

# Communication

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# Magnesiation of Aryl Fluorides Catalyzed by a Rhodium–Aluminum Complex

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**ABSTRACT:** We report the magnesiation of aryl fluorides catalyzed by an Al–Rh heterobimetallic complex. We show that the complex is highly reactive to cleave the C–F bonds across the polarized Al–Rh bond under mild conditions. The reaction allows the use of an easy-to-handle magnesium powder to generate a range of arylmagnesium reagents from aryl fluorides, which are conventionally inert to such metalation compared with other aryl halides.

Complexes that contain metal-metal bonds have received considerable attention in organometallic chemistry due to their unique electronic properties, which differ significantly from those of single-metal systems, especially with respect to achieving novel organic transformations.<sup>1</sup> Among complexes with metal-metal bonds, heterobimetallic metal-metal bonding motifs are particularly reactive towards the cleavage of conventionally inert bonds due to their inherent polarization. In a pioneering study, Bergman showed that complexes activate Zr–Ir can а varietv of thermodynamically strong bonds including O-H and N-H bonds.<sup>2</sup> B-Rh<sup>3</sup> and Si-Rh<sup>4</sup> manifolds have been reported to effectively activate C-F bonds<sup>5</sup> in perfluorinated organic molecules such as pentafluoropyridine and hexafluorobenzene. Moreover, a Zr–Co complex realizes the challenging activation of the C=O bond in benzophenone to afford a cobalt carbene complex.<sup>6</sup> However, catalytic transformations that include these bond-activation events remain elusive. Recently, we have developed an Al–Rh heterobimetallic complex in which an X-type Al moiety<sup>7</sup> is ligated to the Rh center, and demonstrated its reactivity in the alkylation of pyridines.8a An NBO analysis suggested a polarized  $Al^{\delta+}-Rh^{\delta-}$  bond, and this result prompted us to test the reactivity of such Al-Rh bonds in the context of cleaving  $\sigma$ -bonds, which usually exhibit high bonddissociation energies. We previously reported that the energy level of the orbital containing the Al-Rh bond in (Me<sub>2</sub>Al)Rh(PMe<sub>3</sub>)<sub>2</sub> was higher than those containing the B–Rh bond in (Me<sub>2</sub>B)Rh(PMe<sub>3</sub>)<sub>2</sub> and the Si–Rh bond in (Me<sub>3</sub>Si)Rh(PMe<sub>3</sub>)<sub>2</sub>.<sup>8b</sup> We thus expected reactivity of the Al–Rh bonds toward the C–F bond activation higher than that of B–Rh and Si–Rh bonds based on these results. Herein, we report the activation of C–F bonds in fluoroarenes by means of an Al–Rh bond under very mild conditions, which results in an unprecedented catalytic magnesiation of fluoroarenes using easy-to-handle Mg powder.<sup>9</sup>

The reaction of Al–Rh complex 1a. which was generated *in situ* by the reduction of Al–Rh complex 2a<sup>8a</sup> with  $KC_8$ , and fluorobenzene (3a) under N<sub>2</sub> resulted in the activation of the C-F bond at the Al-Rh bond to afford complex 4a in 95% yield (Scheme 1). The solid-state structure of 4a was determined unequivocally by singlecrystal x-ray diffraction analysis. In 4a, the Al(III) moiety coordinates to the Rh center as an electron-accepting Ztype ligand<sup>10</sup> with trigonal bipyramidal geometry. The Rh center adopts a square-pyramidal geometry stabilized by an end-on N<sub>2</sub> ligand. It is noteworthy that the C-F-bond activation proceeds even at -30 °C (for details, see the Supporting Information). To the best of our knowledge. these are the mildest hitherto reported conditions for the activation of unactivated C-F bonds by a homogeneous metal complexes.<sup>3,4,5,11</sup>



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Figure 1. Energy diagram of the C–F bond activation of 3a by 1a.

To gain mechanistic insights into the C-F-bond activation by **1a**, the reaction pathway was theoretically modelled by DFT calculations (Figure 1; for details, see the Supporting Information). The C<sup>2</sup>=C<sup>3</sup> bond of fluorobenzene coordinates to the Rh atom and the F atom occupies the position close to the Al atom in Al-Rh σcomplex **1AD1**. The C–F bond of **1AD1** then changes its orientation to give adduct 1AD2. The activation of the C-F bond occurs at the Al–Rh  $\sigma$ -bond in a cooperative fashion to afford Rh-phenyl complex 4b via transition state TS. After isomerization, which includes a positional change of the Ph group, followed by coordination of N<sub>2</sub>, another Rh-phenyl complex 4a is generated. The Gibbs energy of activation ( $\Delta G^{\circ \ddagger}$ ) and the Gibbs energy of reaction ( $\Delta G^{\circ}$ ) were estimated to be 3.7 kcal mol<sup>-1</sup> and – 63.5 kcal mol<sup>-1</sup>, respectively (blue line in Figure 1). The very small  $\Delta G^{\circ\ddagger}$  stands in sharp contrast to the considerably large  $\Delta G^{\circ\ddagger}$  required for the activation of the C-F bond by Rh alone (24.2 kcal mol<sup>-1</sup>; red lines in Figure 1). The small  $\Delta G^{\circ\ddagger}$  value obtained for the cooperative activation of the C-F bond matches well with the experimentally observed reaction, which proceeds at low temperature.

Next, we turned our attention to developing new catalytic transformations based on the unique reactivity of this Al–Rh manifold toward the activation of C–F bonds. Our working hypothesis is shown in Scheme 2. We anticipated that the C–F-bond activation would afford Z-type Al<sup>III</sup>–Rh<sup>I</sup> complex 4, which could potentially be reduced with Mg to realize a catalytic magnesiation of

Ar–F bonds. The reduction potential of Mg metal should be sufficiently high to reduce the Al center of 4 (Mg<sup>2+</sup>/Mg = -2.4 V; Al<sup>3+</sup>/Al = -1.7 V vs SHE).<sup>12</sup> In contrast to the magnesiation of Ar–X bonds (X = I, Br, Cl),<sup>13</sup> that of Ar– F bonds is extremely difficult, even for highly dispersed Mg.<sup>14</sup> For example, the magnesiation of *p*-fluorotoluene proceeds only in moderate efficiency, even when a large excess of Rieke magnesium is used in refluxing THF.<sup>14a</sup> Although the magnesiation of the C–F bond with Mg(I)– Mg(I) complexes has recently been reported,<sup>5h–k</sup> precedents of the magnesiation of C–F bonds using readily available and easy-to-handle Mg powder remain elusive.



Scheme 2. A Plausible Catalytic Cycle for the Magnesiation of Aryl Fluorides using Al–Rh Complexes such as 2

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The proposed catalytic magnesiation of 1fluoronapthalene (3b, 0.30 mmol) with Mg powder (0.90 mmol), which was pre-activated upon treatment with 1.2dibromoethane (5.0 mol%), was attempted in the presence of various catalysts in THF at room temperature (Scheme 3). Gratifyingly, 1-napthoic acid (5a) was obtained in 88% NMR yield using 2a (5.0 mol% Rh) after quenching of the reaction with  $CO_2$  (1 atm), followed by acidic work-up using 3 M HCl. Al-Rh complex 2b, which bears phenyl groups on the phosphorus atoms instead of isopropyl groups, also furnished 5a in high yield. The reaction did not proceed in the absence of an Al-Rh complex. Catalytic systems based on [RhCl(nbd)]<sub>2</sub> (5.0 mol% Rh; nbd = 2,5-norbornadiene)/phosphorus ligands (10 mol% P)/Et<sub>2</sub>AlCl (20 mol%) did not afford 5a. Adding LiCl, which facilitates the magnesiation of C–Br bonds,<sup>15</sup> or adding a catalytic amount of anthracene, to generate magnesium anthracene,<sup>16</sup> did not show any effect. Using *i*-PrMgCl·LiCl led to the magnesiation of **3b** to afford **5a** in low yield, albeit that this approach is unsuitable for simple aryl fluorides such as 3a.<sup>17</sup> Accordingly, it can be concluded that only Al-Rh complexes 2a and 2b catalyze the magnesiation of aryl fluorides.

# Scheme 3. Screening Catalysts for the Catalytic Magnesiation of 3b



The magnesiation of various aryl fluorides **3** was examined at the 0.50-mmol-scale under the optimized conditions (Scheme 4). Under these conditions, 1naphthoic acid (5a) was obtained from 1fluoronaphthalene (**3b**) and isolated in 99% yield, while benzoic acid (5b) was isolated in 86% yield from the reaction involving fluorobenzene (3a). 5a could be also prepared in 82% yield on a 10 mmol-scale. Electrondonating substituents at the para- or meta-position of fluorobenzene were tolerated to afford the corresponding benzoic acids (5c-5g) in good to high yield, whereas the reaction efficiency was decreased with 4-fluorobiphenyl (3h). It should also be noted here that the C–S bond of 4fluorothioanisole (3f), which is easily functionalized by palladium or nickel catalysts,18 was tolerated in this transformation. Sterically demanding 2-fluorotoluene (3i) and 2,6-dimethylfluorobenzene (3i) furnished the corresponding carboxylic acids (5i and 5j) in 92% and 48% yield, respectively. D<sub>2</sub>O, B(Oi-Pr)<sub>3</sub>, and N-methoxy-N-methylbenzamide<sup>19</sup> can also serve as quenching electrophiles to generate the corresponding deuterated, borylated, and acylated products (5k-5m).





<sup>&</sup>lt;sup>a</sup>Reaction was carried out at room temperature. <sup>b</sup>Reaction was run on a 10 mmol scale. <sup>c</sup>Reaction was carried out at 50 °C. <sup>d</sup>The pinacol ester was isolated after reacting with pinacol. pin = pinacolato

To evaluate the plausible catalytic cycle shown in Scheme 2, stoichiometric reactions were conducted. To gain insights into the reduction of 2 to 1 in Scheme 2, the reaction of 2a (30 µmol) with Mg powder (0.60 mmol) in the presence of nbd (90 µmol) was examined. It proceeded at 60 °C to afford nbd-coordinated Al-Rh complex **1a-nbd** in high yield (Eq 1). The catalytic magnesiation of p-fluorotoluene (3c, 0.25 mmol) with Mg powder (0.75 mmol) in the presence of 4a (20 mol%, 50 µmol) afforded p-toluic acid (5c) in 70% yield (0.18 mmol) based on 3c under concomitant formation of benzoic acid (5b) in 48% yield (24 µmol) based on 4a (Eq These results support the generation of 2). phenylmagnesium species from 4a under the applied conditions, and thus corroborate the catalytic cycle proposed in Scheme 2. In fact, the formation of diphenylmagnesium was implied by <sup>1</sup>H and <sup>13</sup>C NMR spectroscopies of the crude mixture upon magnesiation of **3a** under the optimized conditions (for details, see the Supporting Information).<sup>20</sup>



In conclusion, we have developed a catalytic magnesiation of Ar–F bonds through the C–F bond activation across the X-type heterobimetallic Al–Rh center. It is worth mentioning that the cooperative activation allows the functionalization of C–F bonds in unactivated fluoroarenes under very mild conditions. This is a rare example of successful applications of heterobimetallic catalysis. Further developments of catalytic functionalization of other strong polar  $\sigma$ -bonds by the heterobimetallic systems are currently under investigation in our laboratories.

#### ASSOCIATED CONTENT

The Supporting Information is available free of charge on the ACS Publications website.

Crystallographic data for 2b (CIF)

Crystallographic data for **4a** (CIF)

Detailed experimental procedures and computational details, as well as spectroscopic and analytical data (PDF)

Optimized structures (XYZ)

CCDC 2000480 (**2b**) and 1999655 (**4a**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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#### **Author Contributions**

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## Notes

The authors declare no competing financial interests.

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# REFERENCES

14 (1) (a) Powers, I. G.; Uyeda, C. Metal-Metal Bonds in Catalysis. ACS 15 Catal. 2017, 7, 936-958. (b) Buchwalter, P.; Rosé, J.: Braunstein, P. 16 Multimetallic Catalysis Based on Heterometallic Complexes and 17 Clusters. Chem. Rev. 2015, 115, 28-126. (c) Wheatley, N.; Kalck, P. 18 Structure and Reactivity of Early-Late Heterobimetallic Complexes. 19 Chem. Rev. 1999, 99, 3379-3419. (d) Gade, L. H. Highly Polar Metal-Metal Bonds in "Eary-Late" Heterobimetallic Complexes. Angew. 20 Chem., Int. Ed. 2000, 39, 2658-2678. (e) Cooper, B. G.; Napoline, J. 21 W.; Thomas, C. M. Catalytic Applications of Early/Late 22 Heterobimetallic Complexes. Catal. Rev. Sci. Eng. 2012, 54, 1-40. (f) 23 Mankad, N. P. Selectivity Effects in Bimetallic Catalysis. Chem.-Eur. J. 2016, 22, 5822-5829. (g) Mankad, N. P. Diverse bimetallic 24 mechanisms emerging from transition metal Lewis acid/base pairs: 25 development of co-catalysis with metal carbonyl 26 anions. Chem. Commun. 2018, 54, 1291-1302. (h) Rej, S.; Tsurugi, H.; 27 Mashima, K. Multiply-bonded dinuclear complexes of early-transition 28 metals as minimum entities of metal cluster catalysts. Coord. Chem. Rev. 2018, 355, 223-239. (i) Farley, C. M.; Uyeda, C. Organic 29 Reactions Enabled by Catalytically Active Metal-Metal Bonds. Trends 30 in Chemistry 2019, 1, 497-509. (j) Sevin, A.; Hengtai, Y.; Chaquin, P. 31 Theoretical semi-empirical study of concerted oxidative additions to 32 dinuclear complexes. J. Organomet. Chem. 1984, 262, 391-405. (k) Thomas, C. M. Metal-Metal Multiple Bonds in Early/Late 33 Heterobimetallic Complexes: Applications Toward Small Molecule 34 Activation and Catalysis. Comments Inorg. Chem. 2011, 32, 14-38. (1) 35 Trinquier, G.; Hoffmann, R. Dinuclear Reductive Eliminations. 36 Organometallics 1984, 3, 370-380. (m) Moore, J. T.; Smith, N. E.; Lu, 37 C. C. Structure and dynamic NMR behavior of rhodium complexes supported by Lewis acidic group 13 metallatranes. Dalton Trans. 2017, 38 46, 5689-5701.

40, 5089–5701.
(2) (a) Baranger, A. M.; Bergman, R. G. Cooperative Reactivity in the Interactions of X–H Bonds with a Zirconium–Iridium Bridging Imido Complex. J. Am. Chem. Soc. 1994, 116, 3822–3835. (b) Hanna, T. A.; Baranger, A. M.; Bergman, R. G. Reaction of Carbon Dioxide and Heterocumulenes with an Unsymmetrical Metal–Metal Bond. Direct Addition of Carbon Dioxide across a Zirconium–Iridium Bond and Stoichiometric Reduction of Carbon Dioxide to Formate. J. Am. Chem. Soc. 1995, 117, 11363–11364.

(3) (a) Braun, T.; Salomon, M. A.; Altenhöner, K.; Teltewskoi, M.;
Hinze, S. C–F Activation at Rhodium Boryl Complexes: Formation of 2-Fluoroalkyl-1,3,2-Dioxaborolanes by Catalytic Functionalization of Hexafluoropropene. *Angew. Chem., Int. Ed.* 2009, *48*, 1818–1822. (b)
Teltewskoi, M.; Panetier, J. A.; Macgregor, S. A.; Braun, T. A Highly
Reactive Rhodium(I)–Boryl Complex as a Useful Tool for C–H Bond Activation and Catalytic C–F Bond Borylation. *Angew. Chem., Int. Ed.* 2010, *49*, 3947–3951.

(4) (a) Aizenberg, M.; Milstein, D. Catalytic Activation of Carbon-Fluorine Bonds by a Soluble Transition Metal Complex. *Science* 1994, 265, 359–361. (b) Rhodium(I) Silyl Complexes for C–F Bond Activation Reactions of Aromatic Compounds: Experimental and Computational Studies. Raza, A. L.; Panetier, J. A.; Teltewskoi, M.; Macgregor, S. A.; Braun, T. *Organometallics* 2013, *32*, 3795–3807. (c)

Raza, A. L.; Braun, T. Consecutive C–F bond activation and C–F bond formation of heteroaromatics at rhodium: The peculiar role of FSi(OEt)<sub>3</sub>. *Chem. Sci.* **2015**, *6*, 4255–4260.

(5) (a) Liu, X.-W.; Echavarren, J.; Zarate, C.; Martin, R. Ni-Catalyzed Borylation of Aryl Fluorides via C-F Cleavage. J. Am. Chem. Soc. 2015, 137, 12470–12473. (b) Yoshikai, N.; Matsuda, H.; Nakamura, E. Hydroxyphosphine Ligand for Nickel-Catalyzed Cross-Coupling through Nickel/Magnesium Bimetallic Cooperation. J. Am. Chem. Soc. 2009, 131, 9590-9599. (c) Nova, A.; Reinhold, M.; Perutz, R. N.; Macgregor, S. A.; McGrady, J. E. Selective Activation of the ortho C-F Bond in Pentafluoropyridine by Zerovalent Nickel: Reaction via a Metallophosphorane Intermediate Stabilized by Neighboring Group Assistance from the Pyridyl Nitrogen. Organometallics 2010, 29, 1824-1831. (d) Dugan, T. R.; Sun, X.-R.; Rybak-Akimova, E. V.; Olatunji-Ojo, O.; Cundari, T. R.; Holland, P. L. A Masked Two-Coordinate Cobalt(I) Complex That Activates C-F Bonds. J. Am. Chem. Soc. 2011, 133, 12418-12421. (e) Dugan, T. R.; Goldberg, J. M.; Brennessel, W. W.; Holland, P. L. Low-Coordinate Cobalt Fluoride Complexes: Synthesis, Reactions, and Production from C-F Activation Reactions. Organometallics 2012, 31, 1349-1360. (f) Asako, S.; Ilies, L.; Verma, P.; Ichikawa, S.; Nakamura, E. Theoretical Study on Alkoxydiphosphine Ligand for Bimetallic Cooperation in Nickel-catalyzed Monosubstitution of C-F Bond. Chem. Lett. 2014, 43, 726-728. (g) Li, B. Z.; Qian, Y. Y.; Liu, J.; Chan, K. S. Consecutive Aromatic Carbon-Fluorine Bond and Carbon-Hydrogen Bond Activations by Iridium Porphyrins. Organometallics 2014, 33, 7059-7068. (h) Bakewell, C.; White, A. J. P.; Crimmin, M. R. Addition of Carbon-Fluorine Bonds to a Mg(I)-Mg(I) Bond: An Equivalent of Grignard Formation in Solution. J. Am. Chem. Soc. 2016, 138, 12763-12766. (i) Bakewell, C.; Ward, B. J.; White, A. J. P.; Crimmin, M. R. A combined experimental and computational study on the reaction of fluoroarenes with Mg-Mg, Mg-Zn, Mg-Al and Al-Zn bonds. Chem. Sci. 2018, 9, 2348-2356. (j) Garçon, M.; Bakewell, C.; White, A. J. P.; Crimmin, M. R. Unravelling nucleophilic aromatic substitution pathways with bimetallic nucleophiles. Chem. Commun. 2019, 55, 1805-1808. (k) Gentner, T. X.; Rösch, B.; Ballmann, G.; Langer, J.; Elsen, H.; Harder, S. Low Valent Magnesium Chemistry with a Super Bulky B-Diketiminate Ligand. Angew. Chem., Int. Ed. 2019, 58, 607-611. (1) Bakewell, C.; White, A. J. P.; Crimmin, M. R. Reactions of Fluoroalkenes with an Aluminium(I) Complex. Angew. Chem., Int. Ed. 2018, 57, 6638-6642. (m) Coates, G.; Rekhroukh, F.; Crimmin, M. R. Breaking Carbon-Fluorine Bonds with Main Group Nucleophiles. Synlett 2019, 30, 2233-2246. (n) Kysliak, O.; Görls, H.; Kretschmer, R. C-F bond activation by pentamethylcyclopentadienylaluminium(I): a combined experimental/computational exercise. Chem. Commun. 2020, Advance Article, DOI: 10.1039/d0cc00003e. (o) Talavera, M.; Meißner, G.; Rachor, S. G.; Braun, T. C-F activation reactions at germylium ions: dehydrofluorination of fluoralkanes. Chem. Commun. 2020, 56, 4452-4455. (p) Pietrasiak, E.; Lee, E. Activation of C-F, Si-F, and S-F Bonds by N-Heterocyclic Carbenes and Their Isoelectronic Analogues. Synlett 2020, DOI: 10.1055/s-0040-1707106. (q) Amii, H.; Unevama, K. C-F Bond Activation in Organic Synthesis. Chem. Rev. 2009, 109, 2119-2183. (r) Eisenstein, O.; Milani, J.; Perutz, R. N. Selectivity of C-H Activation and Competition between C-H and C-F Bond Activation at Fluorocarbons. Chem. Rev. 2017, 117, 8710-8753. (6) Marquard, S. L.; Bezpalko, M. W.; Foxman, B. M.; Thomas, C. M. Stoichiometric C=O Bond Oxidative Addition of Benzophenone by a Discrete Radical Intermediate To Form a Cobalt(I) Carbene. J. Am. Chem. Soc. 2013, 135, 6018-6021.

(7) (a) Green, M. L. H. A new approach to the formal classification of covalent compounds of the elements. *J. Organomet. Chem.* **1995**, *500*, 127–148. (b) Fischer, R. A.; Priermeier, T. Transition-Metal-Substituted Alanes: Synthesis and Spectroscopic Studies and the Structure of  $(\eta^5-C_5H_5)(CO)_2Fe-Al[(CH_2)_3NMe_2]('Bu)$ . *Organometallics* **1994**, *13*, 4306–4314. (c) Anand, B. N.; Krossing, I.; Nöth, H. Synthesis and X-ray Crystal Structure of (tmp)\_2Al-Fe(cp)(CO)\_2: An Alanyl-Containing Iron Complex with a Tricoordinated Aluminum Atom. *Inorg. Chem.* **1997**, *36*, 1979–1981. (d) Agou, T.; Yanagisawa, T.; Sasamori, T.; Tokitoh, N. Synthesis and Structure of an Iron-Bromoalumanyl Complex with a Tri-Coordinated

Aluminum Center. Bull. Chem. Soc. Jpn. 2016, 89, 1184–1186. (e) Takaya, J.; Iwasawa, N. Synthesis, Structure, and Catalysis of Palladium Complexes Bearing a Group 13 Metalloligand: Remarkable Effect of an Aluminum-Metalloligand in Hydrosilylation of CO<sub>2</sub>. J. Am. Chem. Soc. 2017, 139, 6074–6077. (f) Hicks, J.; Mansikkamäki, A.; Vasko, P.; Goicoechea, J. M.; Aldridge, S. A nucleophilic gold complex. Nat. Chem. 2019, 11, 237–241. (g) Morisako, S.; Watanabe, S.; Ikemoto, S.; Muratsugu, S.; Tada, M.; Yamashita, M. Synthesis of A Pincer-Ir<sup>V</sup> Complex with A Base-Free Alumanyl Ligand and Its Application toward the Dehydrogenation of Alkanes. Angew. Chem., Int. Ed. 2019, 58, 15031–15035.

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(8) (a) Hara, N.; Saito, T.; Semba, K.; Kuriakose, N.; Zheng, H.; Sakaki, S.; Nakao, Y. Rhodium Complexes Bearing PAIP Pincer Ligands. J. Am. Chem. Soc. **2018**, *140*, 7070–7073. (b) Kuriakose, N.; Zheng, J.-J.; Saito, T.; Hara, N.; Nakao, Y.; Sakaki, S. Characterization of Rh–Al Bond in Rh(PAIP) (PAIP = Pincer-type Diphosphino-Aluminyl Ligand) in Comparison with Rh(L)(PMe<sub>3</sub>)<sub>2</sub> (L = AlMe<sub>2</sub>, Al(NMe<sub>2</sub>)<sub>2</sub>, BR<sub>2</sub>, SiR<sub>3</sub>, CH<sub>3</sub>, Cl, or OCH<sub>3</sub>): Theoretical Insight. *Inorg. Chem.* **2019**, *58*, 4894–4906.

(9) Moore and Lu have reported catalytic hydrogenolysis of aryl C–F bonds using a bimetallic rhodium–indium complex, see: Moore, J. T.; Lu, C. C. Catalytic Hydrogenolysis of Aryl C–F Bonds Using a Bimetallic Rhodium–Indium Complex. Manuscript under revision.

(10) (a) Amgoune, A. Bourissou, D.  $\sigma$ -Acceptor, Z-type ligands for 19 transition metals. Chem. Commun. 2011, 47, 859-871. (b) You, D. 20 Gabbaï, F. P. Tunable  $\sigma$ -Accepting, Z-Type Ligands for 21 Organometallic Catalysis. Trends in Chemistry 2019, 1, 485-496. (c) 22 Vollmer, M. V.; Xie, J.; Lu, C. C. Stable Dihydrogen Complexes of 23 Cobalt(-I) Suggest an Inverse trans-Influence of Lewis Acidic Group 24 13 Metalloligands. J. Am. Chem. Soc. 2017, 139, 6570-6573. (d) Devillard, M.; Nicolas, E.; Ehlers, A. W.; Backs, J.; Mallet-Ladeira, S.; 25 Bouhadir, G.; Slootweg, J. C.; Uhl, W.; Bourissou, D. Dative Au-Al 26 Interactions: Crystallographic Characterization and Computational 27 Analysis. Chem. Eur. J. 2015, 21, 74-79. (e) Cowie, B. E.; Tsao, F. A.; 28 Emslie, D. J. H. Synthesis and Platinum Complexes of an Alane-Appended 1,1'-Bis(phosphino)ferrocene Ligand. Angew. Chem., Int. 29 Ed. 2015, 54, 2165-2169. (f) Rudd, P. A.; Liu, S.; Gagliardi, L.; Young 30 V. G., Jr.; Lu, C. C. Metal-Alane Adducts with Zero-Valent Nickel, 31 Cobalt. and Iron. J. Am. Chem. Soc. 2011, 133, 20724-20727. (g) Saito. 32 T.; Hara, N.; Nakao, Y. Palladium Complexes Bearing Z-type PAIP Pincer Ligands. Chem. Lett. 2017, 46, 1247-1249. 33

(11) Moore reported that Ru(dmpe)<sub>2</sub>H<sub>2</sub> (dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>) cleaved C–F bond of hexafluorobenzene at -78 °C. However, it was limited to C–F bonds of multi-fluorinated arenes. The reactions of dior mono-fluorinated arenes were not reported, see: Whittlesey, M. K.;
Perutz, R. N.; Moore, M. H. Facile intermolecular aromatic C–F bond activation reactions of [Ru(dmpe)<sub>2</sub>H<sub>2</sub>] (dmpe = Me<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PMe<sub>2</sub>). *Chem. Commun.* 1996, 787–788.

(12) CRC Handbook of Chemistry and Physics; 94th ed.; Haynes, W. M., Ed.; CRC Press: Boca Raton, 2013.

(13) (a) Main Group Metals in Organic Synthesis; Yamamoto, H.,
Oshima, K., Eds.; Wiley-VCH: Weinheim, 2004. (b) Ziegler, D. S.;
Wei, B.; Knochel, P. Improving the Halogen–Magnesium Exchange by
using New Turbo-Grignard Reagents. Chem.-Eur. J. 2019, 25, 2695–2703.

45 (14) (a) Rieke, R. D.; Bales, S. E. Activated metals. IV. Preparation 46 and reactions of highly reactive magnesium metal. J. Am. Chem. Soc. 1974, 96, 1775–1781. (b) Tjurina, L. A.; Kombarova, S. V.; Bumagin, 47 N. A.; Beletskaya, I. P. Cryosynthesis of phenylpolymagnesium halides 48 and their interaction with allyl bromide. Metalloorganicheskaya 49 Khimiya 1990, 3, 48-51. (c) Tjurina, L. A.; Smirnov, V. V.; Barkovskii, G. B.; Nikolaev, E. N.; Esipov, S. E.; Beletskaya, I. P. Cluster Grignard 50 Reagents. Organometallics 2001, 20, 2449-2450. (d) Speight, I. R.; 51 Hanusa, T. P. Exploration of Mechanochemical Activation in Solid-52 State Fluoro-Grignard Reactions. Molecules 2020, 25, 570.

53 (15) Piller, F. M.; Appukkuttan, P.; Gavryushin, A.; Helm, M.;
54 Knochel P. Convenient Preparation of Polyfunctional Aryl Magnesium
55 Reagents by a Direct Magnesium Insertion in the Presence of LiCl.
56 Angew. Chem., Int. Ed. 2008, 47, 6802–6806.

(16) Bogdanović, B.; Liao, S.-T.; Mynott, R.; Schlichte, K.; Westeppe, U. Rate of Formation and Characterization of Magnesium Anthracene. *Chem. Ber.* **1984**, *117*, 1378–1392.

(17) Krasovskiy, A.; Knochel, P. A LiCl-Mediated Br/Mg Exchange Reaction for the Preparation of Functionalized Aryl- and Heteroarylmagnesium Compounds from Organic Bromides. *Angew. Chem., Int. Ed.* **2004**, *43*, 3333–3336.

(18) (a) Modha, S. G.; Mehta, V. P.; Van Der Eycken, E. V. Transition Metal-Catalyzed C-C Bond Formation via C-S Bond Cleavage: An Overview. Chem. Soc. Rev. 2013, 42, 5042-5055. (b) Wang, L.; He, W.; Yu, Z. Transition-Metal Mediated Carbon-Sulfur Bond Activation and Transformations. Chem. Soc. Rev. 2013, 42, 599-621. (c) Wenkert, E.; Ferreira, T. W.; Michelotti, E. L. Nickel-induced Conversion of Carbon–Sulphur into Carbon–Carbon Bonds. One-step Transformations of Enol Sulphides into Olefins and Benzenethiol Derivatives into Alkylarenes and Biaryls. J. Chem. Soc., Chem. Commun. 1979, 637-638. (d) Okamura, H.; Miura, M.; Takei, H. Nickel-phosphine complex catalyzed coupling reaction of Grignard reagents with alkenyl or aryl sulfides. Tetrahedron Lett. 1979, 20, 43 - 46

(19) Nahm, S.; Weinreb, S. M. *N*-Methoxy-*N*-methylamides as Effective Acylating Agents. *Tetrahedron Lett.* **1981**, *22*, 3815–3818.

(20) Generation of diphenylmagnesium<sup>18a</sup> was implied by comparing <sup>1</sup>H and <sup>13</sup>C NMR spectra of the crude mixture in C<sub>6</sub>D<sub>6</sub>, with those of independently synthesized diphenylmagnesium in the presence of **2a** or **4a** (5.0 mol% Rh). (a) Tang, H.; Richey, H. G. Reactions of Diorganocadmium Compounds with Other Dialkylmetal Compounds and Macrocycles: Synthesis of Organocadmate Anions. *Organometallics* **2001**, *20*, 1569–1574. In addition, phenylmagnesium fluoride<sup>18b</sup> prepared independently showed very low solubility in THF and C<sub>6</sub>D<sub>6</sub>. (b) Ashby, E. C.; Nackashi, J. The preparation of organomagnesium fluorides by organometallic exchange reactions. *J. Organomet. Chem.* **1974**, *72*, 11–20.

