Volume 61 Number 16 25 February 2025 Pages 3213-3410

# ChemComm

Chemical Communications

rsc.li/chemcomm



ISSN 1359-7345



**COMMUNICATION** Marcus W. Drover *et al.* Ring strain governs transmetalation behaviour at a tucked-in iron complex

### ChemComm



View Article Online View Journal | View Issue

Check for updates

Cite this: Chem. Commun., 2025, 61, 3323

Received 21st November 2024, Accepted 7th January 2025

DOI: 10.1039/d4cc06176d

rsc.li/chemcomm

## Ring strain governs transmetalation behaviour at a tucked-in iron complex<sup>†</sup>

Connor S. Durfy, (1);<sup>a</sup> Michelle Huang, <sup>‡a</sup> Joseph A. Zurakowski, (1)<sup>ab</sup> Paul D. Boyle<sup>a</sup> and Marcus W. Drover (1)\*<sup>a</sup>

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,  $[(\eta^6-C_5Me_4-CH_2)Fe(diphosphine)]$  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 land-scape 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( $\pi$ ) tucked-in complex,  $[(\eta^6-C_5Me_4-CH_2)Fe(dnppe)](dnppe = 1,2-bis(di-n-propylphos$ phino)ethane) (1).<sup>17,18</sup> Despite the prevalence of related sandwich complexes,  $([Cp/Cp^*]_2M; Cp = C_5H_5^-; Cp^* = C_5Me_5^-)$ , the reactivity of tucked-in compounds, especially those with late elements, remains underexplored due to a size 3d 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(1) and Ir(1) 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  $C_6D_6$  solutions of  $1^{17}$  were reacted with 0.5 equiv. of  $[Rh(nbd)Cl]_2$  (nbd = bicyclo[2.2.1]hepta-2,5-diene) or  $[M(COD)Cl]_2$  (M = Rh or Ir, COD = 1,5-cyclooctadiene), affording ring-opened  $\mu$ -Cl heterometallic complexes  $[(\eta^5-C_5Me_4-CH_2-{M(L_n)})Fe^{II}(dnppe)(\mu$ -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

<sup>&</sup>lt;sup>a</sup> Department of Chemistry, Western University, 1151 Richmond St, London, ON, N8K 3G6, Canada. E-mail: marcus.drover@uwo.ca

<sup>&</sup>lt;sup>b</sup> Department of Chemistry and Biochemistry, University of Windsor, 401 Sunset Ave, Windsor, ON, N9B 3P4, Canada

<sup>†</sup> 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

<sup>‡</sup> These authors contributed equally.



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  $\delta_{\rm P}$  = 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(*dn*ppe)Cl] ( $\delta_{\rm P}$  = 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  ${}^{31}P{}^{1}H$ NMR signature for 2 and 3 appears as a Rh-coupled doublet with  $J_{P-Rh} = 3.1$  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  $Cp^*-CH_2-M(L_n)$ group, which shifts from  $\delta_{\rm H}$  = 2.74 ppm in **1** to 1.13 ppm in **2**. Metallation of the Cp\*-CH<sub>2</sub>-M(L<sub>n</sub>) is further cemented by  ${}^{13}C{}^{1}H$ 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  $\delta_{\rm C}$  = 27.5 ppm (<sup>1</sup> $J_{\rm C-Rh}$  = 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( $\iota$ ) 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  $\delta_P = 79.2$  for Fe-dnppe as well as 72.9 (dd, <sup>1</sup>J<sub>Rh-P</sub> = 234.7 Hz, <sup>2</sup>J<sub>P-P</sub> = 26.7 Hz) and 47.0 (dd, <sup>1</sup>J<sub>Rh-P</sub> = 126.6 Hz, <sup>2</sup>J<sub>P-P</sub> = 26.7 Hz) for the Rh-dppe component, attributed to the product **5**,  $[(\eta^5-C_5Me_4-CH_2-{Rh(dppe)})Fe^{II}(dnppe)(\mu-CI)]$  (Scheme 3). A *trans*-influence of the bound Cp\*CH<sub>2</sub> group is borne out in a marked decrease in <sup>1</sup>J<sub>Rh-P</sub> coupling value from 234.7 (*trans*-CI) 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.



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).

 $[Rh(dppe)(\mu-Cl)]_2$  and  $[Rh(dppe)_2]Cl$  (Scheme 3A).<sup>24</sup> Given the preparative route used to access 2: reaction of 1 with 0.5 equiv.  $[Rh(nbd)(\mu-Cl)]_2$ , 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:

$$[M_1] - CR_3 + [M_2]^+ + PR_3 \rightarrow \{[M_1] - PR_3\}^+ + [M_2] - CR_3$$

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,  $[Cp*Fe^{II}(dnppe)(CH_3)]$  with  $[Rh(\mu-Cl)(nbd)]_2$  was also tested. In this case, Fe-C(sp<sup>3</sup>) bond cleavage results to give  $[Cp*Fe^{II}(dnppe)(Cl)]$  by <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy. By <sup>1</sup>H NMR spectroscopy, the related Rh(I)-CH3 compound [Rh(nbd)(µ- $[CH_3]_2$  is not observed. However, the observation of  $CH_4$  is consistent with its implied intermediacy. Indeed, related reactions of  $[Rh(diolefin)(\mu-Cl)]_2$  and  $CH_3Li$ , to generate bridging alkyl Rh complexes, were reported as early as 1987 by Andersen and Muetterties.<sup>25,26</sup> Unlike the Rh(1) alkyl diolefin compounds 2 and 3 presented here,  $[Rh(COD)(\mu-CH_3)]_2$  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 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  $CH_4$  at -30 °C, thwarting isolation.

Expanding our study to the 5d congener Ir(1), 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  $\delta_{\rm H}$  = 3.48 ppm (4H) (and the absence of free COD). Moreover, the observation of two phosphorus resonances at  $\delta_{\rm P}$  = 79.8 and 27.1 ppm of integration 2:2 suggests the formation of a terminal [( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>-{Ir(dppe)(COD)})Fe<sup>II</sup>(dnppe)(CI)] (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  $\mu$ -Cl analogue of 5 – [( $\eta^5$ -C<sub>5</sub>Me<sub>4</sub>-CH<sub>2</sub>-{Ir(dppe)})Fe<sup>II</sup>(dnppe)( $\mu$ -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)] ( $\delta_P = 34.4$  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,  $[Cp^*Fe^{II}(dnppe)(CH_3)]$  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  $[Ir(dppe)(COD)(CH_3)]^{27}$  and  $[Cp^*Fe^{II}(dnppe)(Cl)]$  as the only Fecontaining 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,  $[CpFe(CO)_2I]$  (Cp =  $C_5H_5^-$ ) and Au–C bonds (another 5delement), 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 carbonelement bond formation using Fe.

The authors are grateful to Western University, the Council of Ontario Universities for a John C. Polanyi award to M. W. D., the Canadian Foundation for Innovation (LOF-212442), and the Natural Sciences and Engineering Research Council of Canada (Discovery Grant, RGPIN-2020-04480 (M. W. D.), Discovery Launch Supplement, DGECR-2020-00183), and graduate award (CGS-D/NSERC Vanier to J. A. Z.) for funding. M. H. thanks the Inorganic Chemistry Exchange (ICE) program for the opportunity to conduct research at Western University.

#### 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.

#### References

- 1 J. K. Stille, Angew. Chem., Int. Ed. Engl., 1986, 25, 508-524.
- 2 I. P. Beletskaya and A. V. Cheprakov, *Chem. Rev.*, 2000, **100**, 3009–3066.
- 3 N. Miyaura and A. Suzuki, Chem. Rev., 1995, 95, 2457-2483.
- 4 X. Chen, et al., Angew. Chem., Int. Ed., 2009, 48, 5094-5115.
- 5 C. C. C. Johansson Seechurn, et al., Angew. Chem., Int. Ed., 2012, 51, 5062–5085.
- 6 D. G. Brown and J. Boström, J. Med. Chem., 2016, 59, 4443-4458.
- 7 A. Biffis, et al., Chem. Rev., 2018, 118, 2249-2295.
- 8 X. Yan and C. Xi, Coord. Chem. Rev., 2017, 350, 275-284.
- 9 S. C. Rasmussen, ChemTexts, 2021, 7, 1.
- 10 D. V. Partyka, Chem. Rev., 2011, 111, 1529-1595.
- 11 C. He, et al., Angew. Chem., 2013, 125, 1567-1570.
- 12 A. A. Thomas, et al., J. Am. Chem. Soc., 2017, 139, 3805-3821.
- 13 A. A. Thomas and S. E. Denmark, Science, 2016, 352, 329-332.
- 14 M. J. Demchuk, et al., Chem. Commun., 2022, 58, 68-71.
- 15 M. L. Neidig, et al., Acc. Chem. Res., 2019, 52, 140-150.
- 16 H. Kurosawa and A. Yamamoto, *Fundamentals of Molecular Catalysis*, Elsevier Science, Amsterdam, Netherlands, 2003.
- 17 J. A. Zurakowski and M. W. Drover, Chem. Commun., 2023, 59, 11349-11352.
- 18 J. A. Zurakowski, et al., Chem. Sci., 2024, 15, 10359-10365.
- 19 T. J. Kealy and P. L. Pauson, Nature, 1951, 168, 1039-1040.
- 20 (a) P. J. Chirik, Organometallics, 2010, 29, 1500–1517; (b) T. Ostwald, et al., Organometallics, 2019, 38, 829–843; (c) J. Pinkas, et al., Dalton Trans., 2022, 51, 10198–10215.
- 21 J. A. Zurakowski, et al., Inorg. Chem., 2023, 62, 7053-7060.
- 22 S. Liu and G. S. Girolami, Organometallics, 2021, 40, 714-724.
- 23 T. Shima and Z. Hou, Organometallics, 2009, 28, 2244-2252.
- 24 A. Meißner, et al., ChemPlusChem, 2015, 80, 169-180.
- 25 M. A. Kulzick, et al., J. Organomet. Chem., 1987, 336, 221-236.
- 26 M. A. Kulzick, et al., J. Organomet. Chem., 1987, 333, 105-118.
- 27 M. R. Churchill and S. A. Bezman, *Inorg. Chem.*, 1973, 12, 531–536.
  28 A. S. K. Hashmi and L. Molinari, *Organometallics*, 2011, 30, 3457–3460.