

Dyotropic Rearrangement

Dyotropic Rearrangement of an Iron–Aluminium Complex

Benedek Stadler, Nikolaus Gorgas, Stuart J. Elliott, and Mark R. Crimmin*

Abstract: Ligand exchange processes at metal complexes underpin their reactivity and catalytic applications. While mechanisms of ligand exchange at single site complexes are well established, occurring through textbook associative, dissociative and interchange mechanisms, those involving heterometallic complexes are less well developed. Here we report the reactions of a well-defined Fe–Al dihydride complex with exogenous ligands (CO and CNR, R = Me, ^tBu, Xyl = 2,6-Me₂C₆H₃). Based on DFT calculations we suggest that these reactions occur through a dyotropic rearrangement, this involves initial coordination of the exogenous ligand at Al followed by migration to Fe, with simultaneous migration of a hydride ligand from Fe to Al. Such processes are rare for heterometallic complexes. We study the bonding and mechanism of the dyotropic rearrangement through in-depth computational analysis (NBO, IBOs, CLMO analysis, QTAIM, NCIPLOT, IGMH), shedding new light on how the electronic structure of the heterometallic core responds to the migration of ligands between metal sites. The dyotropic rearrangement fundamentally changes the nature of the hydride ligands, exposing new nucleophilic reactivity as evidenced by insertion reactions with CO₂, isocyanates, as well as isocyanides.

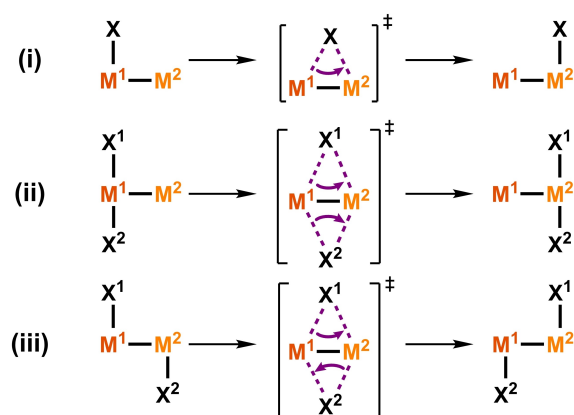
Introduction

Recent years have seen a rapid growth in the interest of heterometallic complexes. Numerous researchers are now actively developing synthetic approaches to heterometallic complexes, studying their properties, and developing their applications as catalysts. One particular area of promise is

heterometallic complexes that contain direct metal–metal bonds. This allows for bimetallic cooperation, i.e. the capability of bimetallic systems for reactivity more diverse than the sum of their parts.^[1–6] The study of these types of complexes and their mechanisms of action, brings with it new fundamental questions about ligand exchange events. For single-site metal complexes, the processes involved in ligand exchange are well described and typically involve associative, dissociative, or interchange pathways. These steps are fundamentally important in catalysis since they underpin substrate binding and product release from the active site.^[7] The proximity of two, bonded, metal centres bring with them new possibilities for intramolecular ligand exchange processes that involve the migration of ligands from one metal site to the other. These include: (i) 1,2-migration of a ligand from one metal to the other, (ii) double 1,2-migration of two ligands from one metal to the other, and (iii) dyotropic rearrangement of two ligands in which they switch position between the two metals (Scheme 1).

1,2-Migration of ligands across metal–metal bonds is an increasingly common phenomenon in the study of heterometallic complexes. For example, Lu and co-workers have reported the 1,2-migration of a mesityl group between Ni and Al sites that could be induced by the coordination of different donor ligands.^[8] Okuda, Maron and co-workers described a heterometallic Zn–Ga system, in which a hydride ligand reversibly migrates between the two metals, with the position of the equilibrium determined by solvent.^[9,10]

Examples of double 1,2-migration of two ligands from one metal to the other are considerably rarer.^[11] Perhaps the



Scheme 1. Metal to metal ligand migration pathways in bimetallic systems: (i) 1,2-migration; (ii) double 1,2-migration; (iii) dyotropic 1,2-migration.

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best characterised example is a simultaneous transfer of two hydride ligands from a Ga to a Rh centre documented by Aldridge and co-workers.^[12] Through isolation and crystallographic characterisation of a series of Ga–Rh complexes, snapshots of the reaction coordinate of the double ligand migration could be obtained. We have suggested that this double 1,2-migration event is an important step in the C–H functionalisation of arenes catalysed by Pd–Al heterometallic complexes.^[13]

Dyotropic rearrangements at heterometallic complexes are rarer still.^[14,15] To the best of our knowledge precedent is limited to one well-defined example; Braunstein, Knorr, Hoffmann and co-workers reported a Fe–Pt system, where ligand exchange can induce a simultaneous transfer of a silyl ligand from Fe to Pt and that of carbonyl or isocyanide from Pt to Fe.^[16–18] There is a parallel between this system and known rearrangements of first row transition metal carbonyl dimers. These species can undergo degenerate dyotropic rearrangements with exchange of CO between the two metal centres.^[19–21]

In this paper, we report the exchange of hydride and carbonyl ligands in a heterometallic Fe–Al complex by a dyotropic rearrangement. Computational analysis suggests that the reaction is initiated by the coordination of the CO ligand to Al, followed by migration of the hydride to Al and carbonyl to Fe. The change in coordination environment fundamentally changes the electronics and the reactivity of the heterometallic complex—switching its properties and exposing new reactivity of hydridic sites that previously did not exist.

Results and Discussion

Dyotropic Rearrangement at an Fe–Al Heterometallic Complex

We have previously reported the synthesis, properties and reactivity of the heterometallic complex **1**.^[22–25] This species possesses a distorted structure with an aluminium-centred LUMO and a HOMO that is largely Fe centred and is responsible for the Fe–Al interaction. Reactions typically occur through initial association a substrate (e.g. pyridine, acetonitrile, alkyne, alkene) at the electrophilic aluminium centre, followed by pathways in which the Fe centre acts as either a base or a nucleophile.

Addition of CO (1 bar) to a solution of **1** in C₆D₆ at 25 °C resulted in an immediate colour change from deep red to pale red-orange. Analysis of the reaction mixture by NMR spectroscopy revealed the complete consumption of **1** and the formation of a new species **2a** in >95 % yield (Scheme 2). In its ³¹P{¹H} NMR spectrum, **2a** features two broad resonances at $\delta_p = 18.60$ and 9.42 ppm, integrating to 1P and 2P each, indicating two different coordination environments of the three P ligands. In the ¹H NMR spectrum, **2a** shows two distinct hydride environments integrating to 1H each. These are assigned as a bridging Fe– μ -H–Al at $\delta_H = -15.00$ ppm (q, $J_{P-H} = 25.0$ Hz), and terminal Al–H observed as a broad resonance at $\delta_H = +5.72$ ppm. EXSY experiments showed no evidence of

chemical exchange between these environments at room temperature. The IR spectrum of **2a** features a characteristic strong vibration at $\nu = 1823$ cm^{−1} assigned as the C=O stretch, typical for a semi-bridging carbonyl ligand (see below). **2a** could be isolated by crystallisation in a 79 % yield and was found to be stable at room temperature under an inert atmosphere over multiple months in its pure form. Characterisation by X-ray crystallography confirmed the presence of an iron-bound CO ligand (Figure 1). Both the bridging and the terminal hydride ligands were located in the Fourier difference map and the solid-state structure is consistent with the solution NMR data. The binding of the carbonyl ligand appears to be non-reversible as the CO cannot be removed under vacuum (3×10^{-2} mbar, 5 h, rt).

Addition of isocyanides CNR (R = Me, ^tBu, Xyl = 2,6-Me₂C₆H₃) to **1** yielded analogous products **2b–d** (Scheme 2). These species all give rise to similar characteristic NMR signatures reminiscent of **2a**. **2b–d** are unstable at room temperature (see below), and they have largely been characterised by NMR spectroscopy in situ at −85 °C. In addition, **2d** could be crystallised at −35 °C and characterised by X-ray diffraction, further supporting the structural assignment as analogues of **2a** (Figure 1).

Complexes **2a** and **2d** feature significantly longer Fe–Al distances compared to complex **1** (**2a**: 2.3948(19) Å, $fsr = 0.99$; **2d**: 2.4314(10) Å, $fsr = 1.01$, d(Fe–Al); **1**: 2.2176(13) Å,

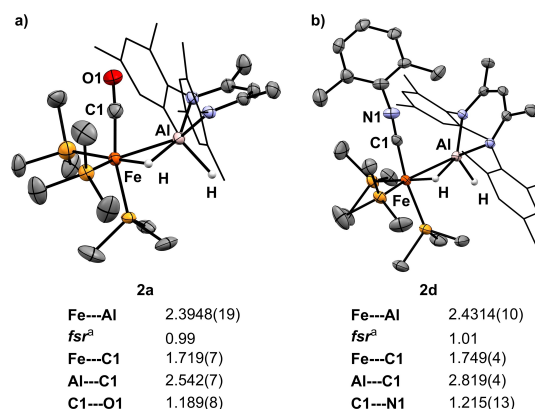
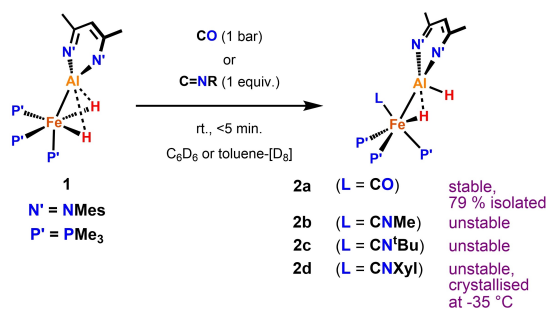


Figure 1. X-ray structure of a) **2a** and b) **2b**. Thermal ellipsoids are shown at the 30% probability level, most hydrogen atoms, atoms in minor occupancy orientations and included solvent molecules are hidden for clarity. ^a $fsr = d(Fe-Al)/(r(Fe) + r(Al))$; r = Pauling radii.^[26]



Scheme 2. Reactivity of **1** with CO and isocyanides.

Mechanism of Rearrangement

DFT calculations were also undertaken to study the underlying mechanism for formation of **2a–d** from **1** (Figure 4). In the case of **2a**, the first step of the reaction is the slightly endergonic coordination of the CO ligand to the Al site of **1** (**INT-1a**, $\Delta G^\circ = 2.0 \text{ kcal mol}^{-1}$), followed by its migration (**TS-1a**, $\Delta G^\ddagger = 2.3 \text{ kcal mol}^{-1}$) to form a bridged species (**INT-2a**, $\Delta G^\circ = -7.6 \text{ kcal mol}^{-1}$). This is then followed by the simultaneous but asynchronous dyotropic migration of the CO and one of the hydride ligands to form the experimentally observed product **2a** (**TS-2a**, $\Delta G^\ddagger = -2.6 \text{ kcal mol}^{-1}$). Overall, this transformation is highly exergonic ($\Delta G^\circ = -27.4 \text{ kcal mol}^{-1}$, $\Delta H^\circ = -39.8 \text{ kcal mol}^{-1}$) and proceeds via a very low barrier ($\Delta G^\ddagger = +5.0 \text{ kcal mol}^{-1}$, $\Delta H^\ddagger = +5.0 \text{ kcal mol}^{-1}$) agreeing with the experimentally observed non-reversibility and fast rate of the reaction. An alternative pathway involving a 1,2-migration of a hydride ligand from Fe to Al (e.g. dissociative with respect to Fe) followed by trapping with CO was also calculated, however, was found not to be competitive ($\Delta\Delta G^\ddagger = 13.0 \text{ kcal mol}^{-1}$, Figure S15). The formation of **2b–d** was calculated to proceed via analogous mechanism to that presented in Figure 4 but with overall higher barriers ($\Delta G^\ddagger = +5.7\text{--}14.7 \text{ kcal mol}^{-1}$), likely due to increased steric clash with the ligands (see Figures S12–S14 for full computed pathways).

In the first step (**TS-1a**), NBO calculations suggest the localisation of negative charges on the CO fragment and positive charges on the Fe and Al atoms (NPA charges $\Sigma(\text{CO})$: **INT-2a** = -0.74; $\Sigma(\text{Fe,Al})$: **1** = +0.15, **INT-2a** = +0.57), mirrored by a loss in Fe–Al bonding (WBIs: **1**: Fe–Al = 0.50, **INT-2a**: Fe–Al = 0.15). QTAIM calculations no longer identify an Fe–Al bond critical path in **INT-2a**, and instead describe **INT-2a** as a bridging carbonyl complex (see below).

The second step (**TS-2a**) is a highly asynchronous transition state. The pre-TS stage is primarily comprised of the rearrangement of the hydride bonding (NPA charge $H^{\delta-}$: **INT-2a** = -0.18 $\rightarrow$ **TS-2a** = -0.39 $\rightarrow$ **2a** = -0.47), whereas the post-TS stage is responsible for the migration of the CO fragment (NPA charges $\Sigma(CO)$: **INT-2a** = -0.74 $\rightarrow$ **TS-2a** = -0.71 $\rightarrow$ **2a** = -0.12). During the migration, the positive charge localised in the bimetallic core is also dissipated (NPA charge $\Sigma(Fe,Al)$: **INT-2a** = +0.57 $\rightarrow$ **TS-2a** = +0.76 $\rightarrow$ **2a** = +0.24), as well as the Fe-Al bonding is re-established (WBI Fe-Al: **INT-2a** = 0.16 $\rightarrow$ **TS-2a** = 0.14 $\rightarrow$ **2a** = 0.26).

To gain further insight into the electronic changes during the rearrangement we conducted analysis of key localised molecular orbitals (LMOs) along the potential energy surface (Figure 5). The LMOs were calculated using the IBO procedure^[29,30] and the procedure described by Vidossich and Lledóss^[31,32] was used to generate centroids of these LMOs (CLMOs). CLMO analysis for **TS-1a** revealed a shift of the former Fe–Al bond in **1** and **INT-1a** forming the Fe–C σ bond in **INT-2a**. As hinted to by lack of metal–metal bonding by NBO and QTAIM analysis earlier, no Fe–Al bonding IBO could be identified in **INT-2a**. Instead, the presence of distinct Fe–C and Al–C IBOs suggest that the bonding in the bimetallic core is entirely based on the bridging CO and the hydride ligands. CLMO analysis also supports the asynchronicity of **TS-2a**. The pre-TS part primarily consists of the transfer of the hydride from Fe to Al, and the weakening of the Al–C bond. This is followed by the strengthening of the Fe–C bond and the reestablishment of the Fe–Al bond in the post-TS stage. To preserve orbital symmetry the same IBO is assigned to the Fe–Al bond in **2a** and **1**, meaning that the two Fe-based bonding orbitals cross in the post-TS stage of **TS-2a**.

The mechanism presented above is different from type I dyotropic rearrangements in organic systems (Scheme 3).^[15] In type I dyotropic rearrangements, the static carbon frame-

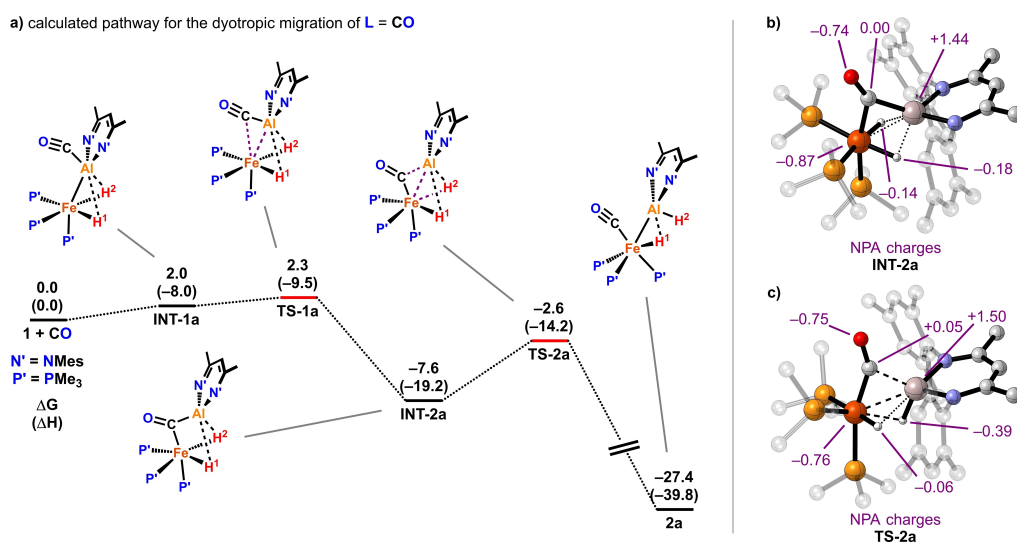


Figure 4. a) Calculated mechanism for the reaction of **1** and CO. b) computed geometry of **INT-2a** and c) **TS-2a** showing NPA charges. Calculations were performed at the B3LYP-D3(BJ)/def2-QZVPP/SMD(benzene)/GoodVibes//B3PW91-D3/6-31G(d,p)/SDDAll/PCM(benzene) level of theory. Gibbs free energies (enthalpies) are given in kcal/mol, calculated at T = 298.14 K and c = 00464 M.

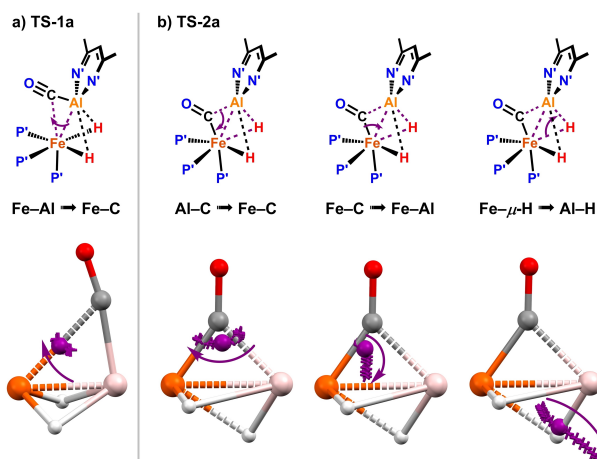
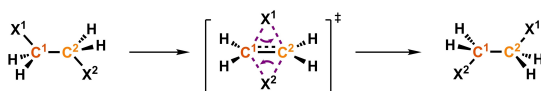
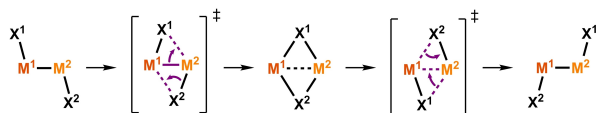


Figure 5. CLMO analysis for a) **TS-1a** and b) **TS-2a**. The centroids of the LMOs are marked with purple crosses, with the CLMO at the transition state geometry marked by the purple sphere. The direction of the electron flow is indicated by the purple arrow. See Supporting Information for computational details.

a) type I dyotropic rearrangement



b) dyotropic rearrangement in a bimetallic system



Scheme 3. Generic Schemes for (type I) dyotropic rearrangements in a) ethylenic organic and b) metal–metal bonded bimetallic systems.

work is stabilised during the transition state due to partial π -bonding enabled by the almost planar geometry of the ethylene scaffold, and thus the reaction barriers arise primarily from the weakening of the bonds between the carbon framework and migrating groups.^[14] In the current case, as the reaction coordinate is traversed, the metal–metal bond is disrupted and then re-formed. Meaning the bonding in static framework is actually weakened during the rearrangement. In addition, the majority of known type I dyotropic rearrangements are concerted. The case reported herein takes place via a stepwise mechanism through an unstable intermediate with a CO ligand occupying a bridging position followed by a dyotropic transition state. Despite these differences, the suggested mechanism is consistent with those proposed for other bimetallic species. This includes the Fe–Pt system reported by Braunstein, Knorr and Hoffmann,^[16–18] and first row transition metal carbonyl dimers. In the former case, variation of the R groups on the migrating SiR_3 and the bridging PR_2 ligands allowed for the isolation intermediates on the reaction pathway. A detailed computational study later established that the dyotropic rearrangement takes place via an intermediate where the CO ligand occupies a bridging position. This is followed by a

dyotropic transition state where both the migrating silyl and CO groups occupy bridging positions across the two metal centres. For transition metal carbonyl dimers (eg. $[\text{CpFe}(\text{CO})_2]_2$), the bridged intermediates are typically a ground state in the solid phase, though the different isomers are often in thermal equilibrium in the solution phase.^[19–21]

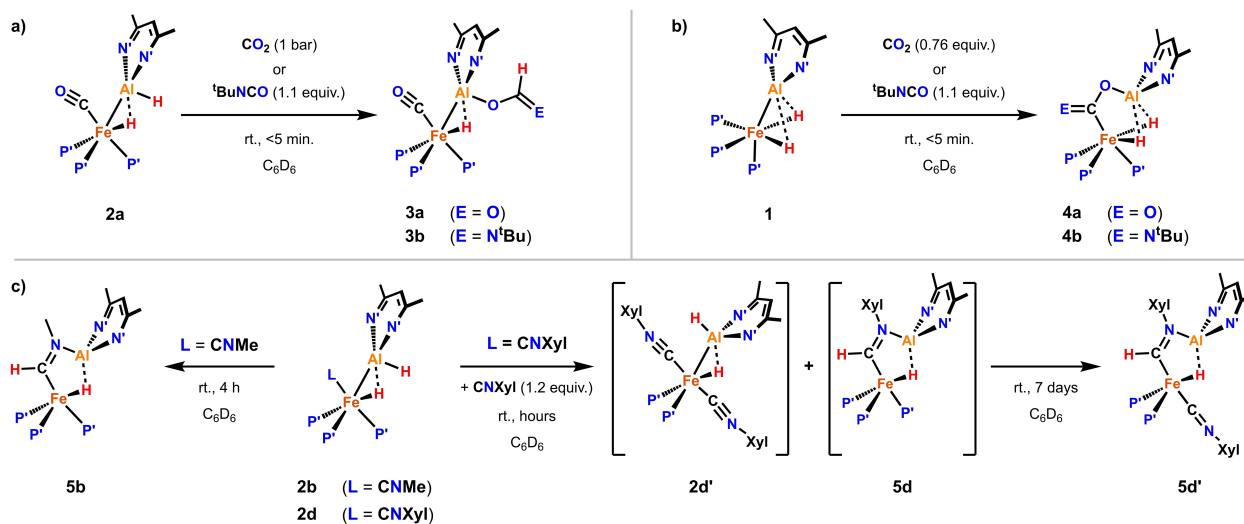
Exposed Reactivity of Migrated Hydride

The hydride ligands of **1**—though essential for the stability of these complexes—are non-nucleophilic and non-basic.^[22–25] The dyotropic rearrangement leads to the establishment of a terminal Al–H bond in **2a** which exposes new reactivity previously not observed with the parent complex **1**. This has been demonstrated by further experiments in which **1** and **2a** were reacted with various electrophiles (Scheme 4).

Addition of CO_2 (1 bar) to a solution of **2a** in C_6D_6 at room temperature results in an immediate colour change from pale red-orange to light orange. The new species formed, **3a**, shows a sharp formate ^1H resonance at $\delta_{\text{H}} = 9.06$ ppm.

Analogous reactivity was achieved using $^t\text{BuNCO}$ (1.1 equiv.) to form aluminium formimidate **3b**. In contrast, reaction of **1** with the same substrates leads to cycloaddition across the metal–metal bond to form **4a–b** respectively.^[33] **4a–b** feature a characteristic mutually coupled doublet (2P) and triplet (1P) resonance in their ^{31}P NMR spectra. In the solid state, the Fe–Al bond lengths of **3a–b** are very similar to **2a** (**3a**: 2.3709(12) Å, $\text{fsr} = 0.98$; **3b**: 2.3860(7) Å, $\text{fsr} = 0.99$). These compounds now show two distinct C=O and C=N vibrations in their IR spectra (**3a**: C=O: $\nu = 1841\text{ cm}^{-1}$, OC=O: $\nu = 1670\text{ cm}^{-1}$; **3b**: C=O: $\nu = 1841\text{ cm}^{-1}$, OC=N: $\nu = 1632\text{ cm}^{-1}$). **4a–b** also have a single characteristic C=N vibration (**4a**: $\nu = 1722\text{ cm}^{-1}$; **4b**: $\nu = 1715\text{ cm}^{-1}$). The structures of **4a–b** are largely similar to other cycloaddition products of this system.^[25] For example, **4b** features an elongated metal–metal bond (**4b**: 2.3946(9) Å, $\text{fsr} = 0.99$) compared with that of **1**, as well as a C–O and C=N bonds approaching the lengths for single and double bonds, respectively.

The isocyanide ligands in **2b–d** were found to be more reactive than the carbonyl in **2a**, reacting with the exposed Al–H hydride by an apparent intramolecular pathway.^[34] Storage of samples of **2b** at room temperature over several hours resulted in its complete consumption and the formation of **5b** in >95% NMR yield. The ^1H NMR spectrum of **5b** features a characteristic quartet resonance at $\delta_{\text{H}} = 11.47$ ppm, as well as the lack of the terminal Al–H signal. X-ray crystallography reveals the migration of the Al–H nucleus onto the isocyanide carbon, with the N now bound to the Al centre (Figure 6). A similar pathway was identified for **2d**. When 2.2 equiv. of CNXyl is added to **1** the reaction yields **5d'** after 7 days at room temperature (>95% NMR yield), which features a similar Fe–CH resonance to **5b** at $\delta_{\text{H}} = 10.62$ ppm. X-ray crystallography reveals that one of the PMe_3 ligands had been replaced by a second equivalent of CNXyl in **5d'**. Following this reaction



Scheme 4. Reactivity of a) **2a** and b) **1** with CO_2 and *tert*-butyl isocyanate. c) Reactivity of **2b**, **d**.

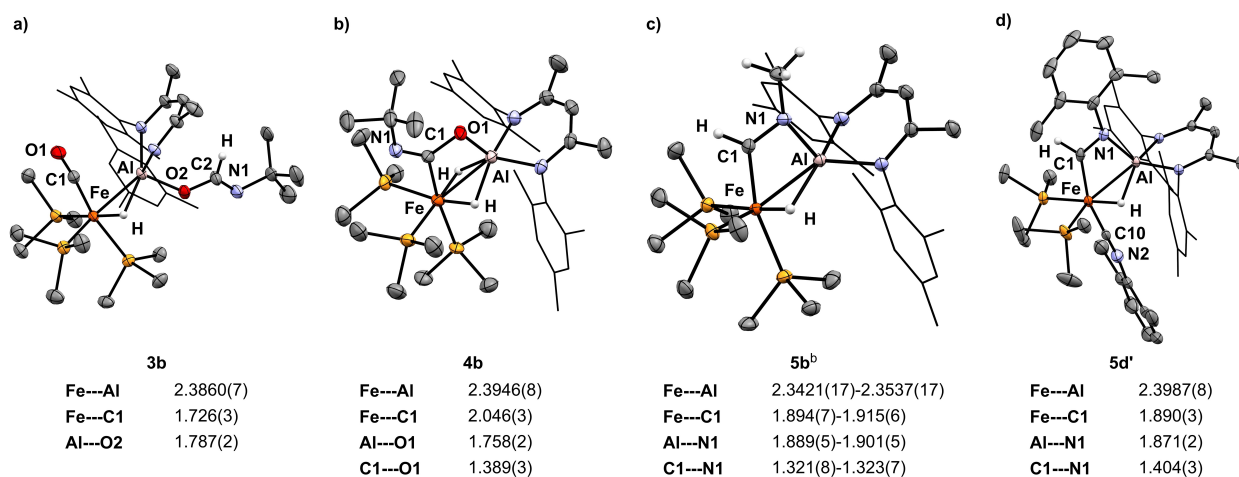


Figure 6. X-ray structures of a) **3b**, b) **4b**, c) **5b^b**, and d) **5d'**. Thermal ellipsoids are shown at the 30% probability level, most hydrogen atoms, atoms in minor occupancy orientations and included solvent molecules are hidden for clarity. ^a $fsr = d(\text{Fe}-\text{Al}) / (r(\text{Fe}) + r(\text{Al}))$; r = Pauling radii.^[26] ^b Range corresponds to the two independent molecules in the asymmetric unit.

by NMR spectroscopy reveals transient intermediates **2d'** and **5d**, resulting from ligand exchange and nucleophilic attack by the hydride, respectively. It appears that the thermodynamic driving force for this reaction is sufficiently large that in the absence of exogenous XylNC, samples of **2d** gave a mixture of **5d'**, **1**, and PMe_3 over the course of several days.^[35]

DFT calculations suggest that in lieu of an external electrophile, the terminal Al-H of **2b** or **2d** is able to afford nucleophilic attack onto the adjacent isocyanide ligand ($\Delta G^\ddagger = 22.6 \text{ kcal mol}^{-1}$, $\Delta G^\circ = -3.3 \text{ kcal mol}^{-1}$, see Figure S12–S14). This is in stark contrast with attack onto the carbonyl in **2a** which is both kinetically and thermodynamically inaccessible at room temperature ($\Delta G^\ddagger = 32.5 \text{ kcal mol}^{-1}$, $\Delta G^\circ = +14.1 \text{ kcal mol}^{-1}$, see Figure S11).

Conclusions

In summary, we report an unusual ligand migration event at an Fe–Al heterometallic complex. This event involves the apparent initial coordination of an exogenous ligand (e.g. CO or CNR) to Al followed by migration to the Fe site which occurs with concurrent migration of a hydride ligand from Fe to Al. The overall process can be conceptualised as a dyotropic rearrangement. DFT calculations are consistent with the characterisation of this reaction as 1,2-dyotropic shift, a rare and understudied process in heterobimetallic systems. This process appears to have some important differences to type I dyotropic rearrangement observed in organic compounds. Detailed computational analysis indicates a stepwise mechanism that involves a bridged intermediate, which is a precursor to a dyotropic transition state. Calculations indicate that the metal–metal bond in the

bimetallic core breaks and then reforms across the reaction coordinate, suggesting it responds to changes in electronic structure brought on by the migration of the ligands between the two metals.

The 1,2-dyotropic shift fundamentally alters the structure of the heterometallic, exposing new types of reactivity. Specifically, migration of hydride from Fe to a terminal position on Al greatly increases its nucleophilicity and facilitates onwards reactions not observed prior to the dyotropic shift. The enhanced reactivity was demonstrated by insertion reactions with CO₂, *tert*-butyl isocyanate and isocyanides.

Our results shed new light on types of ligand exchange processes possible in heterometallic complexes. These events are not only mechanistically divergent from established monometallic complexes and analogous organics systems, but also fundamentally change the properties and reactivity of heterometallic complexes. Our findings might stimulate improved understanding of reactivity patterns in heterometallic complexes of catalytic processes where metal–metal cooperativity is key to successful turnover.

Supporting Information

The data that support the findings of this study are available in the supplementary material (ESI) of this article available at <https://doi.org/10.1002/anie.202408257>, which contains: experimental procedures, characterisation data, details of NMR simulations, crystal structure for compounds **3a**, **S1**, **S2**, and **S3**, and quantum chemical calculations (PDF); computational coordinates (xyz); crystallographic data (cif). Raw NMR and computational data are available at the following repository: <https://doi.org/10.14469/hpc/14352>. Deposition numbers 2341253 (for **2a**), 2341254 (for **2d**), 2341255 (**3a**), 2341256 (for **3b**), 2341257 (for **4b**), 2341258 (for **5b**), 2341259 (for **5d'**), 2341260 (for **S1**), 2341261 (for **S2**), 2341262 (for **S3**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service. The authors have cited additional references within the Supporting Information.^[36–63]

Acknowledgements

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

Keywords: bimetallic chemistry • iron • aluminum • hydride • dyotropic rearrangement

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- [34] **2c** is highly unstable at room temperature and is completely consumed over <1 h to form cyanide bridged complex **S2** via the extrusion of isobutene (see Supporting Information for details).
- [35] NMR and X-ray crystallographic analysis suggests that **5b,d'** can also be described as α -amino Fischer carbene complexes. As such, their crystal structures feature short Fe–C bond lengths (d(Fe–C1): **5b**: 1.894(7)–1.915(6) Å, **5d'**: 1.890(3) Å), and short C–N bonds (d(C1–N1): **5b**: 1.321(8)–1.323(7) Å, **5d'**: 1.406(3) Å). In their NMR spectra the carbene ¹³C resonances appear highly deshielded (δ_c = **5b**: 263.3 ppm, **5d'**: 234.1 ppm), and no FeC=NAl vibrations are discernible in their IR spectra..
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