Nucleophilic Additions to Coordinated 1,10-phenanthroline: Intramolecular, Intermolecular, Reversible and Irreversible

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Abstract: KN(SiMe₃)₂ reacts with [Re(CO)₃(phen)(PMe₃)]OTf via reversible addition to the phen ligand and irreversible deprotonation of the PMe₃ ligand followed by intramolecular attack to phen by the deprotonated phosphane, while MeLi irreversibly adds to phen. The addition of MeLi has been shown to be intermolecular, unlike previously known nucleophilic additions to pyridines.

The relevance of pyridine rings is partly due to their prevalence as donors in transition metal (TM) chemistry. 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) are the most extensively employed among these ligands. Some families of their TM complexes, rhenium carbonyls being a prime example, are promising tools in several areas of contemporary research.^[1] However, the organic chemistry of TM-coordinated bipy and phen remains virtually unexplored.^[2] Additions of main group metal alkyls to free pyridines, including bipy and phen, are well known reactions.^[3] Coordination to a Lewis-acidic metal center could be expected to enhance the electrophilic character of pyridine donors. However, examples of nucleophilic addition to the pyridyl rings of TM-coordinated bipy, phen or other pyridine-containing ligands are scarce,^[4,5] despite a long-time interest in one such reaction, namely, covalent hydration.^[6] Intramolecular additions have been demonstrated in which a nucleophilic group is generated by the reaction of one of the ligands with an external reagent,^[7] but a truly intermolecular addition remains elusive. Here we report, among other reactions, the first examples.

Addition of KN(SiMe₃)₂ to a yellow THF solution of [Re(CO)₃(phen)(PMe₃)]OTf (**1**) at -78°C (IR νCO: 2034, 1945 and 1920 cm⁻¹) immediately produced a purple solution with νCO bands at 2014, 1918 and 1888 cm⁻¹, diagnostic of a neutral fac-Re(CO)₃ complex. After 1 hour at room temperature, the solution darkened, its IR spectrum showed bands at 2010, 1916 and 1888 cm⁻¹, and its NMR revealed a single organometallic product, **2**,

which could be isolated as red crystals in 46% yield. The ¹H and ¹³C NMR spectra of **2** were assigned on the basis of 2D COSY, ¹H-¹³C HSQC and ¹H-¹³C HMBC experiments and showed the dearomatization of one pyridyl ring. ¹H NMR signals at 2.10 and 1.83 ppm (THF-d₈) are assigned to the diastereotopic H atoms of a P-CH₂ group. Their couplings of 9.7 and 5.9 Hz respectively with the 4.63 ppm signal of the C2-H group of the dearomatized ring indicate intramolecular attack on the phen C2(9) position after PMe₃ deprotonation, as depicted in Scheme 1. The nitrogen atoms of **2** occur at 97.7 (dearomatized ring) and 233.2 ppm in the ¹⁵N NMR spectrum (obtained through ¹H-¹⁵N HMBC in THF-d₈; for **1**, δ(¹⁵N NMR) = 226.5 ppm in THF-d₈), reflecting their very different natures. In contrast with its bipy analog,^[7a] which could not be crystallized due to its low stability, solutions of **2** are stable for several days at room temperature, and its crystals are shelf-stable for at least one month. The X-ray structure of **2** (Figure 1), confirmed the connectivity shown in Scheme 1 and the loss of planarity of the N1 ring: alternate single or double C-C bond distances (e. g. C3-C4 = 1.328(8) Å and C4-C12 = 1.449(7) Å) contrast with the intermediate values in the aromatic N10 ring (shortest: C7-C8 = 1.360(7) Å, longest: C14-C7 = 1.409(7) Å). The tetrahedral geometry around C2 (e. g. the N1-C2-C15 angle is 107.1(4)°) agrees with its δ(¹³C) NMR at 64.9 ppm. The sum of the angles around N1, 349.1(4)°, shows a

Scheme 1. Additions to the phen ligand of **1**: (a) Intramolecular attack of a deprotonated P-CH₃ group on C2(9), and (b) intermolecular attack of KN(SiMe₃)₂ on C4(7).

Figure 1. Thermal ellipsoid (30% probability) plots of **2** and **4M-C2**.

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Supporting information for this article is given via a link at the end of the document: Experimental and computational details and data (PDF) and crystallographic information for compounds **2** and **4M-C2** (CIF).

rare pyramidal -rather than planar- geometry for the amido group.^[8]

Low temperature NMR monitoring of the reaction of **1** with KN(SiMe₃)₂ revealed the presence of two intermediates, **3M** and **3m**, in a 17:1 ratio, both with intact PMe₃ ligands and one dearomatized pyridine ring, resulting from amide attack to the C4(7) position of phen (from ¹H-²⁹Si HMQC, COSY, ¹H-¹³C HMBC and ¹H-¹⁵N HMBC NMR).^[9] **3M** and **3m** differ in the relative orientation of the N(SiMe₃)₂ group (shown by the 2D NOESY), **3M** corresponding to the attack to the less hindered side of phen, *anti* with respect to PMe₃ (see Scheme 1). The *ortho* carbons of pyridines are the main target of nucleophilic attack in the Chichibabin^[10] and related reactions.^[11] The failure to detect such products in the reaction of **1** with KN(SiMe₃)₂ is attributed to the metal fragment blocking the approach of the very bulky amide nucleophile.

A ¹H DOSY experiment^[12] of a reaction mixture containing **2**, **3M** and **3m** at 298 K in toluene-*d*₈ afforded diffusion coefficients for **3M** and **2** consistent with their proposed formulations (see Figures S46 and S47 of the SI). Two mechanisms can be envisaged for the evolution of the **3M**, **3m** mixture toward **2**: amide dissociation followed by PMe₃ deprotonation by free amide, or an inner-sphere, concerted deprotonation of PMe₃ by the amide, conceivable at least for **3m**, in which amide and PMe₃ groups are on the same side of phen. The long distance between the amide nitrogen and the phosphane hydrogens (5.118 Å) in a computational model of **3m** militates against the latter mechanism. DFT calculations (vide infra) support that the reaction of **1** with KN(SiMe₃)₂ is reversible (pyridyl rearomatization must provide part of the driving force for amide dissociation), and that PMe₃ is deprotonated by free amide. Reversible, non-productive formation of dearomatized adducts is common as the first step of the reactions of nucleophiles with electron-poor arenes, such as nitroarenes.^[13]

Reaction of MeLi with **1** in toluene produced a green solution from which, after 5 days, **4M-C2** was isolated in 38% yield (see Scheme 2). 2D COSY and ¹H-¹⁵N HMBC NMR showed that **4M-C2** results from methyl addition to C2(phen), and 2D NOESY establishes the position of the methyl group on the side of phen opposite to PMe₃. The structure was confirmed by X-ray diffraction (see Figure 1). The geometry about the amido-like N1 atom is planar, as most often found in TM-complexes, including rhenium carbonyls.^[6] **4M-C2** is an 18 e⁻ complex if a single Re-N1 bond is counted, so the amido lone pair is either delocalized through the aryl ring, donated to the CO ligands through the metal dπ orbitals,^[14] or both. Hence, the pyramidal-at-N1 geometry in **2** is attributed to its constrained cyclic geometry. NMR showed the initial green solution to consist of four products

(**4M-C2**, **4M-C4**, **4m-C2** and **4m-C4** in a 1.0:0.7:0.2:0.2 ratio by ¹H and ³¹P NMR integration 1 hour after the addition of MeLi and quick workup, see Figures S56 and S57), and indicated a composition for **4M-C4** similar to that found for **4M-C2**, but with the methyl group on C4(phen). Although the stereochemistry at C4(phen) in **4M-C4** could not be elucidated, methyl addition to the less hindered phen side (opposite to PMe₃) is proposed. For **4m-C2** and **4m-C4** most ¹H NMR signals were obscured by the signals of the major products, but those of the phen-bonded methyl groups, which could be distinctly observed, showed ¹H-¹³C HMBC cross-peaks identical to those of **4M-C2** and **4M-C4** respectively. Hence, the same connectivity, but methyl groups on the PMe₃ side of phen are proposed for **4m-C2** and **4m-C4** (see Scheme S1). A ¹H DOSY NMR experiment showed that the four products display comparable diffusion coefficients, supporting their formulation as isomers (see Figures S68 and S69). The concentration of the four products in the green solution decreased over time (by ¹H NMR integration against C₆Me₆ as internal standard, see Figure S67)^[15] and a brown material precipitated, consisting of several species containing aromatic phenanthrolines. The precipitate-forming reaction is proposed to be an oxidation, perhaps by traces of dissolved O₂. Supporting this proposal, **4m-C2** and **4m-C4**, with the H atom which would be abstracted on the more accessible phen face (opposite to PMe₃), are the less stable isomers. Dearomatized products resulting from nucleophilic addition to pyridine rings tend to re-aromatize, most often by an elimination step, so that the overall reaction is a nucleophilic aromatic substitution.^[16] In the absence of a good leaving group, hydride can be abstracted by typical oxidants or be transferred to hydride acceptors such as carbonyl groups.^[17] The different rate at which the four products of MeLi addition to **1** decay shows that they do not interconvert, in contrast with several bis(imino)pyridine metal complexes, in which alkyl migration has been established.

In the reactions of bipy, phen and other conjugated diimines with main group metal nucleophiles (MY), following the initial formation of a diimine-MY adduct, a single electron transfer from MY to a low energy, empty molecular orbital of the diimine weakens the M-Y bond, facilitating its homolysis to generate a Y· radical, which eventually adds to the ring.^[18] For the reactions of MY with transition metal complexes in which bipy and phen form robust, non-labile chelates,^[19] such a low-energy^[20] radical pathway is not available.

The mechanism of most dearomatizations of TM-bonded pyridine rings (including the few examples involving bipy or phen) consists of an initial nucleophilic attack to the metal followed by an intramolecular migration of the nucleophile to the ring^[5] reminiscent of the main group chemistry mentioned above. A direct addition to the coordinated pyridine ring has never been demonstrated, and one can wonder if TM fragments do not in fact sterically impede the approach of the nucleophile to the kinetically favored 2(6) position. Moreover, it has been noted that electronically, metal fragments capable of back-donation could deactivate pyridine rings towards nucleophilic attack.^[21] Could the reaction of **1** with MeLi proceed by PMe₃ displacement to form [Re(phen)(CO)₃(Me)] (**5**), followed by intramolecular methyl migration from Re to phen, aided by PMe₃ re-coordination? Treatment of independently synthesized **5** with 1 equivalent of

Scheme 2. Intermolecular attack of MeLi to C2 of phen and bipy in **1** and **6** respectively.

PMe₃ in toluene afforded, after 1 hour at room temperature, unreacted **5**, ruling out this hypothesis.

Part of the driving force in previously known dearomatizations of coordinated pyridyl rings is provided by the strengthening of the N-M bond, due to the π -donation from the created amido group to empty metal orbitals.^[4b,4d,5d] A similar effect could be present in our complexes due to the presence of strongly π -accepting carbonyl co-ligands, to which electron density from the amido group can be transferred through the metal d π orbitals.^[14]

Aiming to obtain an approximate understanding of the reactions (their study is complicated by the formation of salt byproducts, vide infra), and in particular of their reversible (KN(SiMe₃)₂) and irreversible (MeLi) character, the additions to **1** have been investigated by DFT (see Figure 2). In the reaction with KN(SiMe₃)₂, **3M** (-2.6 kcal·mol⁻¹) and **3m** (0.2 kcal·mol⁻¹) form with no barriers. Following PMe₃ deprotonation, intramolecular additions to C10a or to C2, producing **2*** (-9.5 kcal·mol⁻¹) or **2** (-22.2 kcal·mol⁻¹) respectively, present barriers of 4.1 and 3.9 kcal·mol⁻¹. Hence, intermolecular addition is favored at low T. At higher T, free amide, regenerated from **3M** and **3m**, deprotonates PMe₃ and the small barriers for intramolecular addition can be surmounted, ultimately leading to the most stable product **2**. The KOTf product has been modeled as a molecular species without additional donors coordinated to the potassium cation. Preliminary calculations show that including the binding of K⁺ by several THF molecules leads to a lower energy. If, under the reaction conditions, KOTf (or part of it) is a solid, its lattice energy will also lower the energy. Therefore, the very small, yet positive, energy value computed for **3m** is not a concern.

For the reaction with MeLi, the barrier to deprotonation (16.2 kcal·mol⁻¹) is significantly higher than those for the irreversible formation of the products of intermolecular addition (9.6 kcal·mol⁻¹ for **4M-C4** and 11.8 kcal·mol⁻¹ for **4M-C2**), explaining why the latter are the observed products.

Yellow [Re(bipy)(CO)₃PMe₃](OTf) (**6**)^[7a] (2034, 1938, 1915 cm⁻¹ in toluene) reacts with MeLi in toluene affording a red solution with IR bands at 2012, 1917 and 1885 cm⁻¹ containing a single product (as judged by ¹H and ³¹P NMR), **7**, with an asymmetric dearomatized bipy ligand and an intact PMe₃ ligand. COSY, ¹H-¹³C HMBC, ¹H-¹³C HSQC and ¹H-¹⁵N HMBC experiments showed cross-peaks consistent with the methyl group (3H singlet at 1.41 ppm) being bonded to C2(2') of bipy (see Scheme

Figure 2. PCM-B3LYP/6-31+G(d) (LANL2DZ for Re) Gibbs energy profiles (kcal·mol⁻¹) for the reactions of **1** with KN(SiMe₃)₂ in THF (red line) and [MeLi]₂^[22] in toluene (green line). **2*** is the product of the intramolecular attack by the deprotonated group on phen C10a. Energies are referred to the reactants. See pages S100-S112 for absolute energy values and optimized structures.

2). No cross-peaks between that methyl group and PMe₃ were found in the 2D NOESY spectrum, hinting that the methyl group is on the bipy face opposite to PMe₃, as expected on steric grounds.

In summary, the bulky, typically non-nucleophilic amide KN(SiMe₃)₂^[23] reversibly adds to C4(7) of phen in [Re(CO)₃(phen)(PMe₃)]OTf (**1**), yielding two diastereomers which evolve through PMe₃ deprotonation by free amide, followed by intramolecular addition of the P-CH₂ group to C2(9) of phen. MeLi irreversibly adds to C2(9) and C4(7) of phen in **1** in an intermolecular fashion.^[24] Addition of MeLi to [Re(CO)₃(bipy)(PMe₃)]OTf (**6**) takes place exclusively on the quaternary C2(2') position of bipy.^[3a] Therefore, rhenium-coordinated bipy and phen are significantly electrophilic and can undergo the addition of internal and external nucleophiles. Reactions as the ones reported here can provide access to unexplored types of complexes, but also open deactivation pathways of bipy- and phen-containing functional compounds, similar to those known for imine complexes, but previously unrecognized for bipy and phen.^[25]

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- [1] a) S. Oh, J. R. Gallagher, J. T. Miller, Y. Surendranath, *J. Am. Chem. Soc.* **2016**, *138*, 1820-1823; b) K. K. -W. Lo, *Acc. Chem. Res.* **2015**, *48*, 2985-2995; c) L. M. Kiefer, J. T. King, K. J. Kubarych, *Acc. Chem. Res.* **2015**, *48*, 1123-1130; d) A. Zarkadoulas, E. Koutsouri, C. Kefalidi, C. A. Mitsopoulou, *Coord. Chem. Rev.* **2015**, *304-305*, 55-72; e) S. Sato, O. Ishitani, *Coord. Chem. Rev.* **2015**, *282-283*, 50-59; f) R. M. Spada, M. Cepeda-Plaza, M. L. Gómez, G. Günther, P. Jaque, N. Pizarro, R. E. Palacios, A. Vega, *J. Phys. Chem. C* **2015**, *119*, 10148-10159; g) W. -K. Chu, C. -C. Ko, K. -C. Chan, S. -M. Yiu, F. -L. Wong, C. -S. Lee, V. A. L. Roy, *Chem. Mater.* **2014**, *26*, 2544-2550; h) C. W. Machan, S. A. Chabolla, J. Yin, M. K. Gilson, F. A. Tezcan, C. P. Kubiak, *J. Am. Chem. Soc.* **2014**, *136*, 14598-14607; i) C. Bachmann, B. Probst, M. Guttentag, R. Alberto, *Chem. Commun.* **2014**, *50*, 6737-6739; j) A. Leonidova, G. Gasser, *ACS Chem. Biol.* **2014**, *9*, 2180-2193; k) A. E. Pierri, A. Pallaro, G. Wu, P. C. Ford, *J. Am. Chem. Soc.* **2012**, *134*, 18197-18200; l) A. J. Morris, G. J. Meyer, E. Fujita, *Acc. Chem. Res.* **2009**, *42*, 1983-1994; m) A. Cannizzo, A. M. Blanco-Rodríguez, A. El Nahhas, J. Sebera, S. Zális, A. Jr. Vlack, M. Chergui, *J. Am. Chem. Soc.* **2008**, *130*, 8967-8974; n) J. Rohacova, O. Ishitani, *Chem. Sci.* **2016**, DOI: 10.1039/C6SC01913G.
- [2] D. Tzalis, Y. Tor, *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 2666-2668.
- [3] a) C. Weetman, M. S. Hill, M. F. Mahon, *Polyhedron* **2016**, *103*, 115-120; b) S. D. Robertson, A. R. Kennedy, J. J. Liggat, R. E. Mulvey, *Chem. Commun.* **2015**, *51*, 5452-5455; c) Y. Naganawa, T. Namba, T. Aoyama, K. Shoji, H. Nishiyama, *Chem. Commun.* **2014**, *50*, 13224-13227; d) M. Schlosser, *Top. Heterocycl. Chem.* **2013**, *31*, 171-222; e) S. Jakobsen, M. Tilset, *Tetrahedron Lett.* **2011**, *52*, 3072-3074; f) O. Moudam, F. Ajamaa, A. Ekouaga, H. Mamlouk, U. Hahn, M. Holler, R. Welter and J. -F. Nierengarten, *Eur. J. Org. Chem.* **2007**, 417-419; g) W. Clegg, L.

- Dunbar, L. Horsburgh, R. E. Mulvey, *Angew. Chem. Int. Ed.* **1996**, *35*, 753-755; h) D. Barr, R. Snaith, R. E. Mulvey, D. Reed, *Polyhedron* **1988**, *7*, 665-668; i) T. Kauffmann, J. König, A. Woltermann, *Chem. Ber.* **1976**, *109*, 3864-3868; j) R. F. Francis, W. Davis, J. T. Wisener, *J. Org. Chem.* **1974**, *39*, 59-62; k) R. Levine, W. M. Kadunce, *Chem. Commun.* **1970**, 921-922; l) R. A. Abramovitch, B. Vig, *Can. J. Chem.* **1963**, *41*, 1961-1965.
- [4] a) S. Kundu, W. W. Brennessel, W. D. Jones, *Inorg. Chem.* **2011**, *50*, 9443-9453; b) J. Scott, S. Gambarotta, I. Korovkov, P. H. M. Budzelaar, *J. Am. Chem. Soc.* **2005**, *127*, 13019-13029; c) H. Sugiyama, G. Aharonian, S. Gambarotta, G. P. A. Yap, P. H. M. Budzelaar, *J. Am. Chem. Soc.* **2002**, *124*, 12268-12274; d) D. Reardon, F. Conan, S. Gambarotta, G. Yap, Q. Wang, *J. Am. Chem. Soc.* **1999**, *121*, 9318-9325.
- [5] a) C. Gunanathan, B. Gnanaprakasam, M. A. Iron, L. J. W. Shimon, D. Milstein, *J. Am. Chem. Soc.* **2010**, *132*, 14763-14765; b) K. L. Miller, B. N. Williams, D. Benitez, C. T. Carver, K. R. Ogilby, E. Tkatchouk, W. A. Goddard III, P. L. Diaconescu, *J. Am. Chem. Soc.* **2010**, *132*, 342-355; c) J. Cámpora, C. M. Pérez, A. Rodríguez-Delgado, A. M. Naz, P. Palma, E. Álvarez, *Organometallics* **2007**, *26*, 1104-1107; d) K. C. Jantunen, B. L. Scott, J. Hay, J. C. Gordon, J. L. Kiplinger, *J. Am. Chem. Soc.* **2006**, *128*, 6322-6323; e) X. Bei, D. C. Swenson, R. F. Jordan, *Organometallics* **1997**, *16*, 3282-3302; f) S. D. Gray, K. J. Weller, M. A. Bruck, P. M. Briggs, D. E. Wigley, *J. Am. Chem. Soc.* **1995**, *117*, 10678-10693; g) K. J. Weller, S. D. Gray, P. M. Briggs, D. E. Wigley, *Organometallics* **1995**, *14*, 5588-5597; h) P. Berno, S. Gambarotta, *Organometallics* **1994**, *13*, 2569-2571; i) L. M. Kobriger, A. K. McMullen, P. E. Fanwick, I. P. Rothwell, *Polyhedron* **1989**, *8*, 77-81.
- [6] E. C. Constable, *Polyhedron* **2016**, *103*, 295-306.
- [7] a) R. Arévalo, J. Pérez, L. Riera, *Chem. Eur. J.* **2015**, *21*, 3546-3549; b) R. Arévalo, J. Pérez, L. Riera, *Inorg. Chem.* **2013**, *52*, 6785-6787; c) M. A. Huertos, J. Pérez, L. Riera, *J. Am. Chem. Soc.* **2008**, *130*, 5662-5663; d) L. Cuesta, E. Hevia, D. Morales, J. Pérez, V. Riera, M. Seitz, D. Miguel, *Organometallics* **2005**, *24*, 1772-1775; e) L. Cuesta, E. Hevia, D. Morales, J. Pérez, V. Riera, E. Rodríguez, D. Miguel, *Chem. Commun.* **2005**, 116-117.
- [8] E. Hevia, J. Pérez, V. Riera, D. Miguel, *Organometallics* **2002**, *21*, 1966-1974.
- [9] The **3M**, **3m** mixture is stable for 6 hours in THF- d_6 below 233 K (it can be stored overnight in toluene at 253 K). At room temperature, it produces **2** in 20 minutes in THF (or in 12 hours in toluene). The **3M**:**3m** ratio was found to remain constant during the evolution towards **2**.
- [10] C. K. McGill, A. Rappa, *Adv. Heterocycl. Chem.* **1988**, *44*, 1-79.
- [11] P. S. Fier, J. S. Hartwig, *Science* **2013**, *342*, 956-960.
- [12] C. S. Jr. Johnson, *Prog. Nucl. Magn. Reson. Spectrosc.* **1999**, *34*, 203-256.
- [13] K. Blaziak, W. Danikiewicz, M. Makosza, *J. Am. Chem. Soc.* **2016**, DOI: 10.1021/jacs.5b13365.
- [14] K. G. Caulton, *New J. Chem.* **1994**, *18*, 25-41.
- [15] Phen-bonded methyl group ^1H NMR integration against C_6Me_6 as internal standard afforded $t_{1/2}$ of 1 h and 10 h and 40 min for **4m-C2** and **4m-C4** respectively. $t_{1/2}$ of **4M-C2** and **4M-C4** were found to be longer than 3 days, with a faster disappearance of the **4M-C4** methyl signal (in comparison with **4M-C2**).
- [16] A. T. Balaban, D. C. Oniciu, A. R. Katrizky, *Chem. Rev.* **2004**, *104*, 2777-2812.
- [17] D. R. Armstrong, C. M. M. Harris, A. R. Kennedy, J. J. Liggat, R. McLellan, R. E. Mulvey, M. D. T. Urquhart, S. D. Robertson, *Chem. Eur. J.* **2015**, *21*, 14410-14420.
- [18] W. Kaim, *Acc. Chem. Res.* **1985**, *18*, 160-166.
- [19] Compound **1** does not react with 3,4,7,8-tetramethyl-1,10-phenanthroline (Me_4phen) over 2 days at room temperature, nor does $[\text{Re}(\text{CO})_3(\text{Me}_4\text{phen})(\text{PMe}_3)]\text{OTf}$ with phen (see Figures S6-S9) demonstrating that the phen ligands are non-labile.
- [20] P. H. M. Budzelaar, *Eur. J. Inorg. Chem.* **2012**, 530-534.
- [21] P. A. Lay, *Inorg. Chem.* **1984**, *23*, 4775-4777.
- [22] a) M. Nakamura, E. Nakamura, N. Koga, K. Morokuma, *J. Am. Chem. Soc.* **1993**, *115*, 11016-11017. In toluene-diethylether, in which we carried out the reaction, MeLi exists predominantly as tetramer: b) S. Desjardins, K. Flinois, H. Oulyadi, D. Davoust, C. Giessner-Prettre, O. Parisel, J. Maddaluno, *Organometallics* **2003**, *22*, 4090-4097. However, to keep the system manageable we employed the dimer in our calculations.
- [23] Bulky secondary amides, such as $\text{KN}(\text{SiMe}_3)_2$, are usually considered non-nucleophilic due to their bulkiness, see: R. E. Mulvey, S. D. Robertson, *Angew. Chem. Int. Ed.* **2013**, *52*, 11470-11487. Examples of nucleophilic behavior of $\text{KN}(\text{SiMe}_3)_2$, like the one reported here, are rare.
- [24] Since the addition does not proceed via initial attack to Re followed by a Re-to-pyridine migration, intermolecular direct attack to the pyridine seems the most plausible pathway. However, as noticed by one reviewer, we are not excluding possibilities such as initial addition to one of the CO ligands.
- [25] K. G. Caulton, *Eur. J. Inorg. Chem.* **2012**, 435-443.

Entry for the Table of Contents

Layout 1:

COMMUNICATION

Coordinated 1,10-phenanthroline: An excellent electrophile.

Coordinated 1,10-phenanthroline (phen) is usually considered a very inert ligand. However, phen in $[\text{Re}(\text{phen})(\text{CO})_3(\text{PMe}_3)]\text{OTf}$ (**1**) undergoes the nucleophilic addition of internal (the deprotonated trimethylphosphane ligand (**2**)) and external ($\text{KN}(\text{SiMe}_3)_2$ (**3M**, **3m**) and MeLi (**4M-C2**)) nucleophiles under mild conditions.

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