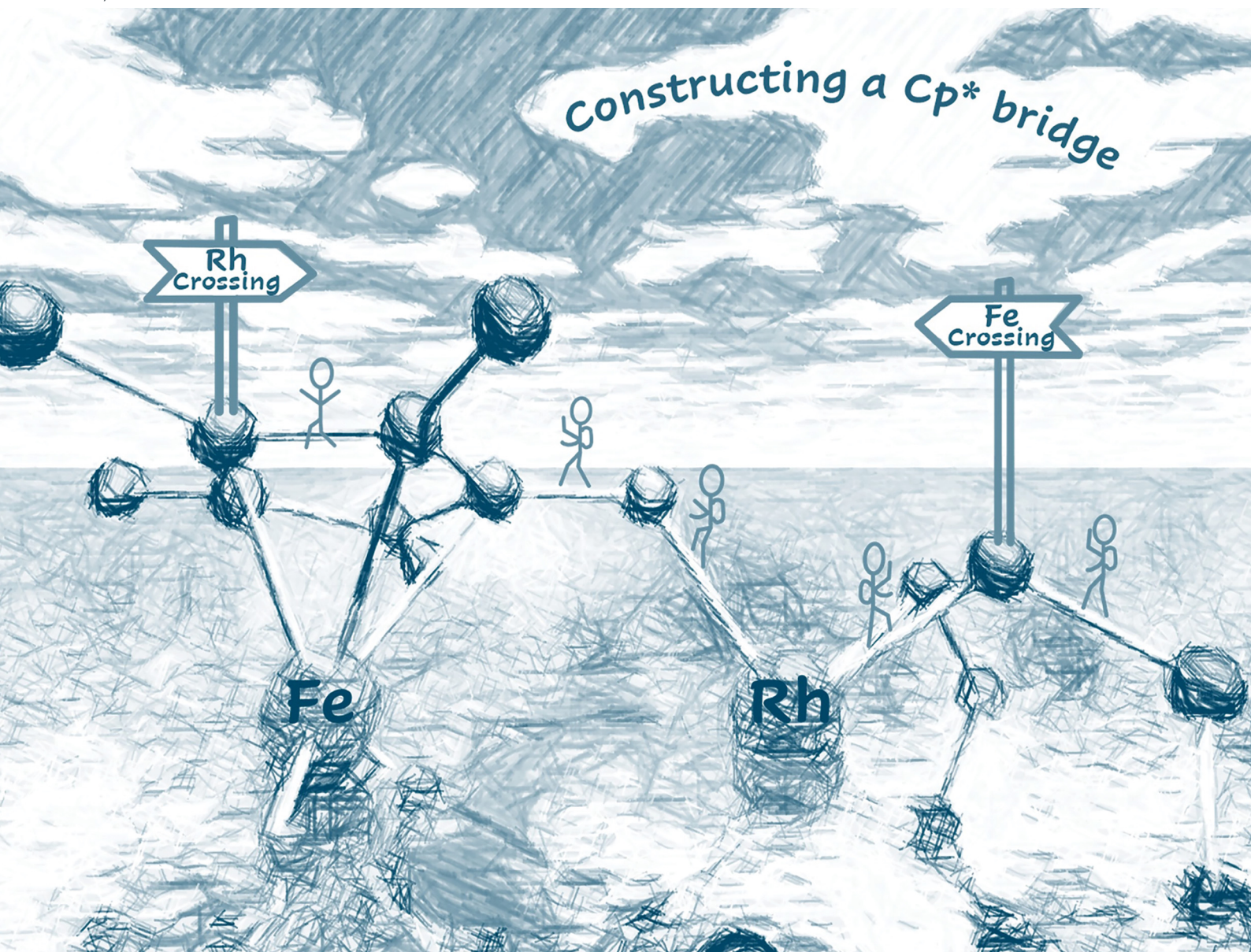


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Studies that independently investigate [M]–C transmetalation reactions using two different metals are uncommon and yet understanding this reactivity is important to unlocking new synthetic approaches and product classes. Here, we show that the strained [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(sp³) bond cleavage and M–C(sp³) (M = Rh or Ir) bond generation.

Carbon-element (C–E) bond forming reactions are key to accessing synthetic diversity.^{1–4} Contributions to the selective generation of C–C bonds, for example, were acknowledged with the 2010 Nobel prize in chemistry.⁵ 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.⁶ Such reactions proceed in the presence of a transition metal often *via* stepwise oxidative addition, transmetalation, and reductive elimination.⁷

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

$[(\eta^6\text{-C}_5\text{Me}_4\text{-CH}_2)\text{Fe}(\text{dnppe})]$ (dnppe = 1,2-bis(di-*n*-propylphosphino)ethane) (**1**).^{17,18} Despite the prevalence of related sandwich complexes, $[(\text{Cp}/\text{Cp}^*)_2\text{M}]$; Cp = C₅H₅[−]; Cp* = C₅Me₅[−], the reactivity of tucked-in compounds, especially those with late 3d elements, remains underexplored due to a size mismatch between the metal and L₂X₂–Cp* ring donor (compared to group 4 metals, for example).^{19,20} 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(sp³) bond cleavage and M–C(sp³) 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(sp³) bond cleavage and the formation of new M–C(sp³) (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 $[\text{Cp}^*\text{Fe}(\text{CH}_3)\text{-}(\text{diphosphine})]$ and Cl–ML_{*n*} (L_{*n*} = 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 C₆D₆ solutions of **1**¹⁷ were reacted with 0.5 equiv. of $[\text{Rh}(\text{nbd})\text{Cl}]_2$ (nbd = bicyclo[2.2.1]hepta-2,5-diene) or $[\text{M}(\text{COD})\text{Cl}]_2$ (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

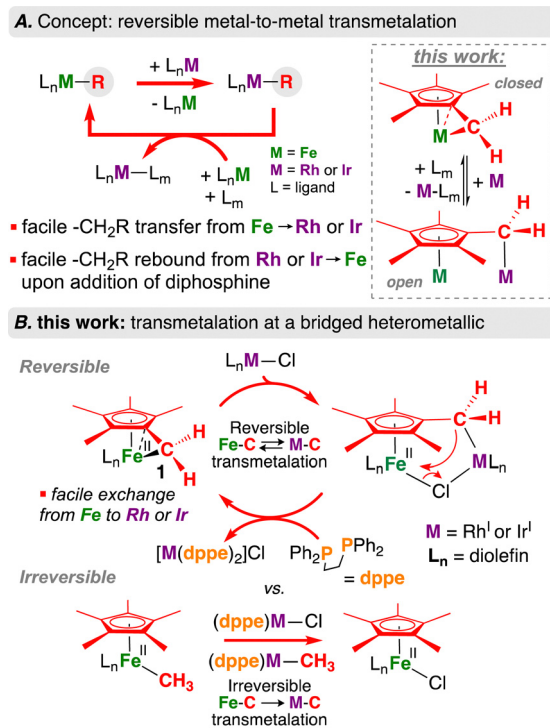
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† Electronic supplementary information (ESI) available: Experimental details, spectroscopic data, and computational methods. CCDC 2380939–2380943. For ESI and crystallographic data in CIF or other electronic format see DOI: <https://doi.org/10.1039/d4cc06176d>

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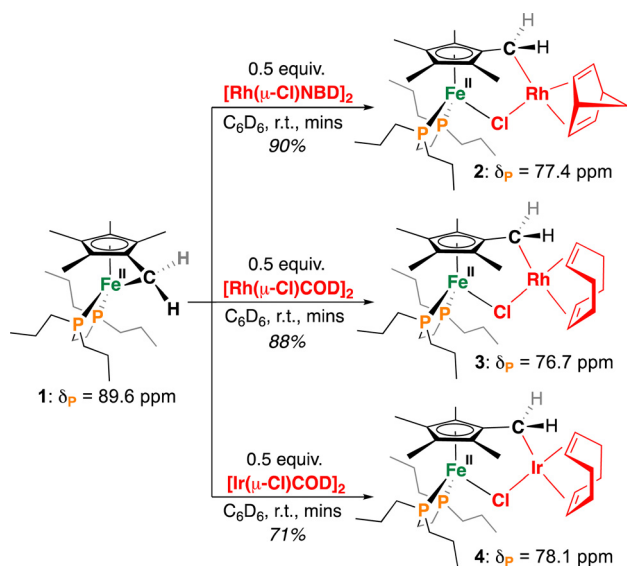




Scheme 1 (A) Concept: reversible metal-to-metal transmetalation; (B) present work: transmetalation at a bridged heterometallic.

tucked-in ring-opening, giving new $\text{M-C}(\text{sp}^3)$ bonds *via* Fe-to-M alkyl transmetalation.

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



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

supporting a $\mu\text{-Cl}$ bridge between Fe and Rh, the $^{31}\text{P}\{^1\text{H}\}$ 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 ^1H NMR spectroscopy, desymmetrization of the $\text{Cp}^*\text{-Me}$ protons proximal (2, 5-) and distal (3, 4-) to the $[\text{M}]\text{-CH}_2$ ($\text{M} = \text{Rh}$ or Ir) bond can be used as an additional means to support a $\text{Cp}^*\text{-bound}$ 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 $\text{Cp}^*\text{-CH}_2\text{-M}(\text{L}_n)$ group, which shifts from $\delta_{\text{H}} = 2.74$ ppm in **1** to 1.13 ppm in **2**. Metallation of the $\text{Cp}^*\text{-CH}_2\text{-M}(\text{L}_n)$ is further cemented by $^{13}\text{C}\{^1\text{H}\}$ and $^1\text{H}\text{-}^{13}\text{C}\{^1\text{H}\}$ 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).²² To the best of our knowledge, compounds **2–4** represent the only known $\text{Fe}(\text{II})/\text{Rh}(\text{I})$ or $\text{Ir}(\text{I})$ complexes merged from a single $\text{Cp}^*\text{-derived}$ ligand scaffold.²³ 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 ($\text{M} = \text{Rh}$ or Ir) ring system having an envelope-type conformation, with the $\mu\text{-Cl}$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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**, $[(\eta^5\text{-C}_5\text{Me}_4\text{-CH}_2\text{-}\{\text{Rh}(\text{dppe})\})\text{Fe}^{\text{II}}(\text{dnppe})(\mu\text{-Cl})]$ (Scheme 3). A *trans*-influence of the bound Cp^*CH_2 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_2).

Single crystals of **5** suitable for analysis by X-ray diffraction confirm a $\mu\text{-Cl}$ 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



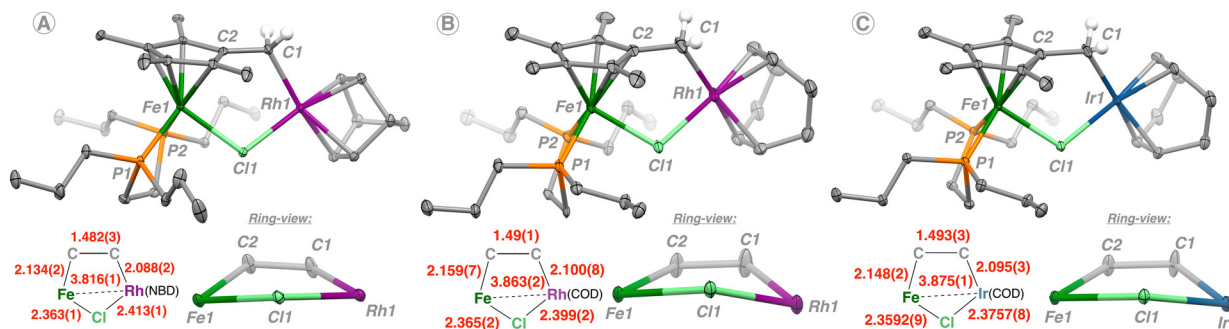
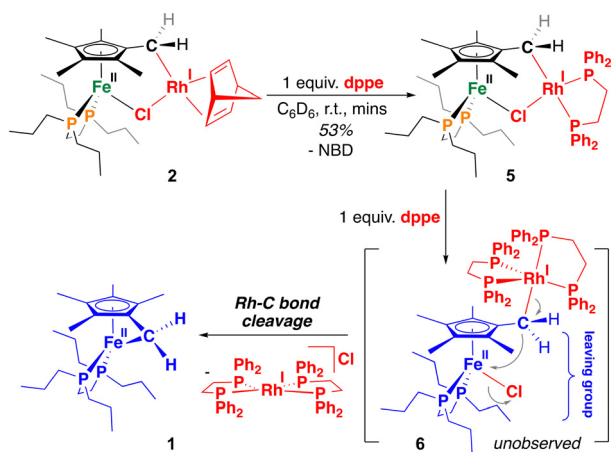
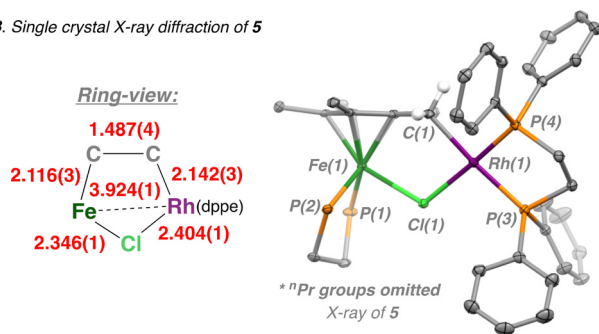


Fig. 1 Molecular structures of (A) **2**, (B) **3**, and (C) **4** with ellipsoids drawn at 40% probability. Hydrogen atoms except for those on C(1) are omitted for clarity.

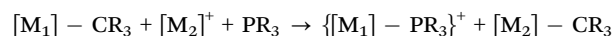


B. Single crystal X-ray diffraction of **5**



Scheme 3 (A) Generation of complex **5** and onwards Rh-to-Fe–C(sp³) 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)]₂ and [Rh(dppe)₂]Cl (Scheme 3A).²⁴ Given the preparative route used to access **2**: reaction of **1** with 0.5 equiv. [Rh(nbd)(μ-Cl)]₂, 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)₂]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:



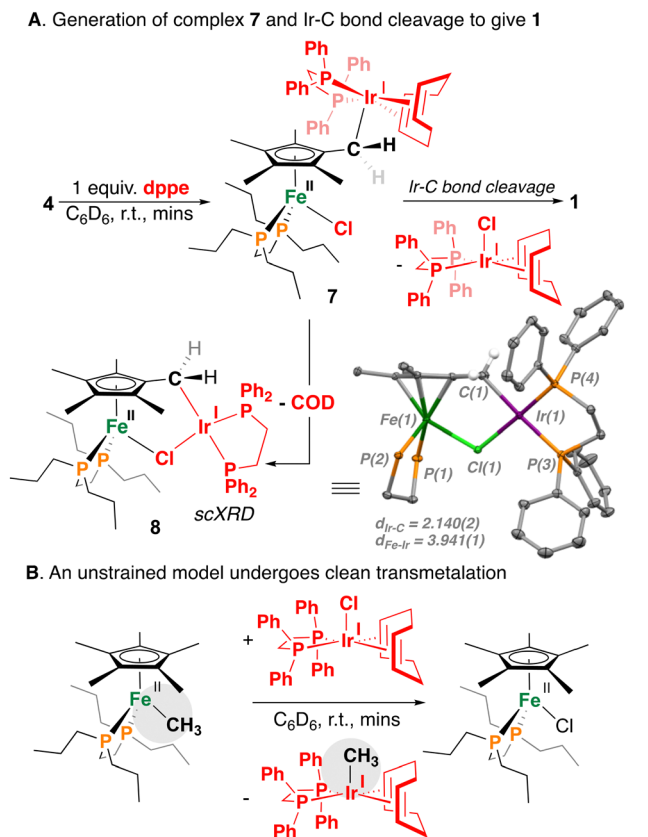
are unusual with the present case benefiting from the leaving group propensity of **1**.

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^{II}(dnppe)(CH₃)] with [Rh(μ-Cl)(nbd)]₂ was also tested. In this case, Fe–C(sp³) bond cleavage results to give [Cp*Fe^{II}(dnppe)(Cl)] by ³¹P{¹H} NMR spectroscopy. By ¹H NMR spectroscopy, the related Rh(i)–CH₃ compound [Rh(nbd)(μ-CH₃)₂] is not observed. However, the observation of CH₄ is consistent with its implied intermediacy. Indeed, related reactions of [Rh(diolefin)(μ-Cl)]₂ and CH₃Li, to generate bridging alkyl Rh complexes, were reported as early as 1987 by Andersen and Muettterties.^{25,26} Unlike the Rh(i) alkyl diolefin compounds **2** and **3** presented here, [Rh(COD)(μ-CH₃)₂] 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 CH₄. Relatedly, they report that efforts to synthesize the nbd analogue, “[Rh(nbd)(μ-CH₃)₂],” result in product decomposition *via* elimination of CH₄ 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 ¹H 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 [(η⁵-C₅Me₄-CH₂-{Ir(dppe)(COD)})Fe^{II}(dnppe)(Cl)] (**7**) (Scheme 4A) *cf.*, bridging chloride, where in the case of the latter, three distinct ³¹P NMR resonances would be expected due to local C_s-symmetry (as seen for **5**). Speaking to COD lability, single-crystal X-ray diffraction analysis of **7** revealed the μ-Cl analogue of **5** – [(η⁵-C₅Me₄-CH₂-{Ir(dppe)})Fe^{II}(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(sp³) 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^{II}(dnppe)(CH₃)] with [Ir(dppe)(COD)(Cl)] was also tested (Scheme 4B). In this case, the Fe–CH₃ complex underwent clean methyl transfer to give [Ir(dppe)(COD)(CH₃)]²⁷ and [Cp*Fe^{II}(dnppe)(Cl)] as the only Fe-containing by-product. For the unstrained analogue, the intermolecular transfer of Fe–CH₃ to Ir–Cl speaks to the drive for Ir–CH₃ 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)₂] (Cp = C₅H₅[−]) and Au–C bonds (another 5d-element), which results in Fe–C bond formation.²⁸

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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