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Ion-pairs as a gateway to transmetalation: aryl transfer from boron to nickel and magnesium†

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Gas-phase ion-ion reactions between tris-1,10-phenanthroline metal dications, [(phen)₃M]²⁺ (where M = Ni and Mg), and the tetraphenylborate anion yield the ion-pairs [(phen)₃M]²⁺[BPh₄][−]. The ion-pairs undergo transmetalation upon loss of a phen ligand to give the organometallic complexes [(phen)₂M(Ph)]⁺. DFT calculations, used to determine the energy barriers for the transmetalation reactions and the hydrolysis reactions, are entirely consistent with the experimental results.

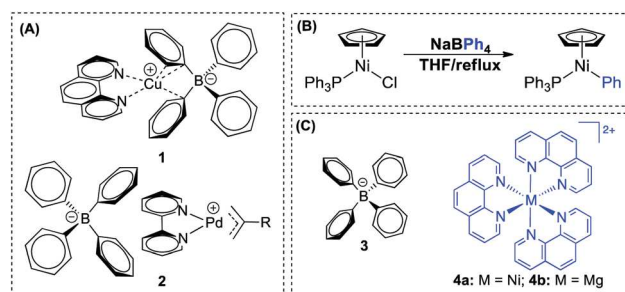
Introduction

Ion-pairs underpin structure, function and reactivity in chemistry¹ and biology.² While X-ray crystallography has revealed an array of ion-pair structures, defining their contribution to the elementary steps associated with transition metal catalysis remains challenging. The choice of both solvent and counter anion can play a crucial role in the type(s) of ion-pairs that are formed and their resultant chemistry. Tetrarylborate anions, BAr₄[−] are particularly interesting since they not only give rise to diverse structures including the inner sphere ion-pair **1** and the outer sphere ion-pair **2** (Scheme 1A)³ but can also be involved in cross-coupling reactions involving a transmetalation step in which the B–C bond is broken and the aryl group is transferred to the transition metal centre.⁴ Although in some instances the resultant organometallic has been isolated (Scheme 1B),⁵ rarely has detailed mechanistic evidence been provided for the specific involvement of ion-pairs in transmetalation.⁶ Here we report the first use of ion-ion reactions in the gas-phase⁷ to directly probe transmetalation reactions⁸ via

formation of ion-pairs. DFT calculations are used to explore the mechanisms and energetics of these reactions.

Results and discussion

Given that N-based ligands such as 1,10-phenanthroline (phen) and 2,2'-bipyridine are known to form metal complexes consisting of ion-pairs (e.g. **1** and **2**, Scheme 1A) containing the tetraphenylborate anion, **3**, here we focus on the gas-phase reactions of **3** with tris-1,10-phenanthroline metal dications, **4** (Scheme 1C). We have chosen the nickel complex **4a** as a representative transition metal known to be involved in transmetalation,⁹ and given the importance of organomagnesium compounds in organic synthesis,¹⁰ the magnesium complex **4b** as a representative main group metal. Both anion **3** and cations **4a** and **4b** are readily transferred from the condensed phase to the gas phase using electrospray ionisation (ESI).¹¹



Scheme 1 Examples of ion-pairs in organometallic chemistry: (A) ion-pairs in which the anion has close contacts with either the metal centre **1**^{3a} or a ligand coordinated to the metal centre, **2**,^{3b} (B) transmetalation from B to Ni where ion-pairs are inferred;⁵ (C) ion-ion reactions in the gas-phase between **3** and **4** to directly probe the role of ion-pairs in transmetalation (this work).

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† Electronic supplementary information (ESI) available: Detailed description of mass spectrometry experiments and DFT calculations; additional mass spectra and DFT calculated energy diagrams; Cartesian coordinates of all structures. See DOI: <https://doi.org/10.1039/d2dt00746k>

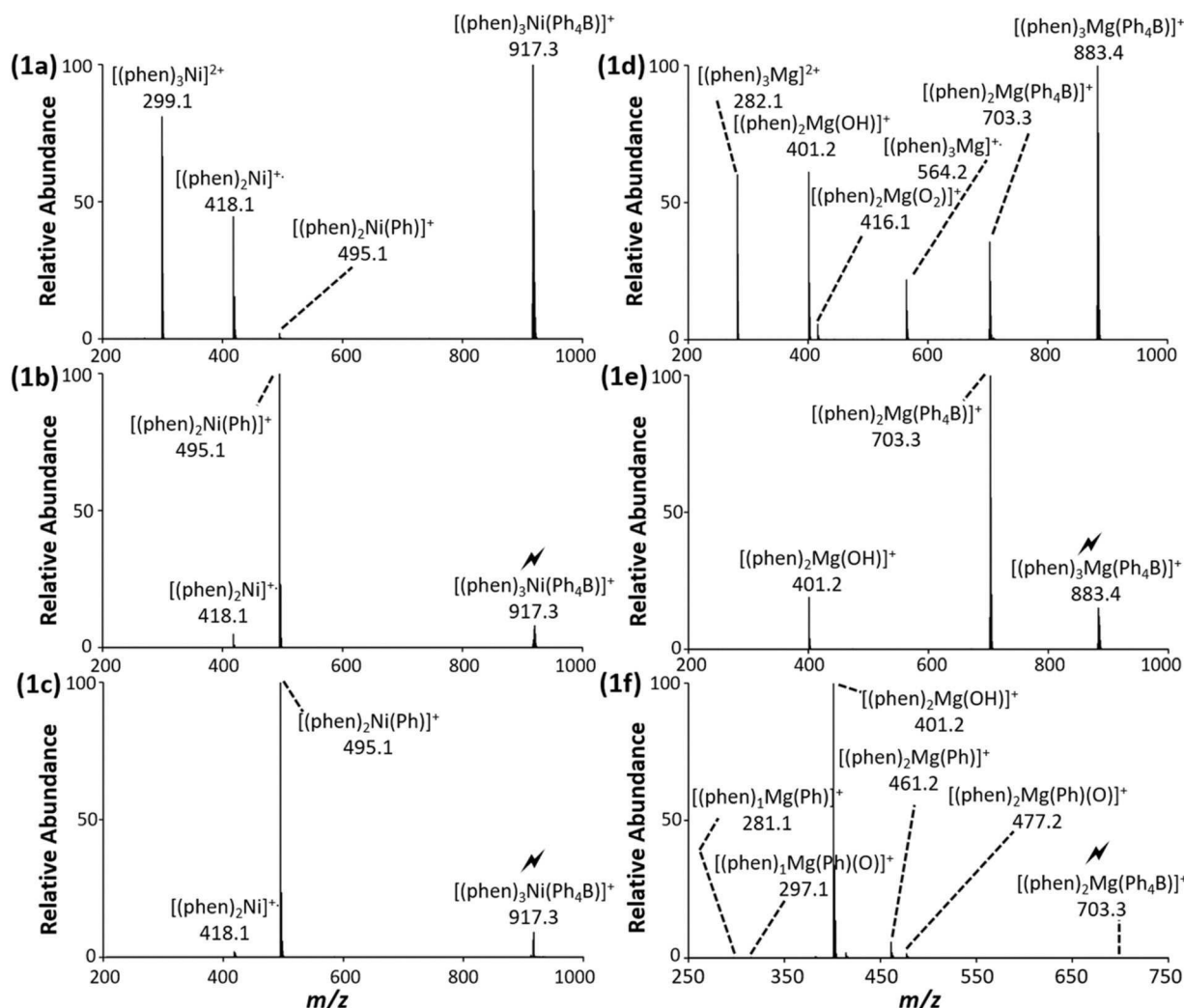
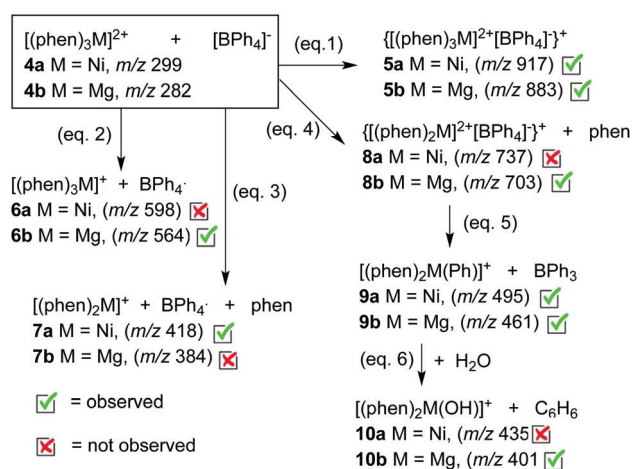


Fig. 1 Gas-phase ion chemistry associated with ion-pair formation and reactivity. (1a) the full spectrum MS1 of **5a** $\{[(phen)_3Ni]^{2+}[BPh_4]^{-}\}^+$, (1b) the CID spectrum MS2 of **5a**, (1c) CID spectrum MS2 of **5a** formed in solution, (1d) the full spectrum MS1 of **5b** $\{[(phen)_3Mg]^{2+}[BPh_4]^{-}\}^+$ + (1e) the MS2 CID spectrum of **5b** and (1f) the MS2 CID spectrum of $\{[(phen)_2Mg]^{2+}[BPh_4]^{-}\}^+$, **8b**.

Fig. 1a shows the positive ion product mass spectrum from the ion-ion reaction between **3** and **4a** (m/z 299). The reactions characterised by mass spectrometry are summarised in Scheme 2. The main peak is due to the formation of the desired ion-pair complex $\{[(phen)_3Ni]^{2+}[BPh_4]^{-}\}^+$, **5a** (m/z 917, eqn (1)). The singly charged Ni complex $[(phen)_3Ni]^+$, **6a** (m/z 598), formed by electron transfer (eqn (2)) is not observed, but the bis complex $[(phen)_2Ni]^+$, **7a** (m/z 418), formed by electron transfer followed by loss of phen (eqn (3)) is observed. This is consistent with the known weak binding of a third phen ligand to a Ni(I) centre.¹² Although the ion-pair $\{[(phen)_2Ni]^{2+}[BPh_4]^{-}\}^+$, **8a**, formed *via* loss of a phen ligand is not observed (eqn (4)), a minor amount of the organometallic ion $[(phen)_2Ni(Ph)]^+$, **9a** (m/z 495), is observed and likely arises from **8a** (eqn (5)). Mass selection of the ion-pair complex **5a** formed from the gas phase ion-ion reaction followed by collision-induced dissociation (CID) gave **9a**, confirmed that



Scheme 2 Summary of reactions detected by mass spectrometry for the interaction of $[(phen)_3M]^{2+}$ with $[BPh_4]^{-}$ in the gas-phase.

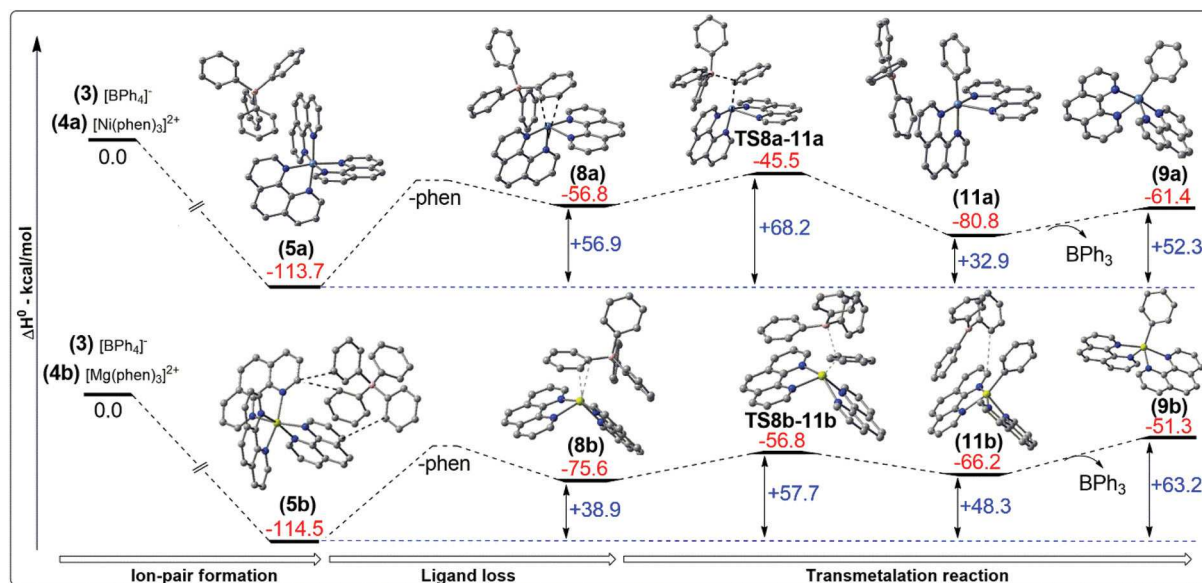


Fig. 2 DFT calculations estimating the energy barriers of transmetalation reaction for the nickel (top) and magnesium (bottom) ion-pairs. The energies are ΔH° obtained at the B3LYP-D3BJ/def2-TZVP//M06/SDD-6-31G(d) level of theory and are relative to the ion pairs **1a** and **1b**. All species are singlets, except for **5a** which has a triplet ground state.¹⁵

transmetalation is preceded by phen loss (Fig. 1b). An identical CID spectrum is produced from the ion-pair **5a** formed *via* ESI of a solution containing nickel acetate, phen and sodium tetraphenylborate (Fig. 1c), highlighting that the ion-pairs formed *via* gas-phase ion-ion reactions undergo the same fragmentation reactions as those transferred to the gas phase from the solution phase.

The ion-ion reaction between **3** and **4b** (m/z 282) also proceeds *via* competing ion-pair formation and electron transfer pathways (Fig. 1d and Scheme 2). The main peak is due to $\{[(\text{phen})_3\text{Mg}]^{2+}[\text{BPh}_4]^{-}\}^+$, **5b** (m/z 883, eqn (1)), and this time $\{[(\text{phen})_2\text{Mg}]^{2+}[\text{BPh}_4]^{-}\}^+$, **8b**, is also observed (m/z 703, eqn (4)). In contrast to the nickel case, the singly charged complex $[(\text{phen})_3\text{Mg}]^+$, **6b** (m/z 564, eqn (2)) is observed but $[(\text{phen})_2\text{Mg}]^+$, **7b** (m/z 384, eqn (3)) is not observed.[‡] The other ions observed, $[(\text{phen})_2\text{Mg}(\text{OH})]^+$ (m/z 401) and $[(\text{phen})_2\text{Mg}(\text{O}_2)]^+$, **10b** (m/z 416), are likely to arise from ion-molecule reactions with adventitious background oxygen and water present in the ion trap (e.g. eqn (6)). Mass selection of the ion-pair complex **5b** formed from the gas phase ion-ion reaction followed by collision-induced dissociation (CID) confirmed the formation of the ion-pair $\{[(\text{phen})_2\text{Mg}]^{2+}[\text{BPh}_4]^{-}\}^+$, **8b** (m/z 703) *via* loss of the phen ligand **8b** (Fig. 1e, eqn (4)). A minor amount of $[(\text{phen})_2\text{Mg}(\text{OH})]^+$, **10b** (m/z 401) is also observed. Mass selection of the ion-pair complex **8b** followed by collision-induced dissociation (CID) gave a minor amount of the organometallic ion $[(\text{phen})_2\text{Mg}(\text{Ph})]^+$, **9b** (m/z 461), with $[(\text{phen})_2\text{Mg}(\text{OH})]^+$, **10b** (m/z 401), being the major product. In

a separate experiment $[(\text{phen})_2\text{Mg}(\text{OH})]^+$, **10b**, was shown to result from ion-molecule reactions between mass-selected $[(\text{phen})_2\text{Mg}(\text{Ph})]^+$ and background water (Fig. S1†). In contrast to the nickel system, we were unable to independently generate **5b** *via* ESI-MS of solutions containing appropriate Mg salts, phen and sodium tetraphenylborate, highlighting that gas-phase ion-ion reactions can be used to prepare ion-pairs that may not readily form in solution.

The large coulombic attraction between oppositely charged ions in gas-phase ion-ion reactions produces the ion-pairs **5a** and **5b** which have an excess energy that can fuel the subsequent gas-phase transmetalation chemistry that we have observed (Scheme 2, eqn (4) and (5)). Fig. 2 shows the DFT calculated energetics associated with the reactants **3** and **4a/4b**, ion-pairs **5a**, **5b**, **8a** and **8b** in two ways. The numbers in red are the exothermicities associated with the ion-ion reactions and are relevant to the experimental data given in Fig. 1(a) and 1(d). The numbers in blue are the endothermicities associated with the ligand loss and transmetalation reactions and these are relevant to the CID experiments on the ion-pairs which are either formed *via* the gas-phase ion-ion reactions (**5a** and **5b**, Fig. 1(b) and 1(e) respectively) or *via* solution phase experiments (only for **5a**, Fig. 1(c)).

An examination of Fig. 2 reveals that: (1) formation of **5a** and **5b** is exothermic by 113.7 and 114.5 kcal mol⁻¹ respectively; (2) the ion-pairs **5a** and **5b** (Fig. 2) consist of the intact tris(phenanthroline) cation complexes with the tetraphenylborate in the second coordination shell (also known as outer sphere ion-pairs);^{1b} (2) phen loss to form **8a** and **8b** is endothermic by 56.9 and 38.9 kcal mol⁻¹, consistent with this reaction requiring CID (Fig. 1(b), (c) and (e)) or being fueled by the excess energy (all numbers in red are exothermic) from the

[‡] Magnesium complexes in the formal +1 oxidation state have attracted considerable interest as reagents for small molecule activation (see ref. 13).

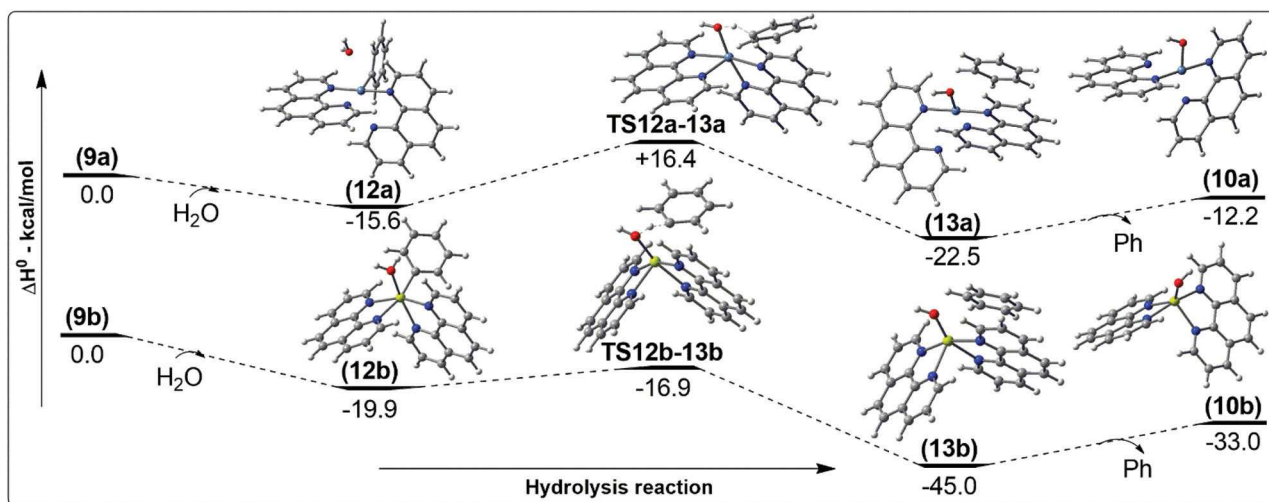


Fig. 3 DFT calculations estimating the energy barriers of the hydrolysis reactions of $[(\text{phen})_2\text{M}(\text{Ph})]^+$ for the $\text{M} = \text{Ni}$ (top) and $\text{M} = \text{Mg}$ (bottom) ion-pairs. The energies are DH0 obtained at the B3LYP-D3BJ/def2-TZVP//M06/SDD-6-31G(d) level of theory (see above text for details).

original ion-ion reaction (Fig. 1(a) and (d)); (3) **8a** and **8b** have interactions between the metal centres and one of the phenyl rings of the tetraphenylborate anion and are thus classified as inner sphere ion-pairs.^{1b} The transition states **TS8a-11a** and **TS8b-11b** for the transmetalation reaction are reminiscent of Wheland species formed in electrophilic substitution reactions.¹⁴ We have not calculated the transition state(s) for formation of **8a** and **8b** due to the fact the overall reaction requires substituting the rigid bidentate phen ligand with the tetraphenylborate anion. Nonetheless, the fact that the barrier for the subsequent transmetalation for the nickel system ($68.2-56.9 = 11.3 \text{ kcal mol}^{-1}$) is less than that for the magnesium system ($57.7-38.9 = 18.8 \text{ kcal mol}^{-1}$) is consistent with the differences in the CID spectra of **5a** (Fig. 1b) and **5b** (Fig. 1e).

Finally, DFT calculations on the hydrolysis of the organo-metallic cations **10a** and **10b** (Fig. 3) reveal that the barrier **TS12a-13a** lies above the energy of the separated reactants while that for **TS12b-13b** lies below, consistent with $[(\text{phen})_2\text{Ni}(\text{OH})]^+$, **10a** not being formed but $[(\text{phen})_2\text{Mg}(\text{OH})]^+$, **10b** being observed under the near thermal conditions of the ion trap.¹⁶ Also, this facile hydrolysis reaction explains why the transmetalated adduct for the Mg complex at m/z 461.2 is not the dominant peak (Fig. 1f).§

The observation of transmetalation from boron to magnesium appears to violate the general expectation that transmetalation occurs if the metal transferring the carbon ligand is more electropositive than the metal receiving the carbon ligand.¹⁸ Indeed, the literature is replete with examples of Grignard reagents, RMgX , transferring their organyl groups, R^- , to boron halides.¹⁹ However, the magnesium dication complex studied here has neutral 1,10-phenanthroline ligands

rather than anionic halide ligands found in typical magnesium salts and is thus a more reactive electrophilic species,[¶] highlighting how ligands can play a key role in tuning the electrophilicity of a metal centre. Comparing the energetics of **8** and **9** (Fig. 2), it is clear that transfer of the phenyl anion from BPh_4^- to the metal centre is more favourable for nickel ($\Delta H^\circ = -4.6 \text{ kcal mol}^{-1}$) than for magnesium ($\Delta H^\circ = 24.3 \text{ kcal mol}^{-1}$). So even for these electrophilic cations, transmetalation from B to Mg is predicted to be endothermic.

Experimental

Materials

HPLC-grade methanol (MeOH) was purchased from Fisher Scientific (Pittsburgh, PA). Magnesium chloride (MgCl_2), nickel(II) acetate tetrahydrate ($\text{Ni}(\text{OCOCH}_3)_2 \cdot 4\text{H}_2\text{O}$), 98%, 1,10-phenanthroline (phen), and sodium tetraphenylborate (NaBPh_4) were purchased from Millipore Sigma (St Louis, MO).

Sample preparation

Solution A. Sodium tetraphenylborate was dissolved in MeOH and diluted to a final concentration of $10 \mu\text{M}$.

Solution B. The divalent metal salts (M^{2+}) and phen were dissolved from powder in MeOH with 1 : 2 (molar ratio) to a final concentration of $40 \mu\text{M}$ to form the metal-phen complex, $[\text{M}(\text{phen})_3]^{2+}$.

Solution C. To generate the ion-pair $\{[(\text{phen})_3\text{Ni}]^{2+}[\text{BPh}_4]^{-}\}^+$ in solution, the previously made solutions of $[\text{BPh}_4]^{-}$ (solution A) and $[\text{Ni}(\text{phen})_3]^{2+}$ (solution B) were mixed together in an equimolar fashion to a final concentration of $20 \mu\text{M}$ in MeOH.

¶Recent attention has focussed on generating highly reactive ligated cationic magnesium complexes with enhanced Lewis acidity. An example is the $(\text{BDI})\text{Mg}^+$ cation (where BDI = β -diketiminate), which has been shown to abstract a neutral triethyl phosphine oxide ligand from $(\text{C}_6\text{F}_5)_3\text{B-OPEt}_3$ (see ref. 20).

§For studies on the gas-phase hydrolysis reactions of related ionic organomagnesium complexes, see ref. 17.

Mass spectrometry experiments

Ion–ion reactions were performed on either a Sciex TripleTOF 5600 hybrid QqTOF mass spectrometer or a Sciex QTRAP 4000 hybrid triple quadrupole/linear ion-trap mass spectrometer that have both been modified to perform ion–ion reactions.²¹ Alternately pulsed nano electrospray ionization (nESI) emitters allow for the sequential injection of anions and cations.²² Using (solution A) tetraphenylborate anions, $[\text{BPh}_4]^-$, were generated *via* nESI, isolated in Q1, and then stored in the high-pressure collision cell, q2. Next, from (solution B) metal–ligand dications, $[\text{M}(\text{phen})_3]^{2+}$, were generated *via* nESI, isolated in Q1, and transferred to q2 where the tetraphenylborate anions were stored. Once the metal–ligand dications were introduced to q2, they were mutually stored with the tetraphenylborate anions for 50 ms to allow for an ion–ion reaction to occur resulting in charge inverted and charge reduced products in the positive ion mode. The resulting ion–ion reaction products were then further interrogated using single frequency ion-trap collision induced dissociation (IT-CID) to perform MS^n experiments. The ion-pair, $\{[(\text{phen})_3\text{Ni}]^{2+}[\text{BPh}_4]^{-}\}^+$, that was formed in solution (solution C) was directly injected into the mass spectrometer using nESI underwent MS^n experiments. Mass analysis was performed *via* orthogonal acceleration time-of-flight for TripleTOF experiments and mass-selective axial ejection (MSAE)²³ mass analysis was employed for QTRAP experiments. All experiments except Fig. S1† were performed on the TripleTOF platform. Fig. S1† was performed on the QTRAP platform for demonstration of the ion–molecule reaction between $[(\text{phen})_2\text{Mg}(\text{Ph})]^+$ water that occurs too quickly on the TripleTOF as the QTRAP platform has a quadrupole after the high-pressure collision cell, q2, that is lower in pressure and contains less water vapour.

DFT calculations

Gaussian 16 was used²⁴ to fully optimize the structures as singlets at the M06 level of density functional theory (DFT).²⁵ The SDD basis set was chosen to describe Ni^{26} and the 6-31G(d) basis set was used for all other atoms.²⁷ This basis set combination is referred as BS1. Frequency calculations were carried out at the same level of theory as those for the structural optimization and were used to confirm that the structures corresponded to either local minima (no imaginary frequencies) or transition states (one imaginary frequency). Transition structures were located using the Berny algorithm. Intrinsic reaction coordinate (IRC) calculations were used to confirm the connectivity between transition structures and minima.²⁸ To take into account long-range correlation for dispersion forces, the energies obtained from the M06/BS1 calculations were further refined for all the structures to include single-point energy calculations carried out with the def2-TZVP basis set (BS2) for all atoms²⁹ at the B3LYP-D3BJ level of theory.³⁰ The enthalpy at 0 K, H_0 , of each species was obtained from B3LYP-D3BJ/BS2 single-point energies corrected for the M06/BS1 zero-point vibrational energies (ZPVE).

Conclusions

This is the first use of gas-phase ion–ion reactions to examine fundamental organometallic chemistry. We are able to directly form ion-pairs which are the precursors to transmetalation reactions. A crucial finding from the present study is that two different types of ion-pairs are involved in transmetalation – the outer sphere ion-pairs $\{[(\text{phen})_3\text{M}]^{2+}[\text{BPh}_4]^{-}\}^+$, **5** and the inner sphere ion-pairs $\{[(\text{phen})_2\text{M}]^{2+}[\text{BPh}_4]^{-}\}^+$, **8**,^{1b} and that these ion-pairs are related to each other *via* a ligand substitution reaction (eqn (4)). While thermolysis of outer sphere ion-pairs $[\text{M}(\text{L})_3][\text{X}]_2$ ($\text{M}^{2+} = \text{Co}, \text{Fe}, \text{Ni}$ etc.; $\text{L} = 2,2'$ -bipyridine (bpy) or 1,10-phenanthroline (phen); $\text{X} = \text{Cl}, \text{Br}, \text{NCS}$ etc.) has been used for decades to synthesise $[\text{M}(\text{L})_2(\text{X})_2]$ complexes *via* ligand substitution in the solid state³¹ or under reflux in non-coordinating solvents,³² these types of ligand substitution reactions appear to be almost unprecedented for weakly coordinating anions such as BPh_4^- .³³ The versatility of our gas-phase ion–ion approach holds great promise for extension to the systematic investigation of the role of ion-pairs in transmetalation reactions. A key feature is the ease of control of the two reactant ions through individual ion isolation and subsequent mutual storage to enable ion–ion reactions. This avoids solvent effects which may disfavour ion pair formation. Future work will examine a wide range of other cationic metal complexes with various neutral ligands, including coordinated solvent molecules, as acceptors of anionic organyl groups, R^- , from anionic complexes RE^- (where $\text{E} =$ various Lewis acids beyond the triphenylboron system studied here). Such studies will provide fundamental information on how ligands can tune the ability of complexes to undergo transmetalation and may guide the design of new reagents and reactions for organic synthesis.||

Author contributions

K. C. F. identified and optimized routes to the gas-phase formation of the dication complexes, carried out the ion–ion reactions and CID experiments and contributed to manuscript preparation. W. A. O. A. carried out the DFT calculations on the nickel system, collated and checked all the DFT data, and contributed to manuscript preparation. A. M. O. A. carried out the DFT calculations on the magnesium system. A. J. C. and S. A. M. contributed to the project design, interpretation of data and writing of the manuscript; R. A. J. O. devised the project, contributed to the design of experiments and interpretation of data, project management and writing of the manuscript.

|| This approach also offers an opportunity to prepare ionic organometallic complexes in the gas phase for subsequent unimolecular and bimolecular reactivity studies. For other approaches to prepare ionic organometallic complexes in the gas phase, see ref. 34.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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