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# Organometallic Complexes with Terminal Imidazolato Ligands and Their Use as Metalloligands

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Compounds [Re(bipy)(CO)$_3$(HIm)]OTf (**1**) and [Mo($\eta^3$-C$_3$H$_4$-R-2)(CO)$_2$(HIm)(phen)]BAr′$_4$ [R = Me (**2a**), H (**2b**); Ar′ = 3,5-bis(trifluoromethyl)phenyl; HIm = 1*H*-imidazole] were prepared from 1*H*-imidazole and either [Re(OTf)(bipy)(CO)$_3$] or [MoCl($\eta^3$-C$_3$H$_4$-R-2)(CO)$_2$(phen)]. Compounds **1**, **2a**, and **2b** were deprotonated to afford the terminal $\kappa$-*N*-imidazolate complexes [Re(bipy)(CO)$_3$(Im)] (**3**) and [Mo($\eta^3$-C$_3$H$_4$-R-2)(CO)$_2$(Im)(phen)] [R = Me (**4a**), H (**4b**)], which were fully characterized, including an X-ray structural determination of **3**. The topological analysis of the electron density (obtained from the X-ray diffraction study) and its Laplacian were used to characterize the differences in the electron density at the five-membered ring ligand between the imidazole and imidazolate complexes **1** and **3**. The reaction of complexes **3**, **4a**, and **4b** with the appropriate organometallic complexes afforded the bimetallic imidazolate-bridged compounds [{Re(bipy)(CO)$_3$}$_2$($\mu$-Im)]OTf (**5**), [{Mo($\eta^3$-C$_4$H$_7$)(CO)$_2$(phen)}$_2$($\mu$-Im)]OTf (**6**), and [{Mo($\eta^3$-C$_3$H$_5$)(CO)$_2$(phen)}($\mu$-Im){Re(phen)(CO)$_3$}]OTf (**7**). The reaction of [Mo($\eta^3$-C$_4$H$_7$)(CO)$_2$(Im)(phen)] (**4a**) with SnClPh$_3$ led to the formation of the trinuclear complex [{Mo($\eta^3$-C$_4$H$_7$)(CO)$_2$(phen)($\mu$-Im)}$_2${SnPh$_3$}]BAr′$_4$ (**8**).

## Introduction

*N*,*N*′-Dialkylimidazolium salts serve as ionic liquids,[1] as hydrogen-bond donors in supramolecular hosts,[2] and as precursors for the synthesis of N-heterocyclic carbenes.[3] Cationic metal complexes with *N*-alkylimidazole ligands can be regarded as N-metalated analogues of *N*,*N*′-dialkylimidazolium cations.[4] We have investigated the ability of the C2−H groups of *N*-alkylimidazole ligands in cationic metal complexes to act as hydrogen-bond donors,[5] as well as the unprecedented reactivity patterns resulting from deprotonation of these groups.[6] Aiming to extend these works, we decided to investigate the possibility of preparing N,N′-dimetalated analogues of *N*,*N*′-dialkylimidazolium cations, i.e., complexes in which an (anionic) imidazolate ligand would bridge two cationic metal fragments, so that the overall dinuclear complex would be cationic.

In our previous studies with imidazole complexes, we have employed allylmolybdenum(II) dicarbonyl and -rhenium(I) tricarbonyl fragments because of their stability (CO-substitution reactions in complexes of this type do not occur easily), ease of preparation, and presence of CO groups, which could serve as a spectroscopic (IR) handle. 2,2′-Bipyridine (bipy) and 1,10-phenanthroline (phen) are stable chelates. Therefore, their presence as ancillary ligands, blocking two coordination sites, would help to prevent the direct formation of dinuclear compounds upon deprotonation (see below). Also, the redox stability of allylmolybdenum(II) dicarbonyl and -rhenium(I) tricarbonyl complexes would ensure that deprotonation of cationic complexes would afford neutral products rather than trigger electron transfer. Therefore, the imidazolato complexes of {Mo(allyl)(CO)$_2$(phen)} and {Re(CO)$_3$(bipy)} fragments were targeted.

Imidazoles form stable complexes with a variety of metal fragments, which, in most cases, are easily prepared through substitution reactions. We therefore thought that the most general route to the synthesis of cationic imidazolate-bridged dinuclear compounds would be deprotonation of a cationic

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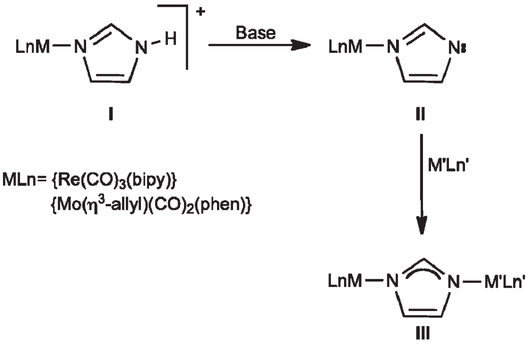
**Scheme 1.** General Reaction Scheme of the Results Included in This Article



mononuclear complex of a parent imidazole. The product would be a neutral complex with a terminal imidazolate ligand. Next this product would be allowed to react with a cationic complex containing a labile ligand, which could be displaced by the uncoordinated nitrogen of the imidazolate ligand (Scheme 1).

Imidazolato-bridged transition-metal complexes have been known since the early 1960s[7] and have attracted considerable interest because the X-ray crystal structure of the enzyme bovine erythrocyte superoxide dismutase showed that the active site consisted of a Zn−Cu bimetallic pair bridged by the imidazolato group of a deprotonated histidine residue.[8] An imidazolato (histidine) bridge has also been proposed to exist between copper and iron in cytochrome *c* oxidase.[9] Therefore, numerous studies have been focused on the synthesis of binuclear imidazolato-bridged complexes to mimic active sites in metalloproteins [the more widely employed metals have been copper(II), zinc(II), nickel(II), and iron(III)].[10] Imidazolato bridges have also been used in the synthesis of zeolitic metal−organic fragments that show potential for gas ($H_2$ and $CO_2$) storage.[11]

The isolation of monomeric imidazolato (Im) complexes has proven to be difficult because of the bidentate nature of Im, which frequently led to oligomeric or polymeric species.[12] As far as we know, just a few terminal imidazolato metal complexes have been reported (fully characterized examples, including the X-ray structure, are very scarce[13]), and none of them is an organometallic complex.[14]

Herein we report the synthesis of a complete series of complexes of rhenium(I) and molybdenum(II), including the parent imidazole species (type I, Scheme 1), the monomeric $\kappa$-*N*-imidazolate derivatives (type II, Scheme 1), and the use of the latter as metalloligands to afford homo- or heteropolymetallic complexes containing $\mu$-$\kappa$-*N*:$\kappa$-*N*′-imidazolate units (type III, Scheme 1).

## Experimental Section

**General Procedures.** All manipulations were carried out under a nitrogen atmosphere using Schlenk techniques. Solvents were distilled from sodium (hexanes), sodium/benzophenone (tetrahydrofuran, THF), and $CaH_2$ ($CH_2Cl_2$). Compounds [Re(OTf)(bipy)$(CO)_3$],[15] [MoCl($\eta^3$-$C_3H_4$-2-R)$(CO)_2$(phen)] (R = H, Me),[16] and NaBAr′$_4$[17] were prepared as previously reported. Deuterated dichloromethane (Cambridge Isotope Laboratories, Inc.) was stored under nitrogen in a Young tube and used without further purification. $^1H$ and $^{13}C$ NMR spectra were recorded on a Bruker Advance 300, DPX-300, or Advance 400 spectrometer. NMR spectra are referred to the internal residual solvent peak for $^1H$ and $^{13}C\{^1H\}$ NMR. IR solution spectra were obtained in a Perkin-Elmer FT 1720-X spectrometer using 0.2 mm $CaF_2$ cells. NMR samples were prepared under nitrogen using Kontes manifolds purchased from Aldrich.

**Crystal Structure Determination. General Description. For Compounds 3, 5, and 8.** Data collection was performed at 293(2) K (compounds **3** and **5**) and 150 (2) K (compound **8**) on a Nonius Kappa CCD single-crystal diffractometer, using Mo Kα radiation ($\lambda$ = 0.710 73 Å). Images were collected up to $2\theta$ = 140° at a 29 mm fixed crystal−detector distance, using the oscillation method. The data collection strategy was calculated with the program *Collect*.[18] Data reduction and cell refinement were performed with the programs *HKL Denzo* and *Scalepack*.[19] A semiempirical absorption correction was applied using the program *SORTAV*.[20] **For Compounds 1 and 7.** Data collection was performed at 150(2) K (compound **1**) and 293(2) K (compound **7**) on an Oxford Diffraction Xcalibur Nova single-crystal diffractometer, using Cu Kα

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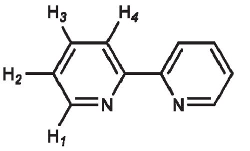
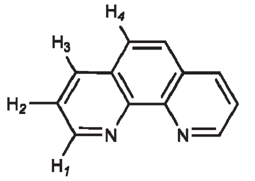
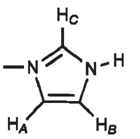
radiation ($\lambda$ = 1.5418 Å) for compound **1** and Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å) for compound **7**. Images were collected at a 65 mm fixed crystal−detector distance, using the oscillation method, with 1° oscillation and variable exposure time per image (4−16 s). The data collection strategy was calculated with the program *CrysAlis CCD*.[21] Data reduction and cell refinement were performed with the program *CrysAlis RED*.[21] An empirical absorption correction was applied using the SCALE3 ABSPACK algorithm, as implemented in the program *CrysAlis RED*.[21] **Structure Solution and Refinement (All).** The structures were solved by direct methods with *SHELXTL*.[22] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were set in calculated positions and refined as riding atoms, with a common thermal parameter. Calculations were made with *SHELXTL* and *PARST*.[23]

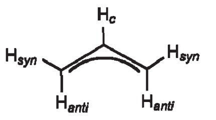
For topological analysis of the electron densities, the MOLFINDER procedure was used.[24]

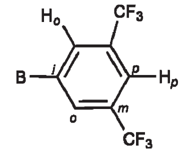
The labeling schemes for $^1$H and $^{13}$C NMR spectra are as follows:











**[Re(bipy)(CO)$_3$(HIm)]OTf (1).** 1*H*-Imidazole (HIm; 0.006 g, 0.088 mmol) was added to a solution of [Re(OTf)(bipy)(CO)$_3$] (0.050 g, 0.087 mmol) in $CH_2Cl_2$ (20 mL), and the mixture was stirred overnight at room temperature. The resulting yellow solution was concentrated under reduced pressure to a volume of 10 mL, and the addition of hexane (20 mL) caused precipitation of a yellow solid, which was washed with hexane (2 × 20 mL) and diethyl ether (2 × 20 mL). The slow diffusion of hexane into a concentrated solution of compound **1** in $CH_2Cl_2$ at −20 °C afforded yellow crystals, one of which was used for the X-ray structure determination. Yield: 0.053 g (96%). IR ($CH_2Cl_2$): 2032vs, 1926s ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 11.85 [s, br, 1H, NH], 9.11 [m, 2H, H1 bipy], 8.33 [m, 2H, H4 bipy], 8.24 [m, 2H, H2 bipy], 7.71 [m, 2H, H3 bipy], 7.12 [s, 1H, HC HIm], 6.94 [s, 1H, HA HIm], 6.71 [s, 1H, HB HIm]. $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 196.3 [2CO], 191.2 [CO], 155.9, 153.6, 141.1, 129.3, 124.7 [bipy], 137.9, 128.8, 119.1 [HIm]. Anal. Calcd for $C_{17}H_{12}F_3N_4O_6ReS$: C, 31.73; H, 1.88; N, 8.71. Found: C, 31.61; H, 2.02; N, 8.60.

**[Mo($\eta^3$-$C_4H_7$)(CO)$_2$(HIm)(phen)]BAr′$_4$ (2a).** NaBAr′$_4$ (0.126 g, 0.140 mmol) was added to a solution of [MoCl($\eta^3$-$C_4H_7$)(CO)$_2$(phen)] (0.060 g, 0.140 mmol) in $CH_2Cl_2$ (20 mL), and it was allowed to stir at room temperature for 15 min. The red solution was filtered from the white solid (NaCl) via a cannula, and HIm (0.010 g, 0.150 mmol) was added. After 1 h, the solution was concentrated under reduced pressure to a volume of 5 mL, and the addition of hexane caused precipitation of a red solid, which was washed with hexane (2 × 20 mL). Compound **2a** was obtained as a red microcrystalline solid. Yield: 0.146 g (79%). IR ($CH_2Cl_2$): 1955vs, 1873s ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 9.85 [s, br, 1H, N*H*], 9.27 [m, 2H, $H_1$ phen], 8.58 [m, 2H, $H_3$ phen], 7.99 [s, 2H, $H_4$ phen], 7.94 [m, 2H, $H_2$ phen], 7.74 [m, 8H, $H_o$ BAr′$_4$], 7.56 [m, 4H, $H_p$ BAr′$_4$], 7.49 [s, 1H, $H_C$ HIm], 6.73 [s, 1H, $H_A$ HIm], 5.84 [s, 1H, $H_B$ HIm], 3.24 [s, 2H, $H_{syn}$], 1.78 [s, 2H, $H_{anti}$], 0.67 [s, 3H, C*H*$_3$]. $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 224.8 [*C*O], 162.2 [q ($^1J_{CB}$ = 49.8 Hz), $C_i$ BAr′$_4$], 152.7, 144.8, 139.5, 130.9, 128.3, 126.1 [phen], 135.2 [$C_o$ BAr′$_4$], 129.3 [q ($^2J_{CF}$ = 31.5 Hz), $C_m$ BAr′$_4$], 124.9 [q ($^1J_{CF}$ = 272.5 Hz), *C*F$_3$, BAr′$_4$], 144.8, 127.3, 121.7 [HIm], 117.8 [$C_p$ BAr′$_4$], 84.0 [$C^2$ $\eta^3$-$C_4H_7$], 56.6 [$C^1$ and $C^3$ $\eta^3$-$C_4H_7$], 18.5 [*C*H$_3$ $\eta^3$-$C_4H_7$]. Anal. Calcd for $C_{53}H_{31}BF_{24}MoN_4O_2$: C, 48.28; H, 2.37; N, 54.25. Found: C, 48.42; H, 2.01; N, 4.09.

**[Mo($\eta^3$-$C_3H_5$)(CO)$_2$(HIm)(phen)]BAr′$_4$ (2b).** Compound **2b** was prepared as described above for compound **2a**, starting from [MoCl($\eta^3$-$C_3H_5$)(CO)$_2$(phen)] (0.060 g, 0.147 mmol), NaBAr′$_4$ (0.130 g, 0.147 mmol), and HIm (0.010 g, 0.147 mmol). Compound **2b** was obtained as a garnet solid. Yield: 0.154 g (80%). IR ($CH_2Cl_2$): 1957vs, 1872s ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 9.61 [s, br, 1H, N*H*], 9.24 [m, 2H, $H_1$ phen], 8.59 [m, 2H, $H_3$ phen], 8.01 [s, 2H, $H_4$ phen], 7.93 [m, 2H, $H_2$ phen], 7.74 [m, 8H, $H_o$ BAr′$_4$], 7.56 [m, 4H, $H_p$ BAr′$_4$], 7.63 [s, 1H, $H_C$ HIm], 6.74 [s, 1H, $H_A$ HIm], 5.80 [s, 1H, $H_B$ HIm], 3.47 [d (*J* = 6.4 Hz), 2H, $H_{syn}$], 2.94 [m, 1H, $H_c$], 1.83 [d (*J* = 9.5 Hz), 2H, $H_{anti}$]. Anal. Calcd for $C_{52}H_{29}BF_{24}MoN_4O_2$: C, 47.88; H, 2.24; N, 4.29. Found: C, 48.03; H, 2.41; N, 4.12.

**[Re(bipy)(CO)$_3$(Im)] (3).** To a solution of **1** (0.050 g, 0.078 mmol) in THF at −78 °C was added KN(SiMe$_3$)$_2$ (0.170 mL of a 0.5 M solution in toluene, 0.085 mmol), and the color of the solution changed immediately from yellow to light green. The mixture was allowed to reach room temperature, and the solvent was evaporated under vacuum. The residue was extracted with $CH_2Cl_2$ (30 mL), filtered via a cannula, and evaporated to dryness. The slow diffusion of hexane (20 mL) into a concentrated solution of compound **3** in THF (5−7 mL) at −20 °C afforded pale-green crystals, one of which was used for X-ray analysis. Yield: 0.031 g (80%). IR (THF): 2017vs, 1911s, 1904s ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 9.15 [m, 2H, $H_1$ bipy], 8.20 [m, 2H, $H_4$ bipy], 8.14 [s, 2H, $H_2$ bipy], 7.61 [m, 2H, $H_3$ bipy], 6.72 [s, 1H, $H_C$ HIm], 6.64 [s, 1H, $H_A$ HIm], 6.35 [s, 1H, $H_B$ HIm]. $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 197.6 [2*C*O], 193.4 [*C*O], 155.6, 153.1, 139.8, 139.6, 127.7 [bipy], 125.7, 123.4, 123.3 [Im]. Anal. Calcd for $C_{16}H_{11}N_4O_3Re$: C, 38.94; H, 2.25; N, 11.35. Found: C, 38.71; H, 2.39; N, 10.96.

**[Mo($\eta^3$-$C_4H_7$)(CO)$_2$(Im)(phen)] (4a).** KN(SiMe$_3$)$_2$ (0.130 mL of a 0.5 M solution in toluene, 0.065 mmol) was added to a solution of **2a** (0.080 g, 0.060 mmol) in THF (20 mL), previously cooled to −78 °C. The reaction mixture was allowed to reach room temperature and then was evaporated to dryness. The dark-red residue was extracted with $CH_2Cl_2$ (30 mL), filtered via a cannula, and concentrated under reduced pressure to a volume of 5 mL. The addition of hexane (20 mL) caused precipitation of a dark-red solid that was washed with hexane (2 × 20 mL). Yield: 0.022 g (80%). IR ($CH_2Cl_2$): 1947vs, 1863s ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 9.13 [m, 2H, $H_1$ phen], 8.52 [m, 2H, $H_3$ phen], 7.98 [s, 2H, $H_4$ phen], 7.84 [m, 2H, $H_2$ phen], 7.20 [s, 1H, HIm], 6.35 [s, 1H, HIm], 5.43 [s, 1H, HIm], 3.08 [s, 2H, $H_{syn}$], 1.65 [s, 2H, $H_{anti}$], 0.63 [s, 3H, C*H*$_3$]. $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 225.9 [*C*O], 152.5, 145.1, 138.9, 130.5, 128.0, 125.7 [phen], 137.7, 127.4, 124.0 [HIm], 83.0 [$C^2$ $\eta^3$-$C_4H_7$], 55.3 [$C^1$ and $C^3$ $\eta^3$-$C_4H_7$], 18.3 [*C*H$_3$ $\eta^3$-$C_4H_7$]. Anal. Calcd for $C_{21}H_{18}MoN_4O_2$: C, 55.52; H, 3.99; N, 12.33. Found: C, 55.61; H, 4.09; N, 12.01.

**[Mo($\eta^3$-$C_3H_5$)(CO)$_2$(Im)(phen)] (4b).** Compound **4** was prepared as described above for complex **3** starting from **2b** (0.080 g, 0.061 mmol) and KN(SiMe$_3$)$_2$ (0.130 mL of a 0.5 M solution in toluene, 0.065 mmol). Compound **4** was obtained as a dark-red microcrystalline solid. Yield: 0.021 g (78%). IR ($CH_2Cl_2$): 1946vs, 1863s ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 9.15 [m, 2H, $H_1$ phen], 8.57 [m, 2H, $H_3$ phen], 8.06 [s, 2H, $H_4$ phen], 7.84 [m, 2H, $H_2$ phen], 6.54 [s, br, 2H, HIm], 6.22 [s, 1H, HIm], 3.29 [d (*J* = 6.3 Hz), 2H, $H_{syn}$], 2.79 [m, 1H, $H_c$], 1.63 [d (*J* = 9.4 Hz), 2H,

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(23) (a) Nardelli, M. *Comput. Chem.* **1983**, *7*, 95. (b) Nardelli, M. *J. Appl. Crytallogr.* **1995**, *28*, 659.

(24) Menéndez-Velázquez, A.; García-Granda, S. *Appl. Crystallogr.* **2003**, *36*, 193.

$H_{anti}$]. Anal. Calcd for $C_{20}H_{16}MoN_4O_2$: C, 54.56; H, 3.66; N, 12.72. Found: C, 54.91; H, 3.29; N, 12.50.

**[{Re(bipy)(CO)$_3$}$_2$($\mu$-Im)}OTf (5).** *Method A*: $KN(SiMe_3)_2$ (0.125 mL of a 0.5 M solution in toluene, 0.062 mmol) was added to a solution of HIm (0.004 g, 0.052 mmol) in THF (10 mL) cooled to −78 °C. After 5 min at low temperature, the mixture was allowed to reach room temperature and was transferred into a solution of [Re(OTf)(bipy)$(CO)_3$] (0.060 g, 0.104 mmol) in THF (15 mL) previously cooled to −78 °C. The reaction mixture was allowed to warm to room temperature and then was stirred for 1 h. The solvent was evaporated to dryness and the residue extracted with $CH_2Cl_2$ (30 mL) and filtered through Celite to afford an orange solution, which was concentrated under reduced pressure to a volume of 10 mL. The addition of hexane (20 mL) caused precipitation of an orange solid, which was washed with hexane (2 × 20 mL). The slow diffusion of hexane into a concentrated solution of compound **5** in $CH_2Cl_2$ (7−10 mL) at −20 °C afforded orange crystals, one of which was used for the X-ray structure determination. Yield: 0.042 g (79%). Anal. Calcd for $C_{30}H_{19}F_3N_6O_9Re_2S$: C, 40.82; H, 2.17; N, 9.52. Found: C, 40.58; H, 2.29; N, 9.43. *Method B*: To a solution of **1** (0.050 g, 0.078 mmol) in THF at −78 °C was added $KN(SiMe_3)_2$ (0.170 mL of a 0.5 M solution in toluene, 0.085 mmol). The mixture was allowed to reach room temperature and then was transferred via a cannula into a solution of [Re(OTf)(bipy)$(CO)_3$] (0.045 g, 0.078 mmol) in THF (20 mL). The reaction mixture was stirred for 1 h and then was evaporated to dryness. The residue was extracted with $CH_2Cl_2$ (20 mL), filtered through Celite, and concentrated under vacuum to a volume of 10 mL. The addition of hexane (20 mL) caused precipitation of an orange solid, which was washed with hexane (2 × 20 mL). Yield: 0.035 g (52%). IR ($CH_2Cl_2$): 2024vs, 1918s ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.88 [m, 4H, $H_1$ bipy], 8.50 [m, 4H, $H_4$ bipy], 8.25 [m, 4H, $H_2$ bipy], 7.58 [m, 4H, $H_3$ bipy], 6.30 [s, 2H, $H_A$ and $H_B$ HIm], 5.84 [s, 1H, $H_C$ HIm]. $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 197.2 [4*C*O], 192.7 [2*C*O], 156.0, 153.4, 144.5, 141.1, 128.2 [bipy], 139.4, 127.8 [HIm]. Anal. Calcd for $C_{30}H_{19}F_3N_6O_9Re_2S$: C, 40.82; H, 2.17; N, 9.52. Found: C, 40.61; H, 2.35; N, 9.35.

**[{Mo($\eta^3$-C$_4$H$_7$)(CO)$_2$(phen)}$_2$($\mu$-Im)]OTf (6).** *Method A*: Compound **6** was prepared following method A as described above for compound **5**, starting from [Mo(OTf)($\eta^3$-$C_4H_7$)$(CO)_2$(phen)] (0.090 g, 0.170 mmol), HIm (0.006 g, 0.088 mmol), and $KN(SiMe_3)_2$ (0.200 mL of a 0.5 M solution in toluene, 0.100 mmol). The slow diffusion of hexane into a concentrated solution of **6** in $CH_2Cl_2$ at −20 °C afforded red crystals. Yield: 0.061 g (70%). Anal. Calcd for $C_{40}H_{33}F_3Mo_2N_6O_7S$: C, 48.50; H, 3.38; N, 8.48. Found: C, 48.22; H, 3.45; N, 8.16. *Method B*: Compound **6** was prepared following method B as described above for compound **5**, starting from **2a** (0.050 g, 0.038 mmol), $KN(SiMe_3)_2$ (0.080 mL of a 0.5 M solution in toluene, 0.040 mmol), and [Mo(OTf)($\eta^3$-$C_4H_7$)$(CO)_2$(phen)] (0.020 g, 0.038 mmol). Compound **6** was obtained as a red microcrystalline solid. Yield: 0.020 g (53%). IR ($CH_2Cl_2$): 1949vs, 1865s ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.90 [m, 4H, $H_1$ phen], 8.64 [m, 4H, $H_3$ phen], 8.10 [s, 4H, $H_4$ phen], 7.86 [m, 4H, $H_2$ phen], 5.93 [s, 1H, $H_C$ HIm], 5.54 [s, 2H, $H_A$ and $H_B$ HIm], 2.98 [s, 4H, $H_{syn}$], 1.48 [s, 4H, $H_{anti}$], 0.56 [s, 6H, $CH_3$]. $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 225.6 [*C*O], 151.9, 144.4, 138.4, 130.3, 127.7, 125.6 [phen], 145.2, 126.8 [HIm], 83.0 [$C^2$ $\eta^3$-$C_4H_7$], 55.3 [$C^1$ and $C^3$ $\eta^3$-$C_4H_7$], 18.3 [$CH_3$ $\eta^3$-$C_4H_7$]. Anal. Calcd for $C_{40}H_{33}F_3Mo_2N_6O_7S$: C, 48.50; H, 3.38; N, 8.48. Found: C, 48.91; H, 3.67; N, 8.74.

**[{Mo($\eta^3$-C$_3$H$_5$)(CO)$_2$(phen)}($\mu$-Im) {Re(phen)(CO)$_3$]OTf (7).** *Method A*: $KN(SiMe_3)_2$ (0.130 mL of a 0.5 M solution in toluene, 0.065 mmol) was added to a cooled (to −78 °C) solution of **2b** (0.080 g, 0.061 mmol) in THF (20 mL). The reaction mixture was allowed to stir at low temperature for 5 min, and then it was transferred via a cannula into a solution of [Re(OTf)$(CO)_3$(phen)] (0.037 g, 0.061 mmol) in THF (15 mL). After 1 h of stirring at room temperature, the solvent was evaporated under vacuum, and the brown residue was extracted with $CH_2Cl_2$ (30 mL) and filtered via a cannula. The resulting solution was concentrated under reduced pressure to a volume of 10 mL, and the addition of hexane (20 mL) caused precipitation of a red solid, which was washed with hexane (2 × 20 mL) and diethyl ether (2 × 20 mL). The slow diffusion of hexane into a concentrated solution of compound **7** in $CH_2Cl_2$ at −20 °C afforded poor-quality crystals. Yield: 0.051 g (80%). Anal. Calcd for $C_{36}H_{24}F_3MoN_6O_8ReS$: C, 41.58; H, 2.33; N, 8.08. Found: C, 41.26; H, 2.66; N, 8.29. *Method B*: Compound **7** was prepared following the procedure described as method A starting from [Re$(CO)_3$(HIm)(phen)]OTf (0.050 g, 0.075 mmol), $KN(SiMe_3)_2$ (0.150 mL of a 0.5 M solution in toluene, 0.075 mmol), and [Mo(OTf)($\eta^3$-$C_3H_5$)$(CO)_2$(phen)] (0.039 g, 0.075 mmol). Yield: 0.59 g (76%). IR ($CH_2Cl_2$): 2026vs, 1948 m, 1919s, 1864 m ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 9.14, 8.87, 8.78, 8.70 [m, 2H each, phen], 8.19, 8.18 [s, 2H each, phen], 7.95, 7.83 [m, 2H each, phen], 5.97, 5.86, 5.71 [s, 1H each, HIm], 3.22 [d ($J$ = 6.4 Hz), 2H, $H_{syn}$], 2.75 [m, 1H, $H_c$], 1.54 [d ($J$ = 9.5 Hz), 2H, $H_{anti}$]. $^{13}$C NMR ($CD_2Cl_2$): $\delta$ 225.4 [2*C*O, Mo−*C*O], 196.5 [2*C*O, Re−*C*O], 192.3 [*C*O, Re−*C*O], 152.8, 152.3, 144.3, 144.1, 139.1, 139.0, 130.9, 130.1, 128.1, 127.8, 126.5, 125.5 [2phen], 146.4, 127.7, 127.3 [HIm], 73.5 [$C^2$ $\eta^3$-$C_3H_5$], 57.5 [$C^1$ and $C^3$ $\eta^3$-$C_3H_5$]. Anal. Calcd for $C_{36}H_{24}F_3MoN_6O_8ReS$: C, 41.58; H, 2.33; N, 8.08. Found: C, 41.63; H, 2.61; N, 7.95.

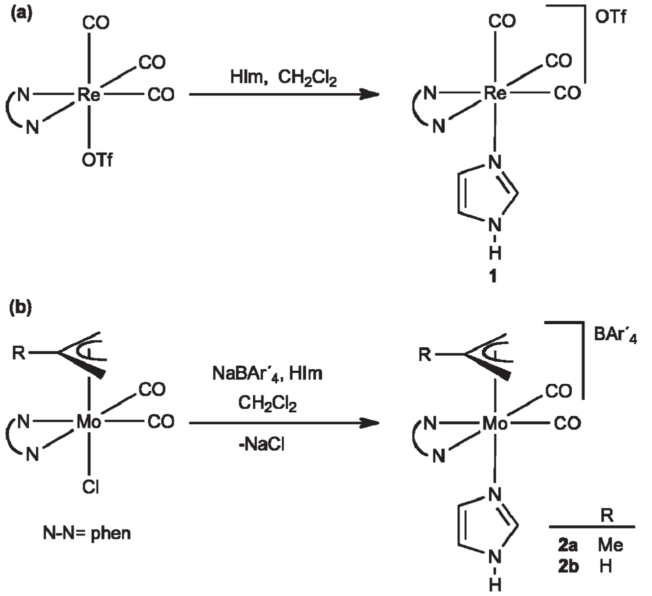
**[{Mo($\eta^3$-C$_4$H$_7$)(CO)$_2$(phen)($\mu$-Im)}$_2${SnPh$_3$}]BAr′$_4$ (8).** To a solution of **2a** (0.080 g, 0.060 mmol) in THF (20 mL) at −78 °C was added $KN(SiMe_3)_2$ (0.120 mL of a 0.5 M solution in toluene, 0.060 mmol), and the mixture was stirred at low temperature for 5 min. A solution of $SnClPh_3$ (0.012 g, 0.030 mmol) in THF (10 mL) was then transferred over the solution described above, and the reaction mixture was allowed to reach room temperature. After 15 min, the solvent was evaporated under vacuum, and the purple residue was extracted with $CH_2Cl_2$ (30 mL) and filtered via a cannula. The resulting solution was concentrated under reduced pressure to a volume of 10 mL, and the addition of hexane (20 mL) caused precipitation of a solid, which was washed with hexane (2 × 20 mL). The slow diffusion of hexane into a concentrated solution of compound **8** in $CH_2Cl_2$ at −20 °C afforded purple crystals. Yield: 0.025 g (83%). IR ($CH_2Cl_2$): 1947vs, 1867 m ($\nu_{CO}$). $^1$H NMR ($CD_2Cl_2$): $\delta$ 8.97 [m, 4H, $H_1$ phen], 8.41 [m, 4H, $H_3$ phen], 7.89 [s, 4H, $H_4$ phen], 7.73 [m, 12H, $H_2$ phen and $H_o$ BAr′$_4$], 7.59 [m, 4H, $H_p$ BAr′$_4$], 7.13 [m, 15H, Ph], 6.20 [s, 2H, $H_C$ HIm], 5.96, 5.58 [s, 2H each, $H_A$ and $H_B$ HIm], 3.04 [s, 4H, $H_{syn}$], 1.60 [s, 4H, $H_{anti}$], 0.58 [s, 6H, $CH_3$]. Anal. Calcd for $C_{92}H_{63}BF_{24}Mo_2N_8O_4Sn$: C, 52.08; H, 2.99; N, 5.28. Found: C, 52.21; H, 3.12; N, 5.01.

## Results and Discussion

The addition of a slight excess of HIm to a solution of [Re(OTf)(bipy)$(CO)_3$] (bipy = 2,2′-bipyridine)[15] in $CH_2Cl_2$ led, in 8 h at room temperature, to the formation of complex **1**, by a simple substitution of the labile triflato ligand by the imidazole (see Scheme 2a).

Compound **1** was obtained as a single product of the reaction in 96% yield and was fully characterized in solution by IR and NMR and in the solid state by X-ray diffraction. The IR $\nu_{CO}$ bands of **1**, indicative of a *fac*-{Re$(CO)_3$} geometry, occur at wavenumber values that are almost identical to those of the triflato precursor, despite the fact that the reaction transforms a neutral complex into a cationic one, reflecting the large $\sigma$-donor ability of the HIm ligand. The incorporation of the HIm moiety into the complex is evidenced by the observation in the $^1$H NMR spectrum of three signals at 7.12, 6.94, and 6.71 ppm, assigned to the three C−H groups of the azole ring, and a characteristically broad singlet at 11.85 ppm, attributable to the N−H group.

**Scheme 2.** Synthesis of Cationic Imidazole Complexes **1**, **2a**, and **2b**



The $^{13}$C NMR spectrum shows three signals at 137.9, 128.8, and 119.1 ppm for the HIm ligand.[25]

In a similar way, complexes **2a** and **2b** were prepared by substitution of the chloride ligand by HIm in the presence of the salt NaBAr′$_4$ [Ar′ = 3,5-bis(trifluoromethyl)phenyl; see Scheme 2b].[26] The $^1$H and $^{13}$C NMR spectra of the new compounds **2a** and **2b** agree with the proposed formulation, showing the existence of a mirror plane in the complex and the incorporation of one HIm ligand per metal center. The observation of three imidazole C−H signals for the rhenium and molybdenum complexes indicates that no fast dissociation−recoordination of imidazole is taking place. Such a fast dissociation would allow the concomitant exchange of the positions of hydrogen and metal (prototropy and metallotropy), giving rise to the observation of only two CH ring signals in the NMR spectra.[27]

The slow diffusion of hexane into a concentrated solution of **1** in CH$_2$Cl$_2$ at −20 °C afforded yellow crystals, one of which was used for the X-ray structure determination (Figure 1a).[28] The solid-state structure is in agreement with the one deduced from the solution spectroscopic data (see above) and similar to the phen analogue previously reported.[29]

The addition of an equimolar amount of the strong base KN(SiMe$_3$)$_2$ to a solution of the imidazole compounds **1**, **2a**, and **2b** in THF at low temperature caused deprotonation of the N−H group, to afford the terminal imidazolate complexes **3**, **4a**, and **4b**, respectively. The transformation was evidenced by a noticeable shift to lower wavenumbers of the $\nu_{CO}$ bands in their IR spectra (from 2032 and 1926 cm$^{-1}$ to 2017 and 1911 cm$^{-1}$ for **1** and from 1955 and 1873 cm$^{-1}$ to 1946 and 1863 cm$^{-1}$ for **2a**), consistent with the formation of neutral products. The most characteristic feature of the $^1$H NMR spectra of the new compounds is the absence of the signal of the N−H group, while a pattern similar to that found for the cationic precursors is encountered for the remaining signals. The solid-state structure of the complex **3** was determined by single-crystal X-ray diffraction, and the results are shown in Figure 1b.[30] The rhenium atom is in an approximately octahedral coordination geometry, and the three carbonyl ligands are in a *facial* disposition. The imidazolate ligand is $\kappa$-N-coordinated and features a noncoordinated nitrogen atom (N3).

The metallic fragments present in **1** and **3** differ only in one hydrogen atom, the one at the N3 nitrogen atom in **1**.[31] The most significant structural consequence of this difference is the shortening of the Re1−N1 distance as a result of deprotonation of the imidazole ligand [from 2.193(3) Å in **1** to 2.157(3) Å in **3**], reflecting the stronger $\sigma$-donor character of imidazolate compared with the imidazole ligand. The C2−N3−C5 angle is slightly more acute in **3** than in **1** [103.0(3)° vs 106.3(4)°], and the N1−C2−N3 angle is broader in **3** [114.9(3)°] than in **1** [108.4(4)°]. These differences can be explained considering that the nonbonding electron pair at N3 in compound **3** is sterically more demanding than the one at the N−H bond in **1** (Table 1).

Admittedly, these differences in distances and angles are small. The topological analysis of the experimental electron density, as obtained from Fourier maps in the X-ray diffraction experiment, can be used as an assessment of bonding beyond the metrical parameters: the bonding properties of the molecular structure are characterized in terms of the charge density at (3, −1) or bond critical points, $\rho_b$.[24,32] In **1** and **3**, all bonds to the rhenium atom have a relatively low value of $\rho_b$, ranging from 0.3 to 0.6 e Å$^{-3}$, diagnostic of the metal−ligand bonds between closed-shell fragments. The values of $\rho_b$ at the Re1−N1 bonds are 0.361 and 0.475 e Å$^{-3}$ in **1** and **3**, respectively, indicating that imidazolate is a stronger $\sigma$ donor than the imidazole ligand.[33]

The electron pairs, either bonding or nonbonding, can be located using the topology of the Laplacian of the charge

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[25] (a) Manganese imidazole complexes closely related to **1** have been studied by Carlos et al.: Aguiar, I. de; Inglez, S. D.; Lima, F. C. A.; Daniel, J. F. S.; McGarvey, B. R.; Tedesco, A. C.; Carlos, R. M.; et al. *Inorg. Chem.* **2008**, *47*, 11519. (b) Rhenium tricarbonylimidazole complexes have been synthesized by Herrick, Ziegler, and co-workers: Franklin, B. R.; Herrick, R. S.; Ziegler, C. J.; Cetin, A.; Barone, N.; Condon, L. R. *Inorg. Chem.* **2008**, *47*, 5902. (c) The behavior of [Re(CO)$_3$(phen)(His)]$^+$ species was studied by Crane, Vlcek, Gray, and co-workers: Blanco-Rodríguez, A. M.; Busby, M.; Gradinaru, C.; Crane, B. R.; Di Bilio, A. J.; Matousek, P.; Towrie, M.; Leigh, B. S.; Richards, J. H.; Vlček, A., Jr.; Gray, H. B. *J. Am. Chem. Soc.* **2006**, *128*, 4365.

[26] The use of $\eta^3$-allyl or $\eta^3$-methallyl does not imply a substantial difference in the chemical behavior of the compounds, although in some cases, it may be crucial for crystallization. The choice of the allyl or methallyl ligand has been done trying to obtain better crystallinity.

[27] Federov, L. A.; Kravtsov, D. N.; Peregudov, A. S. *Russ. Chem. Rev.* **1981**, *50*, 682.

[28] Selected crystallographic data for **1**: C$_{14}$H$_{12}$F$_3$N$_4$O$_6$ReS, $M$ = 643.57, monoclinic, $P21/c$, $a$ = 11.8608(1) Å, $b$ = 6.8182(1) Å, $c$ = 25.4623(3) Å, α = 90.0°, $\beta$ = 102.233(1)°, $\gamma$ = 90.0°, 293(2) K, $V$ = 2012.36(4) Å$^3$, $Z$ = 4, 9474 reflections measured, 3834 independent ($R_{int}$ = 0.0331), R1 = 0.0345, wR2 = 0.0646 (all data).

[29] Connick, W. B.; Di Bilio, A. J.; Hill, M. G.; Winkler, J. R.; Gray, H. B. *Inorg. Chim. Acta* **1995**, *240*, 169.

[30] Selected crystallographic data for **3**: C$_{16}$H$_{11}$N$_4$O$_3$Re, $M$ = 493.49, triclinic, $P\bar{1}$, $a$ = 7.7800 Å, $b$ = 7.9400 Å, $c$ = 12.6460 Å, α = 91.411°, $\beta$ = 100.554°, $\gamma$ = 91.310°, 293(2) K, $V$ = 767.4 Å$^3$, $Z$ = 2, 12 228 reflections measured, 4938 independent ($R_{int}$ = 0.0409), R1 = 0.0405, wR2 = 0.0614 (all data).

[31] Hu, C.; Sulok, C. D.; Paulat, F.; Lehnert, N.; Twigg, A. I.; Hendrich, M. P.; Schulz, C. E.; Scheidt, W. R. *J. Am. Chem. Soc.* **2010**, *132*, 3737.

[32] (a) Bader, R. F. W. In *Atoms in Molecules—A Quantum Theory*; Oxford University Press: Oxford, U.K., 1990. (b) Bader, R. F. W. *Chem. Rev.* **1991**, *91*, 893.

[33] All other bonds are characterized by values of the electron density at the bond critical point from 1.5 to 2.7 e Å$^{-3}$, indicating a shared interaction consistent with covalent bonds. The $\rho_b$ values in both azole rings (in the range 1.6−1.9 e Å$^{-3}$) indicate a bond character intermediate between single and double, consistent with the bonds of highly delocalized, aromatic rings.

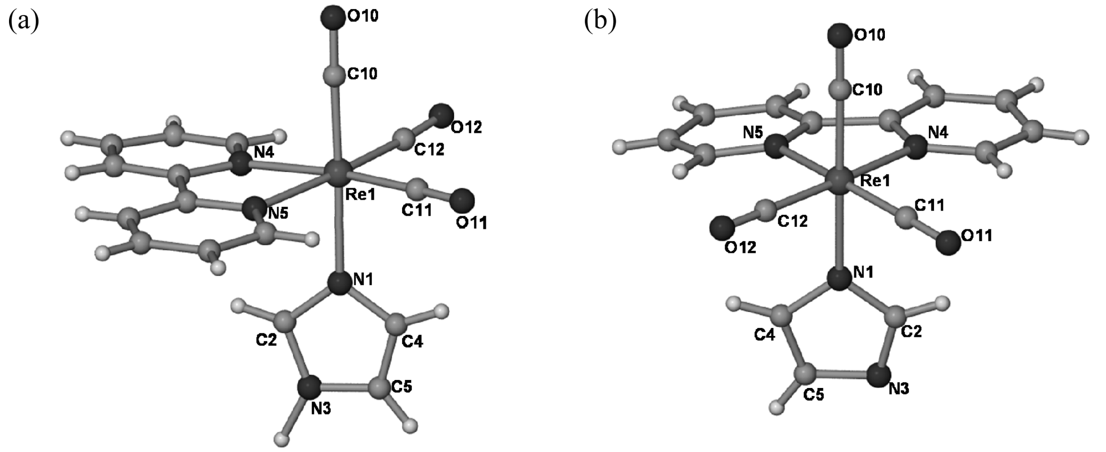


**Figure 1.** (a) Molecular structure of the cation of compound **1**. (b) Molecular structure of complex **3**.

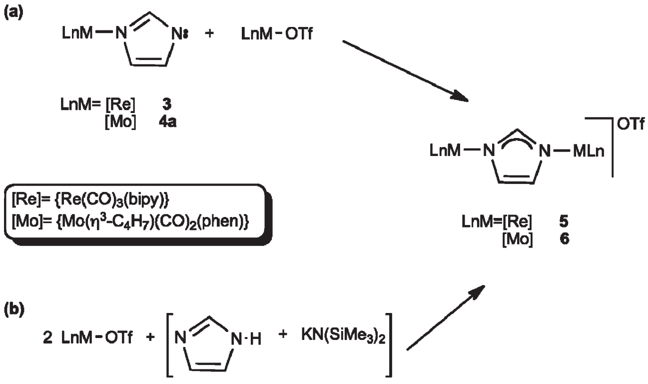
**Table 1.** Selected Bond Distances (Å) and Angles (deg) for Compounds **1** and **3**

| | bond distances (Å) | | | bond angles (deg) | |
|---|---|---|---|---|---|
| | **1** | **3** | | **1** | **3** |
| Re1−N1 | 2.193(3) | 2.157(3) | N1−C2−N3 | 108.3(4) | 114.9(3) |
| N1−C2 | 1.374(6) | 1.355(5) | C2−N3−C5 | 106.4(5) | 103.0(3) |
| C2−N3 | 1.366(7) | 1.330(5) | N3−C5−C4 | 108.2(4) | 110.5(3) |
| N3−C5 | 1.357(7) | 1.384(5) | C5−C4−N1 | 110.7(4) | 107.6(4) |
| C4−C5 | 1.330(6) | 1.360(6) | C4−N1−C2 | 106.4(4) | 104.0(3) |
| C4−N1 | 1.322(6) | 1.383(5) | | | |

distribution: the maxima correspond in number, location, and size to the localized pairs of electrons of a Lewis description.[34] In complex **3**, the imidazolate uncoordinated N3 nitrogen atom exhibits two large nonbonded electron pairs, in the plane of the nuclei ($\nabla^2\rho = -10.1$ e Å$^{-5}$) and perpendicular to that plane ($\nabla^2\rho = -10.3$ e Å$^{-5}$), corresponding to the two nonbonding electron pairs. In contrast, in the imidazole complex of compound **1**, the N3 nitrogen atom shows a maximum perpendicular to the ring plane ($\nabla^2\rho = -10.2$ e Å$^{-5}$) and, in the plane, a less intense one ($\nabla^2\rho = -5.1$ e Å$^{-5}$), indicating nonbonded (the lone pair) and bonded (the N−H bond) charge concentrations, respectively.

With the monomeric imidazolate complexes **3**, **4a**, and **4b** in hand, we aimed at the preparation of homo- and heterobimetallic complexes. The addition of compound **3** to a solution of [Re(OTf)(bipy)(CO)$_3$] afforded, in about 1 h at room temperature, the homobinuclear compound **5**. The homobinuclear molybdenum compound **6** was prepared in a similar way (see Scheme 3a). Complexes **5** and **6** can be prepared in an alternative, straightforward manner by the reaction of the triflato complexes with in situ generated potassium imidazolate in a 2:1 stoichiometry (see Scheme 3b).

**Scheme 3.** Synthesis of the Homobinuclear Compounds **5** and **6**



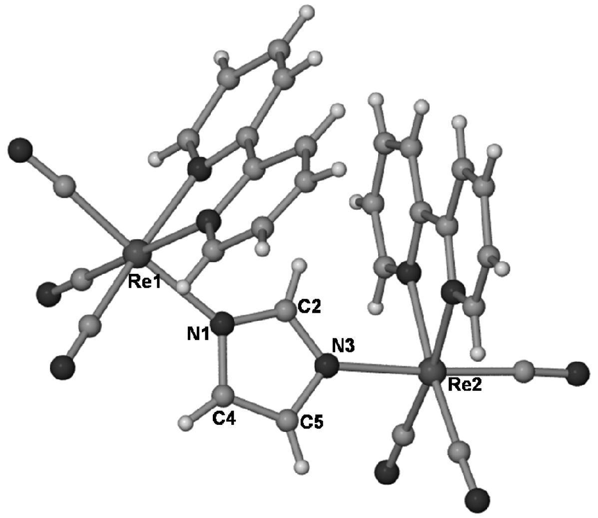


**Figure 2.** Molecular structure of the cation present in **5**. Selected bond distances (Å) and angles (deg): Re1−N1 2.174(7), Re2−N3 2.165(8), N1−C2 1.32(1), C2−N3 1.34(1), N3−C5 1.37(2), C5−C5 134(2), C4−N1 1.37(2); N1−C2−N3 115.4(9), C2−N3−C5 102.1(8), C4−N1−C2 103.8(9).

The binuclear complexes **5** and **6** are symmetric, as evidenced by their spectroscopic data in solution. Hence, $^1$H NMR spectra show only four sets of signals for the bipy (**5**) or phen (**6**) ligands. The signals corresponding to the $\mu$-$\kappa$-$N$:$\kappa$-$N'$-imidazolate ligands are two singlets, one for the NC(H)N group, and one for the two equivalent C−H groups. For compound **6**, the spectrum shows also the typical set of signals of a $\eta^3$-methallyl group in a complex with a mirror plane (equivalent CH$_2$ termini), integrating as two methallyl groups for each Im unit. The $^{13}$C NMR spectra are also consistent with the formation of symmetric binuclear compounds. The slow diffusion of hexane into a concentrated solution of compound **5** in CH$_2$Cl$_2$ at −20 °C afforded yellow

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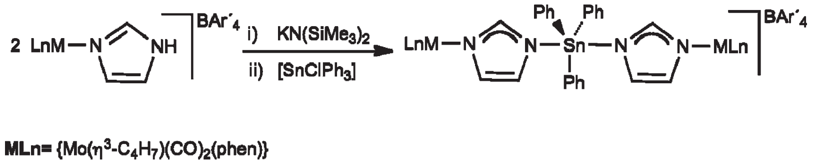
[34] (a) Bader, R. F. W.; Gillespie, R. J.; McDougall, P. J. *J. Am. Chem. Soc.* **1988**, *110*, 7329. (b) Bader, P. J. In *The Lagrangian Approach to Chemistry, in Quantum Theory of Atoms in Molecules: From Solid State to DNA and Drug Design*; Matta, C. F., Boyd, R., Eds.; Wiley-VCH: Weinheim, Germany, 2007; pp 37−59.

**Scheme 4.** Synthesis of the Trimetallic Compound **8**



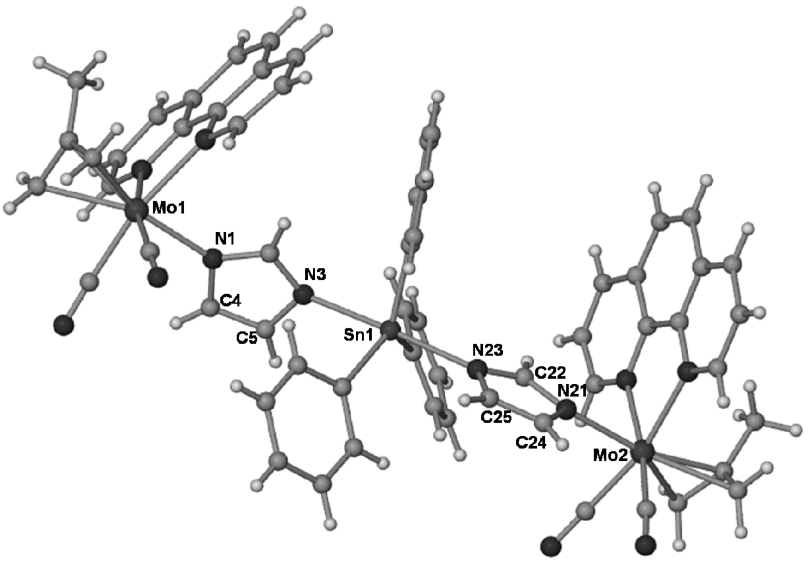


**Figure 3.** Molecular structure of the cation of compound **8**. Selected bond distances (Å) and angles (deg): Mo1−N1 2.224(4), Mo2−N21 2.214(4), Sn1−N3 2.299(4), Sn1−N23 2.296(4); N3−Sn1−N23 177.3(1), N1−C2−N3 113.1(4), N23−C22−N21 113.4(5).

crystals, one of which was used for the X-ray structure determination.[35] Compound **5** is a (triflate) salt with a dirhenium cation, shown in Figure 2. The two virtually identical {Re(CO)$_3$(bipy)} fragments are linked by a *μ*-*κ*-*N*:*κ*-*N*′-imidazolate group. The Re−N(imidazolate) bond distances [Re1−N1 2.174(7) Å and Re2−N3 2.165(8) Å] are intermediate between that of the terminal imidazolate **3** [2.157(3) Å] and the one found in the imidazole complex **1** [2.193(3) Å], reflecting that the anionic character of the bridging ligand is, in compound **5**, shared by two {Re(bipy)(CO)$_3$} fragments, and therefore each one undergoes less electron donation than the one in the terminal imidazolate complex **3**. The bond distances and angles of the five-membered ring are also intermediate between those in the imidazole (as in **1**) and those in the terminal imidazolate (as in **3**).

For compound **5**, the Laplacian of the electron density at the N1 and N3 nitrogen atoms exhibit two pairs of maxima: one perpendicular to the plane ($\nabla^2\rho = -10.0$ e Å$^{-5}$ in N1 and $\nabla^2\rho = -10.1$ e Å$^{-5}$ in N3) and one in the plane ($\nabla^2\rho =$ 5.7 e Å$^{-5}$ in N1 and $\nabla^2\rho = 5.5$ e Å$^{-5}$ in N3). These values are characteristic of nonbonded and closed-shell-bonded (metal−ligand bond) charge concentrations, respectively.

Using a route like the one depicted in Scheme 3a, heterobinuclear imidazolate-bridged complexes can be prepared (while homobinuclear complexes could be prepared via the route shown in Scheme 3b without isolation of mononuclear complexes, route 3a allows the preparation of heterobinuclear complexes). Thus, the reaction of compound [Re(CO)$_3$(Im)(phen)], the phen analogues of **3**, with an equimolar amount of [Mo(OTf)($\eta^3$-C$_3$H$_5$)(CO)$_2$(phen)] led to the formation of **7**. Compound **7** could also be prepared by the inverse route, i.e., the reaction of the molybdenum imidazolate complex **4b** and [Re(OTf)(phen)(CO)$_3$]. The IR spectrum of **7** shows, in the CO region, the bands corresponding to the *fac*-{Re(CO)$_3$} and *cis*-{Mo(CO)$_2$} fragments. The $^1$H and $^{13}$C NMR spectra are in concordance with the proposed formulation and show the signals of two different phen ligands (each C$_s$-symmetric), three different sets of signals for the three C−H groups of the imidazolate bridge, and the signals of a symmetric, static (not undergoing $\eta^3$−$\eta^1$ interconversions), $\eta^3$-allyl. The slow diffusion of hexane into a concentrated solution of **7** in CH$_2$Cl$_2$ afforded poor-quality crystals (see the Supporting Information). The results of the X-ray structure determination are hence of low quality, but the connectivity in the heterobimetallic cation present in **7**, as derived from a topological analysis of the experimental electron density, is unambiguous and in agreement with the structure deduced from the spectroscopic data in solution.

The synthesis of polynuclear compounds using a terminal imidazolato complex as a ligand toward a second metal center is not limited to transition metals. Thus, the imidazole compound **2a** was deprotonated in situ in THF, and the resulting solution was treated with a hemimolar amount of SnClPh$_3$, affording the trinuclear complex **8** (Scheme 4). When the reaction was carried out in a 1:1 stoichiometry, a mixture of **8** and unreacted SnClPh$_3$ was obtained instead of the expected Mo−Sn binuclear product, reflecting the tendency of the Lewis acidic tin center to achieve pentacoordination. A similar formation of 2:1 products in the reaction of tin compounds

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[35] Selected crystallographic data for **5**: C$_{30}$H$_{19}$F$_3$N$_6$O$_9$Re$_2$S, *M* = 1068.97, orthorhombic, *PC*21*n*, *a* = 18.978 Å, *b* = 10.373 Å, *c* = 16.684 Å, α = 90.0°, *β* = 90.0°, *γ* = 90.0°, 293(2) K, *V* = 3284.4 Å$^3$, *Z* = 4, 23 194 reflections measured, 9828 independent ($R_{\text{int}}$ = 0.0396), R1 = 0.0534, wR2 = 0.0660 (all data).

and simple (metal-free) imidazoles has been observed previously, and it was attributed to the formation of hydrogen bonds between the imidazole N−H (a parent imidazole was used) and halide ligands.[36]

Compound **8** was fully characterized, including an X-ray structure determination (see Figure 3).[37] The cationic complex consists of two {Mo($\eta^3$-methallyl)(CO)$_2$(Im)(phen)} fragments linked by a {SnPh$_3$} unit. The Mo−N(imidazolate) distances [2.224(4) Å and 2.214(4) Å] are intermediate between the Mo−N(amine) [2.303(3) Å] and Mo−N(amide) [2.105(4) Å] bond distances found for the corresponding complexes of the analogous {Mo($\eta^3$-methallyl)(bipy)(CO)$_2$} fragment.[38] The tin atom is pentacoordinated with a fairly regular trigonal-bipyramidal configuration, with the three phenyl groups occupying the equatorial positions and an angle N3−Sn1−N23 = 177.3(2)°. The Sn−N(imidazolate) distances are almost identical [2.299(4) Å and 2.296(4) Å] and slightly shorter than the mean value (2.347 Å) found for the Sn−N bond distance for other tin(IV) imidazole adducts (without taking into account their coordination numbers and chemical nature).[39] The bond distances and angles within the imidazolate rings are very similar to each other and to those found in the structure of **5** (see above), showing the slight opening on the N−C−N angle as a consequence of the bridging coordination mode of these ligands. The spectroscopic data in solution are in agreement with the structure found in the solid state. The IR spectrum shows the expected $\nu_{CO}$ pattern for a *cis*-{Mo$^{II}$(CO)$_2$} fragment, and the $^1$H NMR spectrum show the signals corresponding to two equivalent {Mo($\eta^3$-methallyl)(CO)$_2$(Im)(phen)} fragments per bridging {SnPh$_3$} group.

## Conclusions

In summary, we have synthesized the first organometallic complexes with terminal imidazolato ligands by deprotonation of stable, easily prepared, cationic imidazole complexes. Topological analysis of the experimental electron density and its Laplacian were used to provide information about the differences in the electron density between the imidazolato complexes and their imidazole precursors. The imidazolato complexes serve as metalloligands in the rational synthesis of homo- and heteronuclear compounds.

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**Supporting Information Available:** X-ray crystallographic data for compounds **1**, **3**, **5**, and **8** in CIF format, molecular structures and crystallographic data for compounds **1**, **3**, **5**, **7**, and **8**, and IR and NMR spectra of compounds **1**, **2a**, **3**, and **5**−**8**. This material is available free of charge via the Internet at http://pubs.acs.org. The atomic coordinates for these structures have been deposited with the Cambridge Crystallographic Data Centre. The coordinates (CCDC 735954, 735955, 735956, and 735957 for compounds **1**, **3**, **5**, and **8**, respectively) can be obtained, upon request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.

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(36) (a) Pettinari, C.; Marchetti, F.; Pellei, M.; Cingolani, A.; Barba, L.; Cassetta, A. *J. Organomet. Chem.* **1996**, *515*, 119. (b) Pettinari, C.; Pellei, M.; Miliani, M.; Cingolani, A.; Cassetta, A.; Barba, L.; Pifferi, A.; Rivarola, E. *J. Organomet. Chem.* **1998**, *553*, 345.

(37) Selected crystallographic data for **8**: $C_{92}H_{63}BF_{24}Mo_2N_8O_4Sn$, $M$ = 2140.88, monoclinic, $P21/c$, $a$ = 13.685(5) Å, $b$ = 19.135(5) Å, $c$ = 35.816(5) Å, α = 90.0°, $\beta$ = 108.895(5)°, $\gamma$ = 90.0°, 293(2) K, $V$ = 8915(4) Å$^3$, $Z$ = 4, 16 798 reflections measured, 16 259 independent, R1 = 0.0807, wR2 = 0.1675 (all data).

(38) Morales, D.; Pérez, J.; Riera, L.; Riera, V.; Miguel, D.; Mosquera, M. E. G.; García-Granda, S. *Chem.—Eur. J.* **2003**, *9*, 4132.

(39) See ref [36] and references cited therein.