complexes, were reported as early as 1987 by Andersen and Muettterties.<sup>25,26</sup> Unlike the Rh(i) alkyl diolefin compounds **2** and **3** presented here, [Rh(COD)(μ-CH<sub>3</sub>)<sub>2</sub>] requires cryogenic preparation and storage. The authors note that the decomposition of this compound occurs at temperatures as low as 0 °C *via* elimination of CH<sub>4</sub>. Relatedly, they report that efforts to synthesize the nbd analogue, “[Rh(nbd)(μ-CH<sub>3</sub>)<sub>2</sub>],” result in product decomposition *via* elimination of CH<sub>4</sub> at –30 °C, thwarting isolation.

Expanding our study to the 5d congener Ir(i), treatment of **4** with dppe was pursued (Scheme 4A). For this reaction, however, Ir–COD coordination was maintained, as evidenced by a multiplet in the <sup>1</sup>H NMR spectrum at  $\delta_H = 3.48 \text{ ppm}$  (4H) (and the absence of free COD). Moreover, the observation of two phosphorus resonances at  $\delta_P = 79.8$  and 27.1 ppm of integration 2 : 2 suggests the formation of a terminal [(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>-{Ir(dppe)(COD)})Fe<sup>II</sup>(dnppe)(Cl)] (**7**) (Scheme 4A) *cf.*, bridging chloride, where in the case of the latter, three distinct <sup>31</sup>P NMR resonances would be expected due to local C<sub>s</sub>-symmetry (as seen for **5**). Speaking to COD lability, single-crystal X-ray diffraction analysis of **7** revealed the μ-Cl analogue of **5** – [(η<sup>5</sup>-C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>-{Ir(dppe)})Fe<sup>II</sup>(dnppe)(μ-Cl)] (**8**). Chloride interaction (bridging or terminal) in **7**, however, does not dictate group 9 metal loss, which generates the five-coordinate





**Scheme 4** (A) Generation of complex **7** and onwards Ir-to-Fe-C(sp<sup>3</sup>) bond exchange. (B) An unstrained model undergoes clean transmetalation.

[Ir(dppe)(COD)(Cl)] ( $\delta_{\text{P}} = 34.4$  ppm) complex (along with **1**) over time in solution. Consistent with the forward direction of this process, this reaction is irreversible – treatment of **1** with [Ir(dppe)(COD)(Cl)] does not result in **7**.

As an intra- vs. intermolecular point of comparison, reactivity of the unstrained model, [Cp\*Fe<sup>II</sup>(dnppe)(CH<sub>3</sub>)] with [Ir(dppe)(COD)(Cl)] was also tested (Scheme 4B). In this case, the Fe-CH<sub>3</sub> complex underwent clean methyl transfer to give [Ir(dppe)(COD)(CH<sub>3</sub>)]<sup>27</sup> and [Cp\*Fe<sup>II</sup>(dnppe)(Cl)] as the only Fe-containing by-product. For the unstrained analogue, the intermolecular transfer of Fe-CH<sub>3</sub> to Ir-Cl speaks to the drive for Ir-CH<sub>3</sub> and Fe-Cl bond formation. For **5** and **7**, however, this driving force is offset by the stability of **1**, providing a reversal in the predicted outcome. This general reactivity trend additionally contrasts with that noted for the CpFe complex, [CpFe(CO)<sub>2</sub>I] (Cp = C<sub>5</sub>H<sub>5</sub><sup>-</sup>) and Au-C bonds (another 5d-element), which results in Fe-C bond formation.<sup>28</sup>

A family of heterometallic Fe/M (M = Rh or Ir) complexes have been systematically prepared *via* an elementary transmetalation reaction between a strained Cp\*Fe tucked-in complex **1** and group 9 diolefin salts. This work establishes routes for the systematic generation of such a compositionally distinct class of Cp\*{Fe,M} compound and furthers our understanding of the

factors that contribute to metal-to-metal transmetalation, an elementary reaction with direct implications for carbon-element bond formation using Fe.

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## Data availability

The data supporting this article have been included as part of the ESI.† Crystallographic data for **2–5** and **8** have been deposited at the Cambridge Crystallographic Data Centre (CCDC 2380939–2380943†).

## Conflicts of interest

There are no conflicts to declare.

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