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# Two New Imidazole-Based Heteroscorpionate Ligands

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**Keywords:** Ligand design / Rhenium / Ruthenium / Nitrogen heterocycles / Tripodal ligands / Heteroscorpionate

The syntheses of two novel imidazole-based *N*,*N*,*O* and *N*,*N*,*S* ligands, 2,2-bis(*N*-methylimidazol-2-yl)ethanol (Hbmie) and lithium bis(*N*-methylimidazol-2-yl)dithioacetate Li[bmidta], are described. The coordination properties of the two new ligands are studied by the synthesis of rhenium(I) and ruthenium(II) complexes. Single crystal X-ray diffraction analyses of Hbmie, Li[bmidta] together with bis(*N*-methylimidazol-2-yl)methane (bmim) and [Re(bmie)(CO)$_3$] are provided, too.



## Introduction

Facially coordinating heteroscorpionate ligands such as bis(pyrazol-1-yl)acetic acid (Hbpza) or bis(3,5-dimethylpyrazol-1-yl)acetic acid (Hbdmpza) have found broad application both in coordination chemistry as well as in bioinorganic chemistry.[1] In bioinorganic model complexes these ligands mimic the 2-His-1-carboxylate motif of mononuclear non-heme iron oxygenases and zinc peptidases. Only a few tripodal, monoanionic *N*,*N*,*O* ligands with *N*-donor groups are known to mimic histidine more closely than pyrazoles such as imidazoles.[2,3] Approaches to synthesize the corresponding bis(*N*-methylimidazol-2-yl)acetic acid showed that this compound tends to decarboxylate. Thus, so far we and others focused on the synthesis of 3,3-bis(*N*-methylimidazol-2-yl)propionic acid (Hbmip).[3] By now several manganese(I), rhenium(I), copper(II), zinc(II), ferric and ferrous complexes derived from bmip have been reported.[3,4]

Pyrazole-based *N*,*N*,*O* ligands bearing an alcohol moiety such as bis(pyrazol-1-yl)ethanol (Hbpze) and bis(3,5-dimethylpyrazol-1-yl)ethanol (Hbdmpze) have been employed as enzyme models for gluzincins or molybdoenzymes such as the DMSO reductase.[5] Moreover, in the last decade the coordination chemistry of the early transition metals with bdmpze and related ligands as well as of bis(3,5-dimethylpyrazol-1-yl)dithioacetate has been studied intensely.[1,6] Furthermore, in a recent report by Reger and co-workers bis(pyrazol-1-yl)ethanols have been applied as building blocks for coordination polymers.[7] It is also noteworthy that chromium(III) complexes bearing bis(pyrazol-1-yl)ethanol and thioethanol ethers were recently recognized as highly selective ethylene trimerisation catalysts.[8] Herein, we report on the synthesis of bis(*N*-methylimidazol-2-yl)-ethanol (Hbmie), a tripodal *N*,*N*,*O* ligand containing a bis(*N*-methylimidazol-2-yl)methane core and an alcohol functionality as well as on the preparation of lithium bis(*N*-methylimidazol-2-yl)dithioacetate Li[bmidta].

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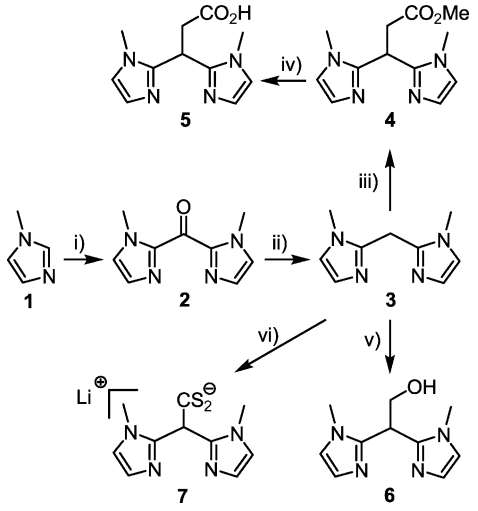
## Results and Discussion

Usually the synthesis of 3,3-bis(*N*-methylimidazol-2-yl)-propionic acid (Hbmip) (**5**) starts from bis(*N*-methylimidazol-2-yl)methane (bmim) (**3**). Following a procedure first reported by Braussaud et al. we synthesized compound **3** by reacting *N*-methylimidazole (**1**) with *n*BuLi and diethyl carbonate and subsequent Wolff–Kishner reduction of the resulting bis(*N*-methylimidazol-2-yl) ketone (bik) (**2**) (Scheme 1).[9] Deprotonation with *n*BuLi at the bridging methylene group followed by the reaction with methyl bromoacetate yields methyl 3,3-bis(*N*-methylimidazol-2-yl)propionate (Mebmip) (**4**), to give 3,3-bis(*N*-methylimidazol-2-yl)propionic acid (Hbmip) (**5**) after saponification and acidic workup (Scheme 1).[3,9]

In this work we chose a rather similar deprotonation of **3** with *n*BuLi followed by reaction with paraformaldehyde which afforded bis(*N*-methylimidazol-2-yl)ethanol (Hbmie) (**6**) after aqueous workup (Scheme 1). This sequence shows some analogy to the synthesis of bis(3,5-dimethylpyrazol-1-yl)ethanol (Hbdmpze) reported by Hammes and Carrano.[5a] The formation of the product is clearly indicated by NMR spectroscopy. Due to the $C_s$ symmetry of the compound in solution only two signals for the two spectroscopically equivalent imidazolyl rings are observed in the $^1$H NMR at $\delta$ = 6.75 ppm and 7.01 ppm. The ethanol building block gives rise to the two tripletts at $\delta$ = 4.97 (OH) and 4.48 ppm (bridging CH group) as well as to a virtual triplet at $\delta$ = 4.08 ppm ($CH_2$ group). The $^{13}$C{$^1$H} NMR spectrum




Scheme 1. Synthesis of Hbmie: i) 1. *n*BuLi, THF, –40 °C, 2. $CO(OEt)_2$, –80 °C; ii) KOH, $N_2H_4$, reflux; iii) 1. *n*BuLi, THF, –80 °C, 2. $BrCH_2CO_2Me$, –40 °C; iv) 1. NaOH (aq.), THF, reflux, 2. $H^+$; v) 1. *n*BuLi, THF, –40 °C, 2. paraformaldehyde, –60 °C, 3. $H_2O$; vi) 1. *n*BuLi, THF, –40 °C, 2. $CS_2$.

exhibits the $CH_2$ group at $\delta$ = 38.9 and the bridging CH at $\delta$ = 62.7 ppm. Hbmie (**6**) was fully characterized by single-crystal X-ray structure analysis, which shows the ligand to possess a geometry similar to the corresponding bis(pyrazol-1-yl)acetic acids or bis(pyrazol-1-yl)ethanols (Figure 1).

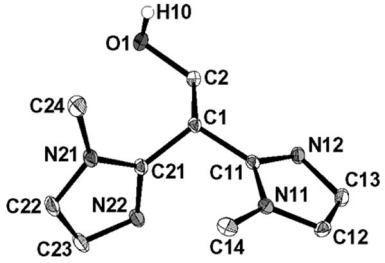



Figure 1. Molecular structure of Hbmie (**6**); thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms, apart from H10, have been omitted for clarity. Selected bond lengths [Å] and angles [°]: C1–C11 1.505(2), C1–C21 1.501(2), C1–C2 1.535(2), C2–O1 1.4155(2), C11–C1–C21 111.4(1).

As an important feature for a comparable application in organometallic chemistry compound **6** is satisfyingly soluble in common organic solvents such as $CH_2Cl_2$ and THF.

The reaction of bmim (**3**) with *n*BuLi and $CS_2$ results in lithium bis(*N*-methylimidazol-2-yl)dithioacetate (Li[bmidta]) (**7**) (Scheme 1). The $^1H$ and $^{13}C\{^1H\}$ NMR spectra of **7** exhibit one set of signals for the imidazole rings as expeced for a $C_s$ symmetrical molecule. The $^{13}C\{^1H\}$ NMR signal of the $CS_2^-$ moiety has been observed at $\delta$ = 249.1 ppm. The IR resonances of this dithioacetate functionality [1030 $\nu_{as}$(C=S) and 840 $\nu_s$(C–S) $cm^{-1}$] is assigned according to the values of the analogous bis(3,5-dimethylpyrazol-1-yl)dithioacetate [1081 $\nu_{as}$(C=S) and 879 $\nu_s$(C–S) $cm^{-1}$] and bis(3,5-diphenylpyrazol-1-yl)dithioacetate [1078 $\nu_{as}$(C=S) and 831 $\nu_s$(C–S) $cm^{-1}$] reported by Otero.[6b]

Crystals suitable for X-ray structure determination were obtained on attempted (but because of partial decomposition largely unsuccessfull) recrystallization of **7** from hot methanol. The molecular structure exhibits the composition Li[bmidta] × bmim (Figure 2) in which $Li^+$ coordinates two imidazole rings of a bmidta anion and two more of a bmim molecule, which was probably formed by decomposition of **7** in hot methanol (see before). Unfortunately, the structure is slightly disordered with bmidta and bmim partly sharing common positions (occupancies 85:15). Therefore, the molecular structure will not be discussed in detail.

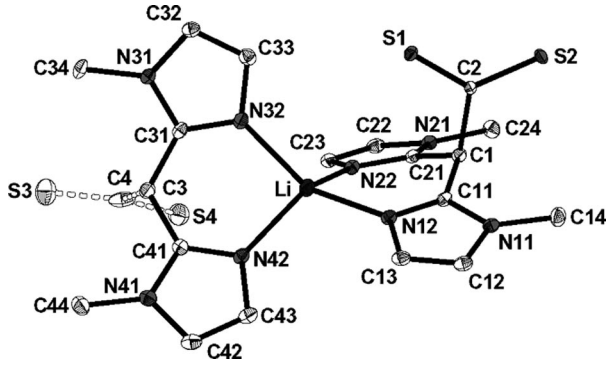



Figure 2. Molecular structure of Li[bmidta] (**7**) × bmim; thermal ellipsoids are drawn at the 50% probability level; the 15% occupancy fraction of the disordered molecule is depicted with dashed bonds. Selected bond lengths [Å] and angles [°]: C1–C11 1.502(2), C1–C21 1.503(2), C1–C2 1.579(2), C2–S1 1.675(2), C2–S2 1.687(2), N12–Li 2.063(3), N22–Li 2.022(3), N32–Li 2.037(3), N42–Li 2.090(3), N12–Li–N22 90.67(13), N32–Li–N42 91.06(13).

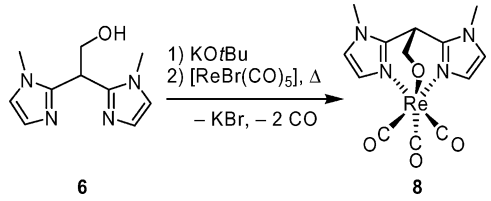
Nevertheless, the molecular structure of Li[bmidta] × bmim confirms the formation of the novel imidazole-based *N*,*N*,*S* heteroscorpionate ligand **7**.

Zinc-containing peptide deformylases (PDFs) from plants as well as from bacteria with ferrous cofactors bind metal ions through two histidines and a cysteine.[10] Thus, this new ligand class might represent a very good model for the metal-binding motif in PDFs.

Group VII metal complexes with several bis(pyrazol-1-yl)acetic and bis(imidazol-2-yl)propionic acids have been reported in literature.[3a,11] But to the best of our knowledge no manganese(I) or rhenium(I) complexes, bearing a bis(pyrazol-1-yl)ethanol or related imidazole-based alcoholate ligand, are reported so far. Thus, we focussed on the synthesis of [Re(bmie)$(CO)_3$] (**8**) in a first coordination experiment. Hence, similar to the synthetic procedure described for [Re(bmip)$(CO)_3$][3a] [$ReBr(CO)_5$] was treated with K[bmie] to give the tricarbonyl rhenium complex [Re(bmie)$(CO)_3$] (**8**) in moderate yield of 41% (Scheme 2).

The lower yield compared to that of [Re(bmip)$(CO)_3$] (yield: 72%[3a]) might arise from the fact, that **6** slowly decomposes, when heated in basic solution for longer times. However, purification of the compound could be accomplished by washing of the crude product with $CH_2Cl_2$. The coordination of bmie towards the rhenium(I) tricarbonyl fragment can be considered as prototype of the ligand's coordination properties in other metal complexes.




Scheme 2. Synthesis of [Re(bmie)(CO)$_3$] (**8**).

Furthermore, the carbonyl vibrations are sensitive probes to investigate the donor properties of the bmie. The IR spectrum of **8** shows the characteristic three carbonyl signals of a facial tricarbonyl complex at 1997 cm$^{-1}$, 1892 cm$^{-1}$, 1847 cm$^{-1}$ appropriate for A′, A′′ and the A′ signals, revealing the $C_s$ symmetry of the complex in solution as well as in solid state (Table 1). The carbonyl signals are shifted to lower wave numbers compared to the corresponding rhenium complexes of bmip and especially the bis(pyrazol-1-yl)acetato complexes, indicating a rather high electron-donating character of the bmie ligand. The $^{13}C\{^1H\}$ NMR of the complex shows two signals for the carbonyl carbon atoms at $\delta$ = 197.7 ppm and 198.9 ppm as well as one signal set for the imidazolyl rings supporting a $C_s$ symmetry of the complex with a $\kappa^3$-coordinated heteroscorpionate ligand.

Table 1. Selected IR signals of [ReL(CO)$_3$] (L = bmie, bpza, bdmpza and bmip.).

| Ligand L | bmie | bmip[3a] | bdmpza[11] | bpza[11] |
|---|---|---|---|---|
| $\tilde{\nu}$(CO) (CH$_3$OH) [ReL(CO)$_3$] | 2017, 1905, 1889 | 2023, 1914, 1896 | 2030, 1926, 1908 | – |
| $\tilde{\nu}$(CO) (KBr) [ReL(CO)$_3$] | 1997, 1892, 1847 | 2018, 1898, 1867 | 2023, 1915, 1903, 1883 | 2028, 1922, 1906, 1895 |

increasing donor strength of the ligand ←

Finally the molecular structure of the rhenium(I) complex [Re(bmie)(CO)$_3$] (**8**) proved the $\kappa^3$-coordination of the ligand (Figure 3). Surprisingly, analogous reactions employing K[bpze], K[bdmpze] or Li[bmidta] instead of K[bmie] did not lead to similar $\kappa^3$-coordinated rhenium(I) complexes.

Very recently Herrick and Ziegler reported on tris(2-pyridyl)methanol and tris(*N*-methylimidazol-2-yl)methoxymethane as tripodal ligands in the formation of tricarbonylrhenium complexes.[12] As a side reaction they observed the formation of OH-bridged dinuclear complexes.[12] Similar species have not been observed in our experiments so far. Imidazolyl donors exhibit σ donor, π donor and π acceptor properties.[3a] Thus, the bond lengths *d*(Re–C3) = 1.913(3) Å and *d*(Re–C5) = 1.905(3) Å are slightly longer than *d*(Re–C4) = 1.896(3) Å, due to the *trans* influence of the imidazolyl donors.

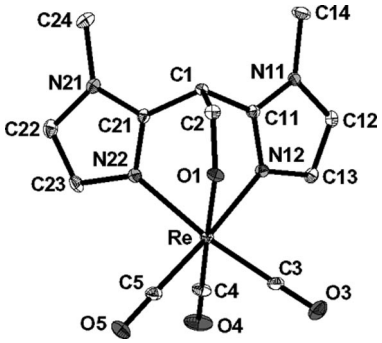
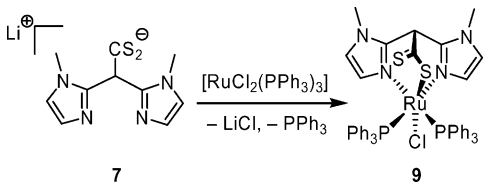



Figure 3. Molecular structure of [Re(bmie)(CO)$_3$] (**8**); thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Re–C3 1.913(3), Re–C4 1.896(3), Re–C5 1.905(3), Re–N12 2.174(2), Re–N22 2.175(3), Re–O1 2.121(2), C3–O3 1.152(4), C4–O4 1.161(4), C5–O5 1.166(4), C1–C2 1.569(4), C1–C11 1.493(4), C1–C21 1.500(4), O1–Re–N12 82.57(8), O1–Re–N22 81.80(9), N12–Re–N22 81.26(9), C3–Re–C4 88.62(14), C3–Re–C5 90.12(13), C4–Re–C5 85.82(13), O1–Re–C4 176.38(10).

It is noteworthy, that Santos and co-workers[13] reported in 2007 on the synthesis of some rhenium(I) and technetium(I) complexes bearing bis- and tris(pyrazol-1-yl)ethanol ethers. The technetium complexes showed to be potent radiotracers for myocardial perfusion imaging. Introduction of imidazole moieties instead of pyrazoles, might lead to interesting novel properties, such as a higher solubility of the complexes in water. As exemplified by [Re(bmie)(CO)$_3$] (**8**), bmie can coordinate tripodal to group VII metals. That makes **8** to a promising lead structure for the design of new myocardial imaging agents.

On the other hand the reaction of the ligand Li[bmidta] with [RuCl$_2$(PPh$_3$)$_3$] resulted in the formation of [Ru(bmidta)Cl(PPh$_3$)$_2$] (**9**) (Scheme 3). In recent years analogous ruthenium complexes derived from bis(pyrazol-1-yl)-acetic acids proved as quite versatile precursors for coordination chemistry and organometallics.[14] Complex **9** precipitates from the reaction mixture, crystallizing with 1 equiv. of THF and was spectroscopically characterised by $^1H$, $^{13}C\{^1H\}$ and $^{31}P$ NMR as well as elemental analysis and IR spectroscopy. As expected, the ruthenium(II) complex exhibits sharp signals in the NMR spectra. In the $^1H$ NMR spectrum, the imidazole protons, as well as the methyl groups are shifted high field, occurring at $\delta$ = 5.99 ppm and 6.03 ppm ($CH_{im}$), and 3.59 ($CH_3$) respectively, indicating the coordination of the ligand. The integration of the PPh$_3$ multiplett signal reasons the coordination of two phosphanes.




Scheme 3. Synthesis of [Ru(bmidta)Cl(PPh$_3$)$_2$] (**9**).

The appearance of one singlet signal in the $^{31}P$ NMR spectrum ($\delta$ = 36.4 ppm) and only one sharp set of signals for the imidazolyl moieties in the $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra, indicates again $C_s$ symmetry of the complex **9** with the phosphanes in *trans* position to the imidazolyl donors. We expected the dithiocarboxylate group (a soft base) to coordinate very strongly by one sulfur atom. Similar to the complexes reported by Cao and co-workers this should result in a significant high field shift of the $CS_2^-$ moiety in the $^{13}C\{^{1}H\}$ NMR spectrum.[15] Indeed the $CS_2^-$ carbon atom of the coordinated ligand appears at $\delta$ = 237.6 ppm, that of the uncoordinated ligand at $\delta$ = 249.1 ppm. But due to either the lability or insolubility of the complex in common organic solvents except $CH_2Cl_2$ and $CHCl_3$ and the insolubility of the ligand Li[bmidta] in the very same solvents, a direct comparison of the NMR spectroscopic data was not possible. Nevertheless, the IR data support the assumption of a tripodal, $\kappa^3$-coordination of the bmidta ligand towards the ruthenium(II) centre indicated by a significant shift of the $\nu_{as}$(C=S) from 1030 $cm^{-1}$ to 1016 $cm^{-1}$. An assignment of the symmetrical dithiocarboxylate vibration was not possible due to several imidazole or phenyl absorptions in the same region. Complex **9** exhibits high stability in solid state and can be stored under aerobic conditions for several days. Unfortunately, so far all efforts to obtain crystals suitable for X-ray structure determination failed, due to decomposition of complex **9**, when kept in solution. Studies regarding the decomposition products are in progress.

## Conclusions

Two novel tripodal, imidazole-based *N*,*N*,*O* and *N*,*N*,*S* ligands were obtained in a three-step synthesis starting from commercially available *N*-methylimidazole. The ligands bind in a $\kappa^3$-coordination mode to rhenium(I) or ruthenium(II). A comparison of their donor properties with those of bis(pyrazol-1-yl)acetic acids and bis(*N*-methylimidazol-2-yl)propionic acid indicated a strong electron-donating character of these ligands.

## Experimental Section

**General Remarks:** All experiments were carried out under nitrogen atmosphere using standard Schlenk techniques. All solvents (analytical-grade purity) were degassed and stored under nitrogen atmosphere. Reported yields refer to analytically pure substances and were not optimized. $^{1}H$ and $^{13}C\{^{1}H\}$ NMR spectra: Bruker DPX 300 AVANCE, $\delta$ values relative to the residual solvent signal. IR spectra: Varian Excalibur FTS-3500 FT-IR spectrometer, $CaF_2$ cuvett (d = 0.2 mm) or KBr matrix. Mass spectra: Jeol JMS-700 using FD technique with NBA as matrix. Elemental analysis: Elemental Analyser Euro EA 3000 Euro Vector instrument. X-ray structure determination: Bruker-Nonius Kappa. Bis(*N*-methylimidazol-2-yl)-keton (bik) (**2**), bis(*N*-methylimidazol-2-yl)methane (bmim) (**3**), $[ReBr(CO)_5]$ and $[RuCl_2(PPh_3)_3]$ were prepared according to published procedures.[9,16,17] All other chemicals were used as purchased.

**Synthesis of Hbmie (6):** A Schlenk flask was charged with bmim (**3**) (6.00 g, 34.0 mmol) and THF (300 mL) and *n*BuLi (21.3 mL, 1.6 M/hexane, 34.1 mmol) was added at –40 °C. The solution was stirred for 1 h, subsequently cooled to –60 °C and paraformaldehyde (2.04 g, 68.0 mmol) was added. The reaction mixture was warmed to ambient temperature and stirred for 2 d. All volatiles were removed in vacuo and the reaction was quenched by addition of $CHCl_3$ (400 mL) and water (5 mL). The mixture was dried with $Na_2SO_4$ and solvents were removed. The white residue was washed with cold $CH_2Cl_2$ (5 × 5 mL) and dried in vacuo to give a white powder (4.30 g, 20.8 mmol, 61%); m.p. 170 °C (dec.). $^{1}H$ NMR ([D$_6$]DMSO): $\delta$ = 3.43 (s, 6 H, $CH_3$), 4.08 (vt, $^{3}J_{H,H}$ = 5.8, $^{3}J_{H,H}$ = 6.7 Hz, 2 H, $CH_2$), 4.48 (t, $^{3}J_{H,H}$ = 7.1 Hz, 1 H, $CH_{bridge}$), 4.97 (t, $^{3}J_{H,H}$ = 5.6 Hz, 1 H, OH), 6.75 (d, $^{3}J_{H,H}$ = 0.5 Hz, 2 H, $CH_{im}$), 7.01 (br. s, 2 H, $CH_{im}$) ppm. $^{13}C\{^{1}H\}$ NMR ([D$_6$]DMSO): $\delta$ = 32.2 ($CH_3$), 38.9 ($CH_2$), 62.7 ($CH_{brigde}$), 121.6 ($CH_{im}$), 126.1 ($CH_{im}$), 145.5 ($C_{im}$) ppm. IR ($CH_2Cl_2$): $\tilde{\nu}$ = 3315 (w), 3200 (w), 3117 (w), 3047 (m), 2955 (m), 1493 (s), 1281 (s), 1056 (s) $cm^{-1}$. IR (KBr): $\tilde{\nu}$ = 3315 (s), 3215 (s), 2949 (sh), 1494 (s), 1285 (m), 1136 (m), 1072 (s), 1998 (m), 774 (s) $cm^{-1}$. FD MS (MeOH): *m*/*z* (%) = 207 (100) [$MH^+$], 177 (65) [bmim$H^+$]. $C_{10}H_{14}N_4O$ (206.24 g mol$^{-1}$): calcd. C 58.24, H 6.84, N 27.17; found C 58.23, H 6.86, N 27.20.

**Synthesis of [Re(bmie)(CO)$_3$] (8):** Hbmie (**6**) (100 mg, 0.485 mmol) was dissolved in THF (15 mL). After deprotonation with KO*t*Bu (50.0 mg, 0.446 mmol) the reaction mixture was stirred for 1 h at ambient temperature whereas a pale yellow precipitate formed. $[ReBr(CO)_5]$ (160 mg, 0.394 mmol) was added and the suspension was heated to reflux overnight. The solvent was removed in vacuo and the residue was washed with degassed water (20 mL) and $CH_2Cl_2$ (3 × 2 mL). Drying in vacuo yielded an off white powder (76.0 mg, 0.160 mmol, 41%); m.p. 270 °C (dec.). $^{1}H$ NMR ([D$_4$]-MeOH): $\delta$ = 3.58 (d, $^{3}J_{H,H}$ = 2.0 Hz, 2 H, $CH_2$), 3.85 (s, 6 H, $CH_3$), 5.02 (t, $^{3}J_{H,H}$ = 1.9 Hz, 1 H, $CH_{bridge}$), 7.14 (d, $^{3}J_{H,H}$ = 1.5 Hz, 2 H, $CH_{im}$), 7.23 (d, $^{3}J_{H,H}$ = 1.6 Hz, 2 H, $CH_{im}$) ppm. $^{13}C\{^{1}H\}$ NMR ([D$_4$]MeOH): $\delta$ = 34.1 ($CH_3$), 37.1 ($CH_2$), 60.2 ($CH_{brigde}$), 123.4 ($CH_{im}$), 130.9 ($CH_{im}$), 145.8 ($C_{im}$), 197.7 (CO), 198.9 (CO) ppm. IR (methanol): $\tilde{\nu}$ = 2017 [s, $\nu$(CO)], 1905 [s, $\nu$(CO)], 1889 [s, $\nu$(CO)], 1513 (w) $cm^{-1}$. IR (KBr): $\tilde{\nu}$ = 3445 [m, $\nu$(OH)], 1997 [s, $\nu$(CO)], 1892 [s, $\nu$(CO)], 1847 [s, $\nu$(CO)], 1633 (w), 1511 (m), 1290 (w), 1180 (w), 1062 (w) $cm^{-1}$. FD MS (MeOH): *m*/*z* (%) = 891 (45) [(2 × M – 2 CO)$^+$], 477 (100) [$MH^+$], 447 (60) [MH – CO]$^+$. $C_{13}H_{13}N_4O_4Re{\cdot}H_2O$ (475.47 g mol$^{-1}$): calcd. C 31.64, H 3.06, N 11.35; found C 31.78, H 2.89, N 11.06.

**Synthesis of Li[bmidta] (7):** A Schlenk flask was charged with bmim (**3**) (5.00 g, 28.4 mmol) and THF (200 mL) and cooled to –40 °C and *n*BuLi (17.7 mL, 1.6 M in *n*-hexane, 28.3 mmol) was slowly added. The solution was stirred for 1 h at –40 °C. Subsequently $CS_2$ (2.06 mL, 2.60 g, 34.1 mmol) was added dropwise by syringe. The reaction mixture was warmed to ambient temperature overnight and all volatiles were removed in vacuo. The residue was washed with THF (3 × 20 mL) and dried in vacuo, yielding an orange powder (6.48 g, 25.1 mmol, 89%); m.p. 203 °C (dec.). $^{1}H$ NMR ([D$_6$]DMSO): $\delta$ = 3.66 (s, 6 H, $CH_3$), 5.66 (s, 1 H, $CH_{bridge}$), 6.65 (br. s, 2 H, $CH_{im}$), 6.94 (br. s, 2 H, $CH_{im}$) ppm. $^{13}C\{^{1}H\}$ NMR ([D$_6$]DMSO): $\delta$ = 33.4 ($CH_3$), 62.7 ($C_{brigde}$), 120.9 ($C_{im}$), 125.4 ($C_{im}$), 146.9 ($C_{im}$), 249.1 ($CS_2$) ppm. IR (KBr): $\tilde{\nu}$ = 3420 (w), 3127 (w), 1526 (w), 1501 (s), 1471 (w), 1282 (m), 1256 (m), 1177 (m), 1155 (m), 1131 (m), 1086 (w), 1030 [s, $\nu_{as}$(C = S)], 1017 (m), 994 (s), 944 (m), 840 (m), 776 (m), 751 (m), 660 (w), 473 (w) $cm^{-1}$. $C_{10}H_{11}LiN_4S_2$ (258.29 g mol$^{-1}$): calcd. C 46.50, H 4.29, N 21.69, S 24.83; found C 46.51, H 4.31, N 21.41, S 24.08.

**Synthesis of [Ru(bmidta)Cl(PPh$_3$)$_2$] (9):** Lithium bis(*N*-methylimidazol-2-yl)dithioacetate Li[bmidta] (**7**) (259 mg, 1.00 mmol) was

Table 2. Details of the structure determination for **6**, **7**× bmim and **8**.

| | **6** | **7**× bmim | **8** |
|---|---|---|---|
| Empirical formula | $C_{10}H_{14}N_4O \times H_2O$ | $C_{19}H_{23}LiN_8S_2$ | $C_{13}H_{13}N_4O_4Re$ |
| Formula mass | 224.27 | 434.51 | 475.47 |
| Crystal colour/habit | colourless plate | orange plate | pale yellow plate |
| Crystal system | monoclinic | monoclinic | triclinic |
| Space group | $P2_1/n$ | $Pc$ | $P\bar{1}$ |
| $a$ [Å] | 7.4297(5) | 9.4278(7) | 7.8701(2) |
| $b$ [Å] | 19.3827(13) | 7.7758(6) | 9.0959(10) |
| $c$ [Å] | 8.1557(5) | 14.5248(10) | 11.2096(9) |
| $\alpha$ [°] | 90 | 90 | 85.533(8) |
| $\beta$ [°] | 106.377(4) | 102.843(6) | 76.987(5) |
| $\gamma$ [°] | 90 | 90 | 67.707(4) |
| $V$ [Å$^3$] | 1126.83(13) | 1038.16(13) | 723.38(10) |
| $\theta$ [°] | 3.04–29.01 | 2.99–29.01 | 2.86–29.5 |
| $h$ | –10 to 10 | –12 to 12 | –10 to 10 |
| $k$ | –26 to 26 | –10 to 10 | –12 to 12 |
| $l$ | –11 to 11 | –19 to 19 | –15 to 15 |
| $F$(000) | 480 | 456 | 452 |
| $Z$ | 4 | 2 | 2 |
| $\mu$ (Mo-$K_\alpha$) [mm$^{-1}$] | 0.095 | 0.428 | 8.423 |
| Crystal size [mm] | 0.28 × 0.16 × 0.04 | 0.30 × 0.29 × 0.05 | 0.21 × 0.16 × 0.06 |
| $D_{calcd.}$ [g cm$^{-3}$], $T$ [K] | 1.322, 150(2) | 1.39, 100(2) | 2.183, 150(2) |
| Reflections collected | 24953 | 27352 | 24985 |
| Indep. reflections | 2994 | 5463 | 4023 |
| Obsd. reflections ($I > 2\sigma I$) | 2242 | 5066 | 3689 |
| Parameter | 154 | 306 | 199 |
| Weight parameter $a$, $b$ | 0.0626, 0.3020 | 0.0386, 0.2588 | 0.0247, 0.1510 |
| $R_1$ (obsd.) | 0.0440 | 0.0296 | 0.0166 |
| $R_1$ (overall) | 0.0686 | 0.0346 | 0.0213 |
| $wR_2$ (obsd.) | 0.1064 | 0.0728 | 0.0464 |
| $wR_2$ (overall) | 0.1198 | 0.0748 | 0.0476 |
| Diff. peak/hole [e/Å$^3$] | 0.258/–0.22 | 0.287/–0.206 | 0.881/–1.010 |

stirred with $[RuCl_2(PPh_3)_3]$ (959 mg, 1.00 mmol) in THF (5 mL). After 10 min an orange product precipitated, which was filtered of and dried in vacuo, yielding a bright orange powder (282 mg, 0.286 mmol, 29%); m.p. 123 °C (dec.). $^1$H NMR ($CDCl_3$): $\delta$ = 1.79 (m, 4 H, THF), 3.59 (s, 6 H, $CH_3$), 3.67 (m, 4 H, THF), 5.99 (br. s, 2 H, $CH_{im}$), 6.03 (br. s, 3 H, $CH_{im}$, $CH_{bridge}$), 6.93–7.29 (m, 30 H, $PPh_3$) ppm. $^{13}$C{$^1$H} NMR ($CDCl_3$): $\delta$ = 25.7 (THF), 33.7 ($CH_3$), 61.0 ($CH_{brigde}$), 68.1 (THF), 119.1 ($C_{im}$), 127.3 (vt, $^3J_{C,P}$ = 4.2 Hz, *m*-$PPh_3$), 128.9 (*p*-$PPh_3$), 131.4 ($C_{im}$), 135.0 (vt, $^3J_{C,P}$ = 4.5 Hz, *o*-$PPh_3$), 135.3, 135.8 (d, $^3J_{C,P}$ = 38.4 Hz, *i*-$PPh_3$), 141.6 ($C_{im}$), 237.6 ($CS_2^-$) ppm. $^{31}$P NMR ($CDCl_3$): $\delta$ = 36.40 ppm. IR (KBr): $\tilde{\nu}$ = 3430 (w), 3142 (w), 3053 (w), 1507 (s), 1481 (w), 1433 (m), 1282 (m), 1261 (m), 1286 (w), 1261 (w), 1086 (m), 1016 [s, $\nu_{as}$(C=S)], 846 (w), 743 (m), 696 (s), 522 (s), 416 (w) cm$^{-1}$. $C_{46}H_{41}ClN_4P_2RuS_2 \cdot$THF (984.55 g mol$^{-1}$): calcd. C 61.00, H 5.02, N 5.69, S 6.51; found C 60.71, H 5.07, N 5.59, S 6.23.

**X-ray Structure Determinations:** Single-crystals of **6** were obtained by slow evaporation of a saturated solution of the compound in $CH_2Cl_2$. Crystals of **7** were grown by recrystallization from hot MeOH. Crystals of **8** suitable for X-ray structure analysis were deposited upon layering a solution of the complex in MeOH with $Et_2O$. Single crystals of **6, 7**× bmim and **8** were mounted with perfluorinated ether on a glass fibre. A Bruker–Nonius Kappa CCD was used for data collection (graphite monochromator, Mo-$K_\alpha$ radiation, $\lambda$ = 0.71073 Å). The structures were solved by using direct methods and refined with full-matrix least-squares against $F^2$ {SHELX-97}.[18] A weighting Scheme was applied in the last steps of the refinement with $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = [2F_c^2 + \max(F_o^2,0)]/3$. The OH proton in **6** was found and refined free. All the other hydrogen atoms were included in their calculated positions and refined in a riding model. The molecular structure of **7** was disordered with occupancies of the two different dithioacetate positions of 85:15. Thus, only a refinement in *Pc* instead of *P*2/*c* was possible. All details and parameters of the measurements are summarised in Table 2. The structures were visualized with Diamond 2.1e.[19]

CCDC-723078 (for **6**) -728290 (for **7**× bmim) and -723079 (for **8**) contain the supplementary crystallographic data. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

**Supporting Information** (see also the footnote on the first page of this article): $^1$H, $^{13}$C and $^{31}$P NMR spectra of [Ru(bmidta)Cl-$(PPh_3)_2$] (**9**).

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