Metal-induced tautomerization of oxazole and thiazole molecules to heterocyclic carbenes†

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Oxazole and thiazole molecules *N*-coordinated to manganese(I) are transformed into their corresponding 2,3-dihydrooxazol-2-ylidene and 2,3-dihydrothiazol-2-ylidene carbene tautomers by acid–base reactions, and subsequently transmetalated to gold(I), *via* isolable heterometallic intermediates.
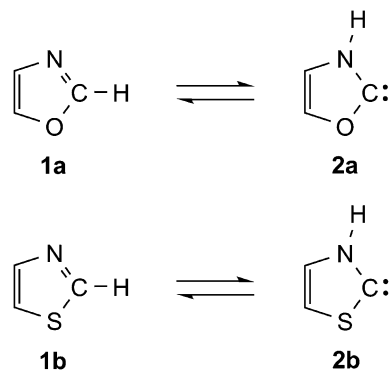
Oxazole (**1a**) and thiazole (**1b**) are simple molecules of great relevance in heterocyclic chemistry and important structural elements in many natural products.[1] Their corresponding carbene tautomers, 2,3-dihydrooxazol-2-ylidene (**2a**) and 2,3-dihydrothiazol-2-ylidene (**2b**), derived from a 1,2-hydrogen shift (Scheme 1) are not stable, and this has been rationalized on the base of theoretical calculations,[2] deuterium exchange NMR measurements[3] and argon matrix experiments.[4] On the other hand, whereas a large number of NHC complexes of imidazol-2-ylidene type are known,[5] many of them successfully applied in homogeneous catalysis,[6] relatively few examples of coordination complexes containing carbene ligands of oxazol-2-ylidene or thiazol-2-ylidene types have been described. Methods for preparing oxazol-2-ylidene carbene complexes are limited to intramolecular cyclization of functionalized hydroxy isocyanides[7] or reaction of epoxides with hydrogen isocyanide complexes,[8] the classical route involving *in situ* deprotonation of oxazolium salts being very infrequently encountered in the literature.[9] A rare case of cyclization of ketones with coordinated isocyanide has been described.[10] Thiazol-2-ylidene carbene complexes are frequently prepared by reaction of lithiated thiazoles with the appropriate metallic fragment and subsequent alkylation or protonation of the corresponding thiazolyl derivative.[11] Methods implying *in situ* deprotonation of thiazolium salts have also been used.[12] Whereas complexes containing carbene **2b** are known,[11b] to the best of our knowledge, so far there has been no report of a complex containing the oxazolin-2-ylidene carbene **2a** itself. We have recently reported that coordinated imidazoles can be transformed into their corresponding NHC complexes by means of acid–base treatments.[13] We have now found that this methodology can be applied to oxazole (**1a**) and thiazole (**1b**) molecules coordinated to manganese(I), which can easily be converted to oxazolin-2-ylidene (**2a**) and thiazolin-2-ylidene (**2b**) ligands, respectively. Preliminary results on the use of

these complexes as carbene transfer agents are also shown herein.

Azoles **1a,b** easily coordinate to Mn(I) when reacting with the precursor complex *fac*-[Mn(OClO₃)(CO)₃(bipy)] (**3**) to afford the cationic complexes **4a,b** (Scheme 2). As can be seen in the X-ray diffraction study carried out on **4b** (Fig. 1),‡ the azole ligands in these complexes are *N*-coordinated. **4a,b** are readily deprotonated at the C2 carbon atom of the azole heterocycle when treated with K^{t}OBu to afford neutral derivatives **5a,b** containing oxazolyl and thiazolyl ligands. Subsequent protonation at the nitrogen atom gives the carbene complexes **6a,b** in quantitative yields, completing the metal and acid–base induced tautomerization of the original azole molecules **1a,b**. It should be mentioned that a low yield transformation of methylthiazole and benzothiazole chromium complexes into *N*-alkyl thiazolin-2-ylidene carbenes, involving deprotonation of the coordinated azole by LiBu and subsequent alkylation, had been previously described,[11c,d] although the experimental approach did not appear to be selective.

Transformation of compounds **4a,b** into **6a,b** according to Scheme 2 was monitored by IR spectroscopy (see ESI†). This showed a strong shift to low frequencies (about 30 cm^{-1} on average) in the νCO bands on passing from **4a,b** to **5a,b**, and a new change to high frequencies when forming **6a,b** after protonation. The stronger donor character of the azolin-2-ylidene ligands with respect to the azole tautomers is evidenced by the lower values of the νCO bands of **6a,b** with respect to **4a,b**.

Amongst the spectroscopic data of compounds **6a,b** (ESI†) it is worth noting the low field singlet signal appearing in the ^{13}C{^{1}H} NMR at 216.8 (**6a**) and 225.5 ppm (**6b**) corresponding to the carbene carbon atom. Fig. 2 shows the crystal structure of the cationic complex **6b**, allowing a comparison with that of


Scheme 1 Tautomerization of oxazole (**1a**) and thiazole (**1b**) molecules to 2,3-dihydrooxazol-2-ylidene (**2a**) and 2,3-dihydrothiazol-2-ylidene (**2b**) carbenes, respectively.

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† Electronic supplementary information (ESI) available: Experimental details and analytical and spectroscopic data. CCDC 716673 (**4b**), 716674 (**6b**), 716675 (**7b**) and 716676 (**8b**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b900955h
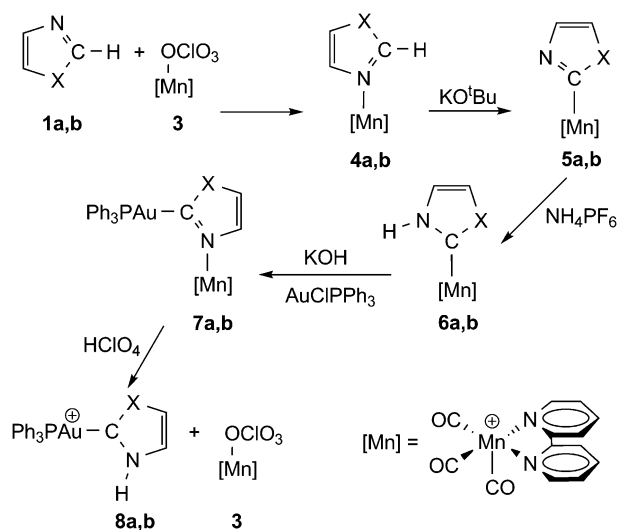
Scheme 2 Formation of azolin-2-ylidene carbene complexes of Mn(I) **6a,b** and subsequent transmetalation process to afford Au(I) carbene complexes **8a,b**.
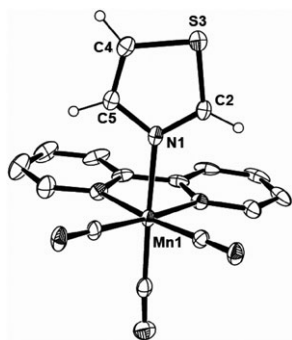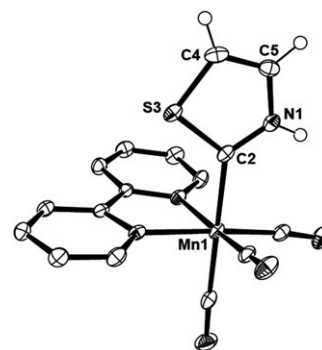

Fig. 1 Molecular structure of the complex **4b**, shown with 30% thermal ellipsoids. Hydrogen atoms of the bipy ligand are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mn1–N1 = 2.074(4), N1–C2 = 1.321(6), C2–S3 = 1.691(5), S3–C4 = 1.705(5), C4–C5 = 1.361(7), C5–N1 = 1.380(6); Mn1–N1–C2 = 124.3(3), Mn1–N1–C5 = 124.9(3), N1–C2–S3 = 114.5(3), C2–S3–C4 = 90.3(2), S3–C4–C5 = 110.2 (4), C4–C5–N1 = 114.3(4), C5–N1–C2 = 110.7(4).

4b (Fig. 1). The Mn–C2 (2.024(2) Å) bond length in **6b** is appreciably shorter than the Mn–N1 (2.074(4) Å) distance in **4b**, in consonance with the stronger donor character of the carbene ligand already showed in the IR data of these complexes (see above). The bond lengths and angles within the azole heterocycle are similar in both complexes, though it should be pointed out that C5–N1–C2 and S3–C2–N1 bond angles in the thiazole cycle are smaller when this features N1- (**4b**) and C2-coordination (**6b**), respectively.

Complexes **6a,b** can be used as carbene transfer agents from manganese to gold, in such a way that allows the isolation of heterometallic intermediates. Thus, treatment of dichloro-methane solutions of **6a,b** with a stoichiometric amount of [AuClPPh₃] in the presence of KOH yields complexes **7a,b** after 1 h of stirring at room temperature (see ESI for full experimental details†).

Complexes **7a,b** contain oxazolyl and thiazolyl bridging ligands, respectively, which are C-coordinated to gold and
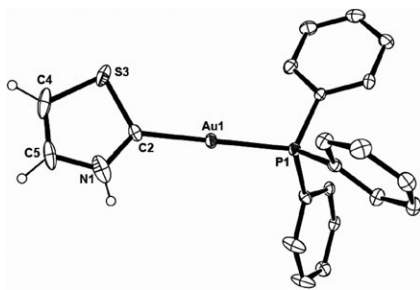

Fig. 2 Molecular structure of the complex **6b**, shown with 50% thermal ellipsoids. Hydrogen atoms of the bipy ligand are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mn1–C2 = 2.024(2), C2–N1 = 1.333(2), N1–C5 = 1.387(2), C4–C5 = 1.339(3), S3–C4 = 1.726(2), C2–S3 = 1.720(2); Mn1–C2–N1 = 128.7(1), Mn1–C2–S3 = 124.9(1), C2–N1–C5 = 118.3(2), N1–C5–C4 = 111.8(2), S3–C4–C5 = 109.6(1), C2–S3–C4 = 93.9(9), N1–C2–S3 = 106.4(1).

N-coordinated to manganese, leading uncoordinated oxygen and sulfur heteroatoms. The preference of Au(I) metal ion, which is softer than Mn(I), to bind carbene carbon atom instead of nitrogen atom appears to be the driving force for generating these heterometallic species, which can also be considered as *N*-metalated azolin-2-ylidene carbene complexes of gold(I). In the case of **7b** an X-ray diffraction study has been undertaken (Fig. 3), confirming the proposed structure for this intermediate species. The Mn–N1 bond length (2.095(2) Å) in **7b** is slightly longer than that in the precursor thiazole complex **4b** (2.074(4) Å), suggesting some weakening of that bond in the heterometallic intermediate, which anticipates the loss of the manganese fragment in the hydrolysis of the complex. Thus, the treatment of **7b** with HClO₄ in CH₂Cl₂ as solvent affords the gold(I) carbene complex **8b** (Scheme 2), together with the starting manganese(I) complex *fac*-[Mn(OClO₃)(CO)₃(bipy)]
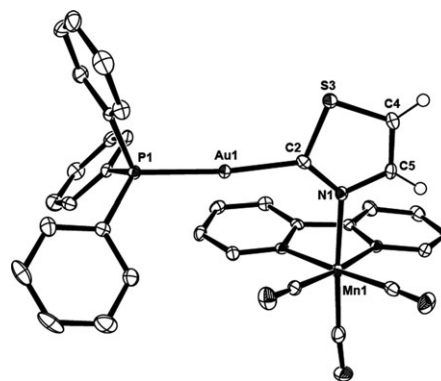
Fig. 3 Molecular structure of the complex **7b**, shown with 50% thermal ellipsoids. Hydrogen atoms of the bipy and PPh₃ ligands are omitted for clarity. Selected interatomic distances (Å) and angles (deg): Mn1–N1 = 2.095(2), N1–C5 = 1.390(4), N1–C2 = 1.336(4), C2–S3 = 1.742(3), S3–C4 = 1.702(3), C4–C5 = 1.348(4), C2–Au1 = 2.040(3), Au1–P1 = 2.301(9); Mn1–N1–C2 = 129.5(2), Mn1–N1–C5 = 117.7(2), C2–N1–C5 = 112.6(3), N1–C5–C4 = 115.6(3), N1–C2–S3 = 110.2(2), C2–S3–C4 = 92.4(2), S3–C4–C5 = 109.2(2), N1–C2–Au1 = 132.9(2), S3–C2–Au1 = 116.9(2), C2–Au1–P1 = 176.4(9).

Fig. 4 Molecular structure of complex **8b**, shown with 30% thermal ellipsoids (only the major disorder component is shown). Hydrogen atoms of the bipy and PPh₃ ligands are omitted for clarity. Selected interatomic distances (Å) and angles (deg): C2–Au1 = 2.031(7), C2–N1 = 1.312(19), C2–S3 = 1.714(8), S3–C4 = 1.715(11), C4–C5 = 1.348(17), N1–C5 = 1.370(20), Au1–P1 = 2.283(1); C2–Au1–P1 = 177.6(3), Au1–C2–N1 = 127.6(1), Au1–C2–S3 = 124.1(4), N1–C2–S3 = 108.3(1), C2–S3–C4 = 91.9(5), S3–C4–C5 = 111.0(6), C4–C5–N1 = 110.5(1), C2–N1–C5 = 118.2(2).

(**3**), completing the transmetalation process of carbene **2b** from manganese to gold.[14] The crystal structure of **8b** (Fig. 4) shows no significant differences in the structural parameters of the heterocyclic carbene with respect to those in complex **7b**.

In conclusion, we report herein an experimental approach for the synthesis of oxazolin-2-ylidene and thiazolin-2-ylidene carbene complexes of manganese(I) involving tautomerization of the corresponding oxazole and thiazole heterocycles mediated by the metal center. The new carbene ligands can be transferred to gold(I) through isolable heterometallic intermediates. Experiments aiming to make use of complexes **6a,b** as carbene transfer agents to other metallic centers are currently in progress in our laboratory.

Notes and references

‡ Crystal data for **4b**: C₁₇H₁₃Cl₃MnN₃O₇S, M = 564.66, monoclinic, $P2_1/n$, a = 10.1874(5), b = 12.8131(5), c = 16.3439(7) Å, β = 93.621(2)°, V = 2129.15(16) Å³, Z = 4, T = 100(2) K, 33 014 measured reflections, 3647 independent reflections (R_{int} = 0.0672), $R1$ = 0.0755, w$R2$ = 0.2284 (all data). **6b**. C₁₆H₁₁F₆MnN₃O₃PS, M = 525.25, triclinic, $P\bar{1}$, a = 8.6199(3), b = 10.0390(3), c = 11.5074(3) Å, α = 78.487(1), β = 80.485(2), γ = 84.597(2)°, V = 960.41(5) Å³, Z = 2, T = 100(2) K, 15 455 measured reflections, 3416 independent reflections (R_{int} = 0.0275), $R1$ = 0.0338, w$R2$ = 0.0648 (all data). **7b** C₃₄H₂₅AuF₆MnN₃O₃P₂S, M = 983.48, triclinic, $P\bar{1}$, a = 11.0938(3), b = 11.4700(4), c = 15.1096(5) Å, α = 94.041(2), β = 101.191(2), γ = 112.355(2)°, V = 1722.13(10) Å³, Z = 2, T = 100(2) K, 57 416 measured reflections, 6738 independent reflections (R_{int} = 0.0305), $R1$ = 0.0398, w$R2$ = 0.0519 (all data). **8b** C₂₁H₁₈AuClNO₄PS, M = 643.81, monoclinic, $P2_1/n$, a = 9.7030(3), b = 16.6091(6), c = 13.9180(4) Å, β = 101.338(2)°, V = 2199.22(12) Å³, Z = 4, T = 100(2) K, 57 620 measured reflections, 4051 independent reflections (R_{int} = 0.0314), $R1$ = 0.0516, w$R2$ = 0.0658 (all data).

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14 The oxazolin-2-ylidene carbene complex of gold(I) **8a** is formed from **7a** in a similar way, as detected by NMR spectroscopy, through in this case purification of the compound was not feasible owing to the appearance of variable amounts of secondary products.