Double Activation of an *N*-alkylimidazole

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Despite the extensive coordination chemistry of imidazoles, metal-mediated imidazole activation is very rare.^[1] It has been shown that deprotonation of the central C-H group of coordinated *N*-alkylimidazoles can serve, after reaction of the resulting imidazolyl intermediate with an electrophile, as a new synthetic route to *N*-heterocyclic carbene (NHC) complexes.^[2,3] NHC ligands, which attract much ongoing interest, have been compared to tertiary phosphanes, although it has been shown that NHCs can participate in C-H or C-C activation of *N*-alkyl or *N*-aryl substituents,^[4] and, occasionally, adopt abnormal binding modes.^[5] We have found that the outcome of the deprotonation of coordinated *N*-alkylimidazoles dramatically depends on the nature of the imidazole substituent and the ancillary ligands, and in some examples C-C coupling products are obtained instead of NHC complexes.^[3a,b, 6] Even highly inert ligands, such as 2,2-bipyridine,^[6] or additional *N*-alkylimidazoles,^[3a,b] afforded C-C coupling products, presumably reflecting a high nucleophilic character of the deprotonated species. Here we report the extension of our studies to $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PR}_3)]\text{BAR}'_4$ (*N*-MeIm = *N*-methylimidazole; Ar' = 3,5-bis(trifluoromethyl)phenyl) compounds, showing that the nature of the phosphane substituents crucially determines the type of product. For the triphenylphosphane derivative, treatment with excess of base followed by MeOTf leads to an unprecedented double activation of the *N*-alkylimidazole ligand. The product, a binuclear complex, features a bridging ligand that is both an abnormal NHC and a Fischer carbene.

$[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PR}_3)]\text{BAR}'_4$ (R = Me, **1**; Ph **2**) compounds were prepared in good yields by substitution of the triflate ligand by the tertiary phosphane, assisted by the salt NaBAR'₄. Compounds **1** and **2** were spectroscopically characterized and the solid-state structure of **2** was determined by X-ray diffraction.^[7, 8]

The reaction of **1** with $\text{KN}(\text{SiMe}_3)_2$ in THF at -78 °C afforded immediately the deprotonation of the central C-H group of an *N*-MeIm ligand, as shown by a large shift to lower wavenumbers in the IR ν_{CO} bands (from 2034, 1938 and 1912 cm⁻¹ to 1999, 1899 and 1877 cm⁻¹). The NMR data in solution are in accordance with the formation of the imidazol-2-yl complex **1a**^[7] as a result of changing the coordination mode of the heterocyclic ligand (from *N*- to C- rhenium bonded) upon deprotonation (Scheme 1). Imidazol-2-yl complexes are very reactive, and only in a few cases have been isolated.^[1d-f, 3]

Scheme 1. Reactivity of compound **1**.

Compound **1a** was methylated at the non-substituted nitrogen to afford the NHC complex **1b** (see Scheme 1). The IR (ν_{CO} bands at 2028, 1935 and 1914 cm⁻¹) and NMR spectra showed the formation of a cationic species and the formation of an NHC ligand. The ¹³C NMR spectrum shows three signals for the CO ligands, reflecting the lack of symmetry, and a low intensity doublet at 174.6 ppm characteristic of the carbene carbon bonded to the Re atom and coupled to the *cis*-phosphane ligand (J_{CP} = 11.2 Hz). The solid state structure of **1b** (Figure 1), determined by X-ray diffraction,^[9] confirmed the formation of the NHC ligand, and a Re-C2 bond distance (2.198(4) Å) similar to those found for previously reported Re^I-NHC complexes.^[3, 10]

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Figure 1. Molecular structure of the cation of **1b**.

The reaction of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PPh}_3)]\text{BAR}'_4$ (**2**) with the equimolar amount of $\text{KN}(\text{SiMe}_3)_2$ in THF at -78°C led to a mixture of unreacted **2** and a new species in a 1:1 ratio. The deprotonation of **2** with the potassium amide in a 1:2 stoichiometry afforded the new species mentioned above, which was too unstable to be isolated. Addition of MeOTf (excess) to the reactant mixture allowed the isolation of crystals of compound **2b** (see Scheme 2). An X-ray structure determination showed that **2b** is a triflate salt of the cationic binuclear Re^I complex which molecular structure is showed in Figure 2.^[11]

Figure 2. Molecular structure of the cation of **2b**.

Two different rhenium fragments are bridged by an imidazole ligand that has undergone a double activation.^[12] The central carbon of an *N*-MeIm ligand, once deprotonated, has attacked the carbon atom of a *cis*-CO (C11), affording a four membered metallacycle. A similar coupling between a CO ligand and a C-deprotonated, *N*-coordinated *N*-alkylimidazole has been recently located as an intermediate in the reaction profile transforming an *N*-imidazolyl complex into the more stable C-metal bonded tautomer (imidazol-2-yl).^[13] The oxygen atom of the involved carbonyl (O11) has been methylated leading to the formation of a methoxycarbene ligand. The Re1-C11 bond distance, of 2.036(7) Å is close to those found for previously known Re^I hydroxy- or methoxycarbene complexes.^[14] Another deprotonation at the backbone of the same *N*-MeIm ligand afforded an abnormal NHC ligand bonded to the Re2 atom. In agreement with the higher σ -donor character of abnormal NHC ligands, the Re2-C5 bond distance (2.148(7) Å) is slightly shorter than normal NHC Re-C_{carbene} distances.^[3, 10] The coordination of the abnormal NHC ligand to Re2 forces the substitution of one carbonyl (C21-O21) which is involved in the formation of a new *N,N*-bidentate ligand by its formal coupling with a deprotonated *N*-MeIm and one *N*-MeIm ligands, both coordinated to the Re2 atom. The resulting unsaturated oxygen (O21) has been subsequently methylated affording a more stable product.

Scheme 2. Reactivity of compounds **2** and **3**.

In the deprotonation and subsequent methylation of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PPh}_3)]\text{BAR}'_4$ (**2**) a minor product, **2c**, was also isolated by crystallization.^[15] As shown in Figure 3, the cationic complex of **2c** consists of a *cis-trans*- $\{\text{Re}(\text{CO})_2(\text{PPh}_3)_2\}$ fragment bonded to a *N,N*-bidentate chelate. The latter results from trapping of CO (displaced by the second phosphane) by the two imidazole ligands through a C-C dehydrogenative coupling.

Figure 3. Molecular structure of the cation of **2c**.

Treatment of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PMePh}_2)]\text{BAR}'_4$ (**3**) with a twofold excess of $\text{KN}(\text{SiMe}_3)_2$ and MeOTf showed the same reactivity pattern as that found for **2** leading to the formation of **3b** and **3c**, analogous to **2b** and **2c** respectively (see Supporting Information for full experimental details and for the X-ray structure of **3b**).^[16]

The complex rearrangements involved in the formation of the binuclear compounds **2b** and **3b**, virtually instantaneous at low temperature, prompted us to try to isolate an intermediate by using a different basic reagent. The addition of the equimolar amount of *n*BuLi to a solution of compound **2** in THF at -78°C , afforded an imidazolyl complex. The formation of a neutral complex was clearly evidenced by the ν_{CO} bands in the IR spectrum (a *fac*- $\{\text{Re}(\text{CO})_3\}$ pattern at 2004, 1906 and 1882 cm^{-1}). This species, because of its high instability, was reacted with HOTf to afford the NH-NHC complex **2d**, which was fully characterized including the solid-state structure determined by X-ray diffraction (Figure 4).^[17]

Strong reactivity differences depending on the base used for imidazolium salts deprotonation have been previously noted.^[18] On the basis of these previous observations the large difference of reactivity found in our case could be due to a stabilization of the carbene-alkaline-metal adduct when the lithium base is used.

Figure 4. Molecular structure of the cation of **2d**.

In summary we have studied the deprotonation reactions of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PR}_3)]\text{BAR}'_4$ (**1-3**) compounds showing that the substituent of the phosphane ligand is crucial to determine the reactivity pattern. For PMe_3 complex **1**, the product is an imidazol-2-yl complex that, after methylation, leads to an NHC derivative. In contrast, for arylphosphane compounds **2** and **3**, an *N*-methylimidazole is doubly activated affording binuclear $\text{Re}^{\text{I}}\text{-Re}^{\text{I}}$ complexes. These unexpected products display several interesting features: an abnormal NHC ligand bonded to Re (for the first time generated by deprotonation of a coordinated imidazole), the formation of a Fischer carbene by CO activation, and the substitution of a CO group which is involved in an intramolecular ligand coupling. Preliminary studies suggest that the base can be non-innocent, and that the choice of the alkaline cation could play a role in determining the nature of the product.

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- [1] a) R. J. Sunberg, R. F. Bryan, I. F. Taylor Jr. H. Taube, *J. Am. Chem. Soc.* **1974**, *96*, 381-392; b) K. L. Tan, R. G. Bergman, J. A. Ellman, *J. Am. Chem. Soc.* **2002**, *124*, 3202-3203; c) J. C. Lewis, S. H. Wiedemann, R. G. Bergman, J. A. Ellman, *Org. Lett.* **2004**, *6*, 35-38; d) V. Miranda-Soto, D. B. Grotjahn, A. G. DiPasquale, A. L. Rheingold, *J. Am. Chem. Soc.* **2008**, *130*, 13200-13201; e) K. Araki, S. Kuwata, T. Ikariya, *Organometallics* **2008**, *27*, 2176-2178; f) V. Miranda-Soto, D. B. Grotjahn, A. L. Cooksy, J. M. A. Golen, C. E. Moore, A. L. Rheingold, *Angew. Chem.* **2011**, *123*, 657-661; *Angew. Chem. Int. Ed.* **2011**, *50*, 631-635.
- [2] J. Ruiz, B. F. Perandones, *J. Am. Chem. Soc.* **2007**, *129*, 9298-9299.
- [3] a) M. A. Huertos, J. Pérez, L. Riera, A. Menéndez-Velázquez, *J. Am. Chem. Soc.* **2008**, *130*, 13530-13531; b) M. A. Huertos, J. Pérez, L. Riera, J. Díaz, R. López, *Chem. Eur. J.* **2010**, *16*, 8495-8507; c) M. A. Huertos, J. Pérez, L. Riera, J. Díaz, R. López, *Angew. Chem.* **2010**, *122*, 6553-6556; *Angew. Chem. Int. Ed.* **2010**, *49*, 6409-6412.
- [4] a) R. F. R. Jazzar, S. A. Macgregor, M. F. Mahon, S. P. Richards, M. K. Whittlesey, *J. Am. Chem. Soc.* **2002**, *124*, 4944-4945; b) N. M. Scott, R. Dorta, E. D. Stevens, A. Correa, L. Cavallo, S. P. Nolan, *J. Am. Chem. Soc.* **2005**, *127*, 3516-3526; c) B. R. Galan, M. Gembicky, P. M. Dominiak, J. B. Keister, S. T. Diver, *J. Am. Chem. Soc.* **2005**, *127*, 15702-15703; d) L. N. Applehans, D. Zuccaccia, A. Kovacevic, A. R. Chianese, J. R. Miecznikowski, A. Macchioni, E. Clot, O. Eisenstein, R. H. Crabtree, *J. Am. Chem. Soc.* **2005**, *127*, 16299-16311; e) E. Becker, V. Stingl, G. Dazinger, M. Puchberger, K. Mereiter, K. Kirchner, *J. Am. Chem. Soc.* **2006**, *128*, 6572-6573; f) S. Burling, M. F. Mahon, R. E. Powell, M. K. Whittlesey, J. M. J. Williams, *J. Am. Chem. Soc.* **2006**, *128*, 13702-13703; g) S. H. Hong, A. Chlenov, M. W. Day, R. H. Grubbs, *Angew. Chem.* **2007**, *119*, 5240-5243; *Angew. Chem. Int. Ed.* **2007**, *46*, 5148-5151; h) K. Vehlouw, S. Gessler, S. Bleichert, *Angew. Chem.* **2007**, *119*, 8228-8231; *Angew. Chem. Int. Ed.* **2007**, *46*, 8082-8085; i) C. E. Cooke, M. C. Jennings, R. K. Pomeroy, J. A. C. Clyburne, *Organometallics* **2007**, *26*, 6059-6062; j) B. R. Galan, M. Pitak, M. Gembicky, J. B. Keister, S. T. Diver, *J. Am. Chem. Soc.* **2009**, *131*, 6822-6832.
- [5] a) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.* **2007**, *251*, 596-609; b) O. Schuster, L. Yang, H. G. Rabenheimer, M. Albrecht, *Chem. Rev.* **2009**, *109*, 3445-3478.
- [6] M. A. Huertos, J. Pérez, L. Riera, *J. Am. Chem. Soc.* **2008**, *130*, 5662-5663.
- [7] See Supporting Information.
- [8] CCDC 831342 (**1b**), 831343 (**2**), 831344 (**2b**), 831345 (**2c**), 831346 (**2d**) and 831347 (**3b**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [9] Selected crystallographic data for **1b**: $\text{C}_{16}\text{H}_{23}\text{F}_3\text{N}_4\text{O}_6\text{PREs}$, $M = 673.61$, triclinic, $P-1$, $a = 8.9655(4)$ Å, $b = 11.7102(4)$ Å, $c = 12.3789(5)$ Å, $\alpha = 105.885(2)^\circ$, $\beta = 100.370(3)^\circ$, $\gamma = 104.814(2)^\circ$, $150.0(2)$ K, $V = 1163.96(9)$ Å³, $Z = 2$, 35464 reflections measured, 4761 independent ($R_{\text{int}} = 0.0386$). $R_1 = 0.0266$, $wR_2 = 0.0640$ (all data).
- [10] a) C. Y. Liu, D. Y. Chen, G. H. Lee, G. H.; S. M. Peng, S. T. Liu, *Organometallics* **1996**, *15*, 1055-1061; b) W.-M. Xue, M. C.-W. Chan, Z.-M. Su, K.-K. Cheung, S.-T. Liu, C.-M. Che, *Organometallics* **1998**, *17*, 1622-1630; c) O. Kaufhold, A. Stasch, P. G. Edwards, F. E. Hahn, *Chem. Commun.* **2007**, 1822-1824; d) O. Hiltner, E. Herrdtweck, M. Drees, W. A. Herrmann, F. E. Kühn, *Eur. J. Inorg. Chem.* **2009**, 1825-1831; e) O. Kaufhold, A. Stasch, T. Pape, A. Hepp, P. G. Edwards, P. D. Newman, F. E. Hahn, *J. Am. Chem. Soc.* **2009**, *131*, 306-317; f) T. A. Martin, C. E. Ellul, M. F. Mahon, M. E. Warren, D. Allan, M. K. Whittlesey, *Organometallics* **2011**, *30*, 2200-2211.
- [11] Selected crystallographic data for **2b**: $\text{C}_{30}\text{H}_{72}\text{BCl}_4\text{F}_{24}\text{N}_8\text{O}_6\text{P}_2\text{Re}_2$, $M = 2452.55$, triclinic, $P-1$, $a = 11.8058(2)$ Å, $b = 18.9552(4)$ Å, $c = 22.3487(3)$ Å, $\alpha = 82.549(2)^\circ$, $\beta = 79.672(2)^\circ$, $\gamma = 84.678(2)^\circ$, $293(2)$ K, $V = 4866.2(1)$ Å³, $Z = 2$, 41399 reflections measured, 17883 independent ($R_{\text{int}} = 0.0335$). $R_1 = 0.0455$, $wR_2 = 0.1494$ (all data).
- [12] No double activation of *N*-alkylimidazole ligands has been previously reported. There are a few examples of doubly activated imidazolium salts, see: a) P. L. Arnold, M. Rodden, C. Wilson, *Chem. Commun.* **2005**, 1743-1745; b) P. L. Arnold, S. T. Liddle, *Organometallics* **2006**, *25*, 1485-1491; c) C. E. Ellul, M. F. Mahon, O. Saker, M. K. Whittlesey, *Angew. Chem.* **2007**, *119*, 6459-6461; *Angew. Chem. Int. Ed.* **2007**, *46*, 6343-6345; d) A. A. Danopoulos, D. Pugh, J. A. Wright, *Angew. Chem. Int. Ed.* **2008**, *47*, 9911-9913; *Angew. Chem. Int. Ed.* **2008**, *47*, 9765-9767; e) U. J. Scheele, S. Dechert, F. Meyer, *Chem. Eur. J.* **2008**, *14*, 5112-5115; f) Y. Wang, Y. Xie, M. Y. Abraham, P. Wei, H. F. Schaefer III, P. v. R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2010**, *132*, 14370-14372.
- [13] a) J. Ruiz, B. F. Perandones, J. F. Van der Maelen, S. García-Granda, *Organometallics* **2010**, *29*, 4639-4642; b) M. Brill, J. Díaz, M. A. Huertos, R. López, J. Pérez, L. Riera, *Chem. Eur. J.* **2011**, *17*, 8584-8595; c) A nucleophilic attack of an NHC onto a metal carbonyl has been reported, but in that case the result was an acyl ligand: A. Wacker, C. G. Yan, G. Kaltenpoth, A. Ginsberg, A. M. Arif, R. D. Ernst, H. Pritzkow, W. Siebert, *J. Organomet. Chem.* **2002**, *641*, 195-202.
- [14] See for example: a) C. Bianchini, N. Mantovani, A. Marchi, L. Marvelli, D. Masi, M. Peruzzini, R. Rossi, A. Romerosa, *Organometallics* **1999**, *18*, 4501-4508; b) E. Hevia, J. Pérez, V. Riera, D. Miguel, *Organometallics* **2003**, *22*, 257-263.
- [15] Selected crystallographic data for **2c**: $\text{C}_{79}\text{H}_{52}\text{BF}_{24}\text{N}_4\text{O}_3\text{P}_2\text{Re}$, $M = 1820.2$, monoclinic, $P2_1/n$, $a = 11.6507(1)$ Å, $b = 18.8112(2)$ Å, $c = 36.5114(5)$ Å, $\alpha = 90^\circ$, $\beta = 94.208(1)^\circ$, $\gamma = 90^\circ$, $150(2)$ K, $V = 7980.4(1)$ Å³, $Z = 4$, 38305 reflections measured, 15849 independent ($R_{\text{int}} = 0.044$). $R_1 = 0.0449$, $wR_2 = 0.1445$ (all data).
- [16] The combination of low solubility and limited stability in solution of **2b-c** and **3b-c** compounds precluded the acquisition of their ¹³C NMR spectra.
- [17] Selected crystallographic data for **2d**: $\text{C}_{61}\text{H}_{39}\text{BF}_{24}\text{N}_4\text{O}_3\text{PRE}$, $M = 1559.94$, triclinic, $P-1$, $a = 13.8092(3)$ Å, $b = 16.3315(3)$ Å, $c = 16.4347(3)$ Å, $\alpha = 111.156(2)^\circ$, $\beta = 105.166(2)^\circ$, $\gamma = 106.655(2)^\circ$, $100(2)$ K, $V = 3022.6(1)$ Å³, Z

= 2. 35287 reflections measured, 11948 independent ($R_{\text{int}} = 0.0236$). $R_1 = 0.0362$, $wR_2 = 0.0909$ (all data).

- [18] a) G. Guisado-Barrios, J. Bouffard, B. Donnadiu, G. Bertrand, *Angew. Chem.* **2010**, *122*, 4869-4872; *Angew. Chem. Int. Ed.* **2010**, *49*, 4759-4762; b) E. Aldeco-Pérez, A. J. Rosenthal, B. Donnadiu, P. Parameswaran, G. Frenking, G. Bertrand, *Science*, **2009**, *326*, 556-559; c) V. Lavallo, C. A. Dyker, B. Donnadiu, G. Bertrand, *Angew. Chem.* **2008**, *120*, 5491-549; *Angew. Chem. Int. Ed.* **2008**, *47*, 5411-5414; d) V. Lavallo, Y. Ishida, B. Donnadiu, G. Bertrand, *Angew. Chem.* **2006**, *118*, 6804-6807; *Angew. Chem. Int. Ed.* **2006**, *45*, 6652-6655; e) V. Lavallo, Y. Canac, B. Donnadiu, W. W. Schoeller, G. Bertrand, *Science* **2006**, *312*, 722-724; f) D. : Khramov, A. J. Boydston, C. W. Bielawski, *Angew. Chem.* **2006**, *118*, 6332-6335; *Angew.*
-

Chem. Int. Ed. **2006**, *45*, 6186-6189. g) R. W. Alder, M. E. Blake, L. Chaker, J. N. Harvey, F. Paolini, J. Schütz, *Angew. Chem.* **2004**, *116*, 6020-6036; *Angew. Chem. Int. Ed.* **2004**, *43*, 5896-5911.

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Imidazole activation: make it double! A coordinated *N*-methylimidazole has been transformed, by a double activation, in a bridging ligand that is simultaneously an abnormal NHC and a Fischer carbene.

Double Activation of an N-Alkylimidazole

Miguel A. Huertos, Julio Pérez and Lucía Riera

Supporting Information

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Experimental Section

All manipulations were performed under an inert atmosphere of nitrogen by using standard Schlenk techniques. Dry, oxygen-free solvents were employed. ^1H and ^{13}C NMR spectra were recorded on Bruker Avance 400 and DPX 300 spectrometers. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer. Compounds $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$,^[1] and NaBAR'_4 ^[2] were prepared following the reported procedures.

Labelling scheme for BAR'_4 :

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PMe}_3)]\text{BAR}'_4$ (1). A solution of $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (60 mg, 0.10 mmol), NaBAR'_4 (89 mg, 0.10 mmol) and PMe_3 (9 μL , 0.10 mmol) in CH_2Cl_2 (20 mL) was stirred at room temperature for 1 h. The reaction mixture was filtered via canula and the solvent was evaporated under reduced pressure. Compound **1** was obtained as a white microcrystalline solid that was washed with hexane (2 $\times$ 15 mL). Yield: 106 mg (77 %). IR (CH_2Cl_2 , cm^{-1}): 2034, 1928, 1912 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 7.94 (s, 8H, H_o BAR'_4), 7.62 (s, 2H, NCHN N-MeIm), 7.59 (s, 4H, H_p BAR'_4), 7.00 (m, 2H, CH N-MeIm), 6.79 (m, 2H, CH N-MeIm), 3.74 (s, 6H, CH_3 N-MeIm), 1.43 (d (J = 8.5 Hz) 9H, CH_3 PMe_3). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 193.3 (2CO), 190.3 (d (J_{CP} = 67.7 Hz) CO), 141.9 (NCHN N-MeIm), 131.8 (CH N-MeIm), 122.9 (CH N-MeIm), 161.8 (q (J = 49.9 Hz), C_i BAR'_4), 134.8 (C_o BAR'_4), 128.8 (q (J = 34.5 Hz), C_m BAR'_4), 124.6 (q (J = 272.3 Hz), CF_3), 117.5 (C_p BAR'_4), 34.6 (CH_3 N-MeIm), 15.3 (d (J_{CP} = 30.5 Hz), PMe_3). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 32.2. Anal. Calcd. for $\text{C}_{46}\text{H}_{33}\text{BF}_{24}\text{N}_4\text{O}_3\text{PRe}$: C 40.22, H 2.42, N 4.08. Found: C 40.58, H 2.65, N 3.96.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PPh}_3)]\text{BAR}'_4$ (2). Compound **2** was prepared as described above for **1** starting from $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (60 mg, 0.10 mmol), NaBAR'_4 (89 mg, 0.10 mmol) and PPh_3 (26 mg, 0.10 mmol). Yield: 126 mg (81 %). IR (CH_2Cl_2 , cm^{-1}): 2036, 1943, 1914 (ν_{CO}). ^1H NMR (CD_2Cl_2): δ 7.74 (s, 8H, H_o BAR'_4), 7.59 (s, 4H, H_p BAR'_4), 7.42 (m, 15H, PPh_3), 6.85 (s, 2H, NCHN N-MeIm), 6.78 (s, 2H, CH N-MeIm), 6.67 (s, 2H, CH N-MeIm), 3.49 (s, 6H, CH_3 N-MeIm). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 194.0 (2CO), 190.2 (CO), 142.2, 135.2, 133.8, 133.7, 130.5, 130.4, 119.5 (PPh_3 and N-MeIm), 161.8 (q (J = 49.9 Hz), C_i BAR'_4), 134.8 (C_o BAR'_4), 128.8 (q (J = 34.5 Hz), C_m BAR'_4), 124.6 (q (J = 272.3 Hz), CF_3), 117.5 (C_p BAR'_4), 35.1 (CH_3 N-MeIm). $^{31}\text{P}\{^1\text{H}\}$ NMR (CD_2Cl_2): δ 19.9. Anal. Calcd. for $\text{C}_{61}\text{H}_{39}\text{BF}_{24}\text{N}_4\text{O}_3\text{PRe}$: C 46.97, H 2.52, N 3.59. Found: C 47.21, H 2.31, N 3.72.

Synthesis of $[\text{Re}(\text{CO})_3(\text{N-MeIm})_2(\text{PMePh}_2)]\text{BAR}'_4$ (3). Compound **3** was prepared as described above for **1** starting from $[\text{Re}(\text{OTf})(\text{CO})_3(\text{N-MeIm})_2]$ (60 mg, 0.10 mmol), NaBAR'_4 (89 mg, 0.10 mmol) and

PMePh₂ (19 μ L, 0.10 mmol). Yield: 139 mg (90 %). IR (CH₂Cl₂, cm⁻¹): 2031, 1936, 1911 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.74 (s, 8H, H_o BAr'₄), 7.60 (s, 4H, H_p BAr'₄), 7.41 (m, 10H, C₆H₅ PMePh₂), 7.06 (s, 2H, NCHN *N*-MeIm), 6.84 (s, 2H, CH *N*-MeIm), 6.67 (s, 2H, CH *N*-MeIm), 3.53 (s, 6H, CH₃ *N*-MeIm), 2.15 (d (J = 7.8 Hz), 3H, CH₃ PMePh₂). ³¹P {¹H} NMR (CD₂Cl₂): δ -0.9. Anal. Calcd. for C₅₆H₃₇BF₂₄N₄O₃PRe: C 44.90, H 2.49, N 3.74. Found: C 45.09, H 2.78, N 3.53.

Synthesis of 1a. KN(SiMe₃)₂ (0.17 mL of a 0.5 M solution in toluene, 0.09 mmol) was added to a solution of compound [Re(CO)₃(*N*-MeIm)₂(PMe₃)]BAr'₄ (**1**) (100 mg, 0.07 mmol) in THF (20 mL) at -78 °C. The solution was allowed to reach room temperature, and the resulting yellow solution was evaporated under vacuum. The residue was redissolved in CH₂Cl₂ (20 mL), filtered via canula and the solvent was evaporated under reduced pressure to a volume of 5 mL. Addition of hexane caused the precipitation of compound **2a** as a pale yellow solid, which was washed with hexane (2 $\times$ 15 mL) and dried under vacuum. Yield: 27 mg (73 %). IR (CH₂Cl₂, cm⁻¹): 1999, 1899, 1877 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.63 (s, 1H, NCHN *N*-MeIm), 7.29 (s, 1H, CH *N*-MeIm), 6.96 (s_{br}, 2H, 2 $\times$ CH imidazol-2-yl), 6.83 (s, 1H, CH *N*-MeIm), 3.80 (s, 3H, CH₃), 3.62 (s, 3H, CH₃), 1.34 (d (J = 6.9 Hz), 9H, CH₃ PMe₃). ¹³C {¹H} NMR (CD₂Cl₂): δ 197.6 (d (J_{CP} = 8.4 Hz), CO), 196.4 (d (J_{CP} = 6.9 Hz), CO), 196.3 (d (J_{CP} = 108.1 Hz), CO), 171.9 (d (J_{CP} = 13.6 Hz), Re-C), 143.2, 134.3, 121.6, 120.9, 120.6 (*N*-MeIm and imidazol-2-yl), 30.1, 34.4 (CH₃), 15.5 (d (J_{CP} = 29.9 Hz), CH₃ PMe₃). ³¹P NMR {¹H} (CD₂Cl₂): δ -29.7. Anal. Calcd for C₁₄H₂₀N₄O₃PRe: C 33.00, H 3.96, N 10.99. Found: C 33.23, H 4.09, N 11.08.

Synthesis of 1b. MeOTf (11 μ L, 0.10 mmol) was added to a solution of compound **1a** (50 mg, 0.10 mmol) in CH₂Cl₂ (20 mL), and the reaction mixture was stirred at room temperature for 5 min. The solvent was evaporated under reduced pressure to a volume of 5 mL and addition of hexane (20 mL) caused the precipitation of a yellow solid, which was washed with hexane (2 $\times$ 20 mL) and dried under vacuum. Slow diffusion of hexane (20 mL) into a concentrated solution of **1b** in CH₂Cl₂ at -20 °C afforded yellow crystals, one of which was employed for an X-ray determination. Yield: 49 mg (74 %). IR (CH₂Cl₂, cm⁻¹): 2028, 1935, 1914 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.80 (s, 1H, NCHN *N*-MeIm), 7.17 (s_{br}, 2H, 2 $\times$ CH NHC), 7.10 (s, 1H, CH *N*-MeIm), 6.88 (s, 1H, CH *N*-MeIm), 3.87 (s, 3H, CH₃ *N*-MeIm), 3.61 (s, 6H, CH₃ NHC), 1.53 (d (J = 8.1 Hz), 9H, CH₃ PMe₃). ¹³C {¹H} NMR (CD₂Cl₂): δ 193.8 (d (J_{CP} = 7.5 Hz), CO), 193.0 (d (J_{CP} = 8.9 Hz), CO), 190.7 (d (J_{CP} = 60.3 Hz), CO), 174.6 (d (J_{CP} = 11.2 Hz), Re-C), 143.0, 133.2, 124.1, 123.7, 120.9 (*N*-MeIm and NHC), 39.5 (s, 2 $\times$ CH₃ NHC), 34.4 (CH₃ *N*-MeIm), 34.8 (d (J_{CP} = 30.4 Hz), CH₃ PMe₃). ³¹P {¹H} NMR (CD₂Cl₂): δ -36.8. Anal. Calcd. for C₁₆H₂₃F₃N₄O₆PSRe: C 28.53, H 3.44, N 8.32. Found: C 28.59, H 3.62, N 8.06.

Synthesis of 2b. KN(SiMe₃)₂ (0.60 mL of a 0.5 M solution in toluene, 0.30 mmol) was added to a solution of [Re(CO)₃(*N*-MeIm)₂(PPh₃)]BAR'₄ (**2**) (200 mg, 0.12 mmol) in THF (20 mL) previously cooled to -78 °C. The color of the solution changed immediately from colorless to red, and the solvent was evaporated to dryness. The residue was redissolved in CH₂Cl₂ (20 mL), MeOTf (28 μL, 0.26 mmol) was added and the mixture was allowed to stir at room temperature for 15 min. The resulting red solution was filtered via canula and the solvent was evaporated under reduced pressure to a volume of 5 mL. Slow diffusion of hexane (20 mL) at -20 °C afforded red crystals, one of which was employed for an X-ray determination. Yield: 63 mg (43 %). IR (CH₂Cl₂, cm⁻¹): 1929, 1907, 1844, 1835 (ν_{CO}) ¹H NMR (CD₂Cl₂): δ 7.76 (s, 8H, H_o BAR'₄), 7.60 (s, 4H, H_p BAR'₄), 7.21 (m, 30H, PPh₃), 7.03 (s, 1H, CH), 6.99 (s, 1H, CH), 6.95 (s, 1H, CH), 6.92 (s, 1H, CH), 6.89 (s, 1H, CH), 6.77 (s, 1H, CH), 6.42 (s, 1H, CH), 5.49 (s, 1H, CH), 5.20 (s, 1H, CH), 4.52 (s, 3H, OCH₃), 4.03 (s, 3H, NCH₃), 3.80 (s, 3H, NCH₃), 3.60 (s, 3H, NCH₃), 3.32 (s, 3H, NCH₃), 2.47 (s, 3H, OCH₃). ³¹P{¹H} NMR (CD₂Cl₂): δ 30.3, 21.5. Anal. Calcd. for C₉₂H₆₉BF₂₄N₈O₆P₂Re₂: C 48.39, H 3.05, N 4.91. Found: C 49.01, H 3.18, N 4.96.

Synthesis of 2c. Compound **2c** was obtained as a minor product in the synthesis of compound **2b**. Slow diffusion of hexane into a concentrated solution of the mother liqueur that afforded **2b** at -20 °C afforded pale yellow crystals of **2c**. Repetition of the reaction of compound **2** with KN(SiMe₃)₂, and followed by MeOTf afforded both products **2b** and **2c** in approximately the same ratio. Yield: 12 mg (10 %). IR (CH₂Cl₂, cm⁻¹): 1936, 1865 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.74 (s, 8H, H_o BAR'₄), 7.57 (s, 4H, H_p BAR'₄), 7.25 (m, 30H, 2PPh₃), 6.85 (s, 2H, CH) 6.65 (s, 2H, CH), 3.85 (s, 6H, NCH₃) ³¹P{¹H}NMR (CD₂Cl₂): δ 20.5. Anal. Calcd. for C₇₉H₅₂BF₂₄N₄O₃P₂Re: C 52.13, H 2.88, N 3.08. Found: C 52.42, H 3.09, N 2.87.

Synthesis of 3b. Compound **3b** was prepared as described above for **2b** starting from [Re(CO)₃(*N*-MeIm)₂(PMePh₂)]BAR'₄ (**3**) (200 mg, 0.14 mmol), KN(SiMe₃)₂ (0.60 mL of a 0.5 M solution in toluene, 0.30 mmol) and MeOTf (30 μL, 0.26 mmol). Yield: 64 mg (46 %). IR (CH₂Cl₂, cm⁻¹): 1929, 1904, 1841, 1826 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.76 (s, 8H, H_o BAR'₄), 7.60 (s, 4H, H_p BAR'₄), 7.24 (m, 23H, PMePh₂ and 3 × CH), 7.06 (s, 1H, CH), 6.90 (s, 1H, CH), 6.58 (s, 1H, CH), 6.54 (s, 1H, CH), 5.95 (s, 1H, CH), 5.52 (s, 1H, CH), 4.46 (s, 3H, OCH₃), 3.84 (s, 3H, NCH₃), 3.79 (s, 3H, NCH₃), 3.68 (s, 3H, NCH₃), 3.34 (s, 3H, NCH₃), 2.44 (s, 3H, OCH₃), 1.95 (d (*J*_{HP} = 7.3 Hz), 3H, CH₃ PMePh₂), 1.85 (d (*J*_{HP} = 6.9 Hz), 3H, CH₃ PMePh₂). ³¹P{¹H} NMR (CD₂Cl₂): δ 10.3, 4.2. Anal. Calcd. for C₈₂H₆₅BF₂₄N₈O₆P₂Re₂: C 45.60, H 3.03, N 5.19. Found: C 45.45, H 3.33, N 4.98.

Synthesis of 3c. Compound **3c** was obtained in the same way as it has been described for **2c**. **3c** was obtained as pale yellow crystals. Yield: 12 mg (11 %). IR (CH₂Cl₂, cm⁻¹): 1932, 1855 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 7.74 (s, 8H, H_o BAR'₄), 7.57 (s, 4H, H_p BAR'₄), 7.22 (m, 20H, PMePh₂), 7.06 (s, 2H, CH) 6.70 (s, 2H, CH), 3.91 (s, 6H, NCH₃), 1.90 (s_{br}, 6H, CH₃ PMePh₂). ³¹P{¹H}NMR (CD₂Cl₂): δ 12.8. Anal. Calcd. for C₆₉H₄₈BF₂₄N₄O₃P₂Re: C 48.86, H 2.85, N 3.30. Found: C 48.56, H 3.04, N 3.13.

Synthesis of 2d. *n*BuLi (40 μ L of a 1.6 M solution in hexane, 0.06 mmol) was added to a solution of compound [Re(CO)₃(*N*-MeIm)₂(PPh₃)]BAr'₄ (**2**) (100 mg, 0.06 mmol) in THF (20 mL) at -78 °C. The reaction mixture was allowed to reach room temperature and then the solvent was evaporated to dryness. The residue was extracted with toluene (20 mL), HOTf was added, and the reaction was stirred for 30 min. The solvent was concentrated under vacuum to a volume of 5 mL and slow diffusion of hexane (15 mL) at -20 °C afforded yellow crystals of **2d**, one of which was employed for an X-ray structure determination. Yield: 49 mg (74 %). IR (CH₂Cl₂, cm⁻¹): 2031, 1943, 1917 (ν_{CO}). ¹H NMR (CD₂Cl₂): δ 8.59 (s_{br}, *NH* NHC), 7.74 (s, 8H, H_o BAr'₄), 7.60 (s, 4H, H_p BAr'₄), 7.39 (m, 15H, PPh₃) 6.98, 6.94, 6.85, 6.77, 6.68 (s, 1H each, *NCHN* and *CH N*-MeIm and NHC), 3.87, 3.61 (s, 3H each, *CH*₃ *N*-MeIm and NHC). ¹³C{¹H} NMR (CD₂Cl₂): δ 194.2 (d (J_{CP} = 7.4 Hz), CO), 193.0 (d (J_{CP} = 7.9 Hz), CO), 190.2 (d (J_{CP} = 60.0 Hz), CO), 172.0 (d (J_{CP} = 10.1 Hz), Re-C), 161.8 (q (J = 49.9 Hz), C_i BAr'₄), 134.8 (C_o BAr'₄), 128.8 (q (J = 34.5 Hz), C_m BAr'₄), 124.6 (q (J = 272.3 Hz), CF₃), 117.5 (C_p BAr'₄), 143.4, 133.8, 131.4, 129.5, 124.0 (*N*-MeIm and NHC), 39.0, 35.1 (*CH*₃ *N*-MeIm and NHC). ³¹P {¹H} NMR (CD₂Cl₂): δ 14.6. Anal. Calcd. for C₆₁H₃₉BF₂₄N₄O₃PRe: C 46.97, H 2.52, N 3.59. Found: C 47.34, H 2.66, N 3.43.

Crystal Structure Determination.

For Compounds 2b, 2c, and 2b. Data collection was performed at 150(2) K (for **2b**) or 100(2) K (for **2c** and **2d**) on a Oxford Diffraction Xcalibur Nova single crystal diffractometer, using Cu-K α radiation (λ = 1.5418 Å). Images were collected at a 65 mm fixed crystal-detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (4-16 s). Data collection strategy was calculated with the program CrysAlis^{Pro} CCD.³ Data reduction and cell refinement was performed with the program CrysAlis^{Pro} RED.³ An empirical absorption correction was applied using the SCALE3 ABSPACK.³

For Compounds 2 and 3b. Data collection was performed at 150(2) K on a Nonius KappaCCD single crystal diffractometer, using Mo-K α radiation (λ = 0.71073 Å). Images were collected at a 29 mm fixed crystal-detector distance, using the oscillation method, with 2° oscillation and 40 s exposure time per image. Data collection strategy was calculated with the program Collect.⁴ Data reduction and cell refinement were performed with the programs HKL Denzo and Scalepack.⁵ A semi-empirical absorption correction was applied using the program SORTAV.⁶

For compound 1b. Crystal data were collected on a Bruker APPEX II diffractometer using graphite-monochromated Mo K α radiation (λ = 0.71073 Å) from a fine-focus sealed tube source at 150 K. Computing data and reduction were made with the APPEX II software.⁷ In all cases empirical absorption corrections were applied using SADABS.⁸

Crystal structures were solved by direct methods, using the program SIR-92.⁹ Anisotropic least-squares refinement was carried out with SHELXL-97.¹⁰

Figure S1. Molecular Structure of the cation of compound 2.

Table S1. Selected bond distances (Å) and angles (°) of compound 2.

Selected Bond Distances (Å)			
Re1-C12	1.929(7)	N3-C5	1.37(1)
Re1-C13	1.960(7)	C5-N4	1.29(1)
Re1-C11	1.957(7)	N4-C7	1.35(1)
C11-O11	1.129(8)	C7-C6	1.410(1)
C12-O12	1.154(8)	C6-N3	1.37(1)
C13-O13	1.138(9)	N1-C1	1.42(1)
C18-C17	1.44(39)	N1-C2	1.40(1)
Re1-P1	2.499(2)	C1-N2	1.27(1)
Re1-N1	2.195(6)	N2-C3	1.41(2)
Re1-N3	2.231(6)	C3-C2	1.46(2)
Selected Bond Angles (°)			
O12-C12-Re1	177.2(6)	C13-Re1-P1	179.0(2)
O13-C13-Re1	179.2(7)	C11-Re1P1	89.8(2)
O11-C11-Re1	178.4(6)	N1-Re1-N3	87.8(3)

Figure S2. Molecular Structure of the cation of Compound 3b.

Table S2. Selected bond distances (Å) and angles (°) of compound 3b.

Selected Bond distances (Å)			
Re1-C11	2.070(14)	Re2-C20	1.861(16)
Re1-C12	1.900(14)	Re2-C23	1.856(13)
Re1-C13	1.908(14)	Re2-P2	2.415(3)
Re1-N1	2.287(9)	Re2-N22	2-213(9)
Re1-N2	2.240(12)	Re2-N21	2-196(10)
Re1-P1	2.427(3)	Re2-C5	2.169(11)
N1-C2	1.314(15)	C26-C21	1.465(19)
C4-N1	1.344(16)	C22-C21	1.479(18)
C2-C11	1.389(19)	C21-O21	1.423(16)
C11-O11	1.332(15)	O21-C10	1.402(16)
O11-C1	1.436(15)	N22-C27	1.323(17)
C2-N3	1.373(16)	C27-C28	1.352(17)
C5-C4	1.385(16)	C28-N24	1.375(8)
C5-N3	1.368(15)	N24-C26	1.346(16)
N21-C22	1.331(14)	C22-N23	1.386(16)
N23-C25	1.366(17)	C25-C24	1.356(18)
C24-N21	1.367(16)	C26-N22	1.330(15)
Selected Bond Angles (°)			
O11-C11-Re1	141.3(11)	C22-C21-C26	112.3(11)
C2-C11-Re1	97.9(8)	C22-C21-O21	105.4(10)
O11-C11-C2	120.7(13)	C26-C21-O21	114.7(12)

References

1. M. A. Huertos, J. Pérez, L. Riera, J. Díaz, R. López, *Angew. Chem. Int. Ed.* **2010**, *49*, 6409.
2. M. Brookhart, B. Grant, A. F. Volpe Jr., *Organometallics* **1992**, *11*, 3920.
3. *CrysAlis^{Pro} CCD, CrysAlis^{Pro} RED*. Oxford Diffraction Ltd., Abingdon, Oxfordshire, UK.
4. *Collect* data collection software. Bruker AXS, Delft, The Netherlands.
5. Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1997**, *276*, 307.
6. Blessing, R. H. *Acta Cryst.* **1995**, *A51*, 33.
7. *APPEX II*; Bruker AXS Inc.; Madison, WI, USA, 2004.
8. G. M. Sheldrick. *SHELX-97 (SHELXS 97 and SHELXL 97), Programs for Crystal Structure Analyses*; University of Göttingen: Göttingen (Germany), 1996.
9. A. Altomare, G. L. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori, M. Camalli, *J. Appl. Cryst.* **1994**, *27*, 435.
10. G. M. Sheldrick, *Acta Cryst.* **2008**, *A64*, 112.