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N-Heterocyclic Carbenes

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Westfälische Wilhelms-Universität, Münster, Germany

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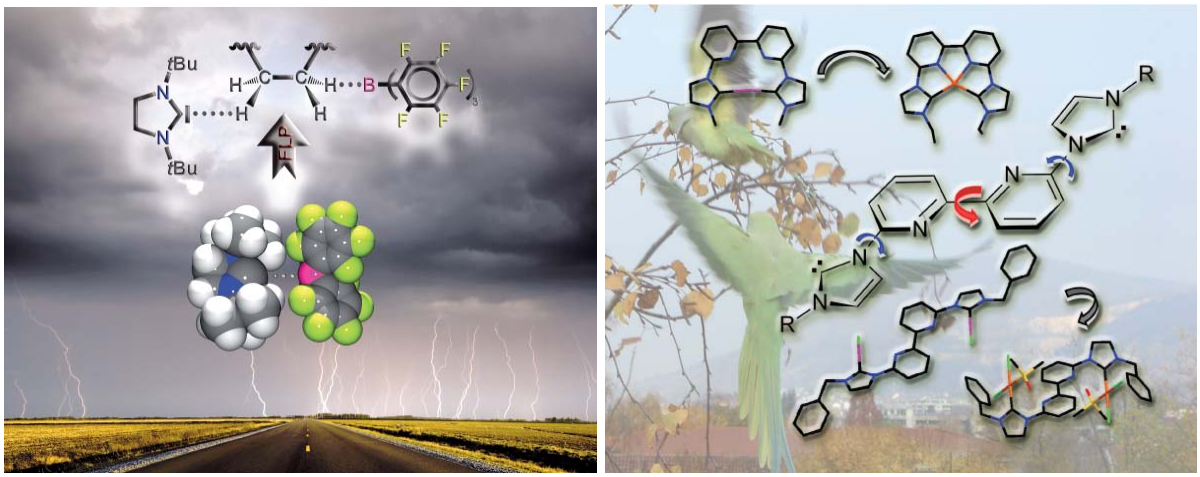

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NHC–manganese(I) complexes as carbene transfer agents†

Javier Ruiz,* Ángela Berros, Bernabé F. Perandones and Marilín Vivanco

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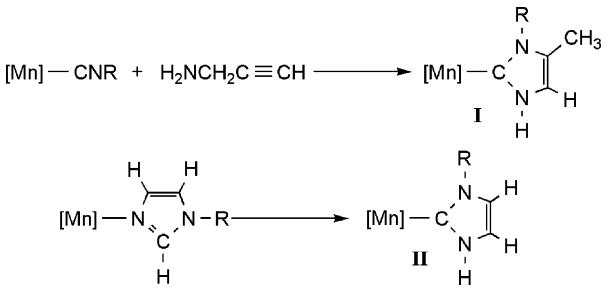
Tautomerization of coordinated azoles to their corresponding *N*-heterocyclic carbenes (NHCs) has been carried out by reaction of complexes *fac*-$[Mn(L)(CO)_3(dppe)]^+$ (L = *N*-phenylimidazole) and *fac*-$[Mn(L)(CO)_3(bipy)]^+$ (L = *N*-methylbenzimidazole, benzoxazole, benzothiazole) with KO^{t}Bu and subsequent protonation of the azolyl intermediates with NH_4PF_6. Several NHC–manganese(I) complexes bearing an N–H residue of general formula *fac*-$[Mn(NHC)(CO)_3(dppe)]^+$ and *fac*-$[Mn(NHC)(CO)_3(bipy)]^+$ have been tested as carbene transfer agents to the gold fragments $[Au(L)]^+$ (L = PPh_3, CNPh, CNXylyl), allowing isolation or spectroscopic detection of various Mn(I)/Au(I) heterometallic intermediates containing azolyl bridging ligands, which liberate the gold(I) carbene complexes $[Au(NHC)(L)]^+$ by means of acid hydrolysis. By contrast, when using the silver(I) fragment $[Ag(PPh_3)]^+$ as carbene acceptor no transmetallation process occurred but instead inverse tautomerization of the NHC to the corresponding imidazole ligand was observed.

Introduction

Several methods are known to accomplish the synthesis of NHC transition metal complexes.[1] Out of them those consisting of *in situ* deprotonation of imidazolium salts or direct reaction of free NHC with the appropriate metallic fragment have been extensively used. The first approach have been successfully applied by Lin and co-workers to obtain NHC–Ag(I) complexes through reaction of Ag_2O with a variety of imidazolium cations.[2] The silver carbenes are of remarkable interest as carbene transfer agents for the preparation of NHC complexes of other metals by transmetallation reactions.[3] Isocyanide complexes are also useful starting materials for the synthesis of NHC metal complexes, either by intermolecular or intramolecular coupling. Thus, reaction of coordinated isocyanides with haloamines leads to the formation of cyclic diaminocarbenes,[4] whereas intramolecular cyclization of amino-functionalized isocyanides to afford benzannulated NHC complexes has also been described in the literature.[5]

We have recently reported two new methods for the generation of NHC ligands assisted by coordination of the precursor species to manganese(I). As summarized in Scheme 1, one of them implies the coupling of isocyanides with propargylamines (compound **I**),[6] whereas the other one is based on tautomerization reactions of *N*-coordinated imidazoles (compound **II**).[7] Preliminary results on the use of these complexes as carbene transfer agents have also been described.[7] In this paper, we report the extension of the tautomerization methodology to the synthesis of new NHC complexes of manganese(I), including benzannulated ones, as well as an account of the scope and limitations of the use of NHC–Mn(I) complexes in transmetallation processes of the NHC ligand.



Scheme 1 Formation of NHCs by reaction of isocyanides with propargylamine (**I**) and by tautomerization of imidazoles (**II**), in manganese complexes. [Mn] = *fac*-$[Mn(CO)_3(bipy)]^+$.

Results and discussion

The tautomerization process observed in imidazole ligands *N*-coordinated in manganese(I) complexes containing bipy chelating ligand[7] (Scheme 1), also takes place when a more strongly donating and bulkier chelating ligand such as dppe is present in the complex (Scheme 2). The precursor compound *fac*-$[Mn(L)(CO)_3(dppe)]ClO_4$ ([**2**]ClO_4: L = *N*-phenylimidazole) is readily obtained by reaction of *fac*-$[Mn(OClO_3)(CO)_3(dppe)]$ with *N*-phenylimidazole in CH_2Cl_2 at room temperature. Complex **2** is transformed into the corresponding imidazolin-2-ylidene tautomer **4** by treatment with KO^{t}Bu and subsequent protonation of the imidazolyl intermediate **3** with NH_4PF_6 (Scheme 2).[8]

The acid–base promoted tautomerization of coordinated azoles to NHCs is also feasible when using benzannulated derivatives (Scheme 3). The precursor compounds *fac*-$[Mn(L)(CO)_3(bipy)]ClO_4$ ([**6a**]ClO_4: L = *N*-methylbenzimidazole, [**6b**]ClO_4: L = benzoxazole, [**6c**]ClO_4: L = benzothiazole) were prepared using the same experimental procedure as for compound **2**. The azole ligands in complexes **6a–c** are *N*-coordinated, but in the case of **6c** a little amount (20%) of the *S*-coordinated isomer is present in the isolated product, as detected by ^{1}H NMR spectroscopy (see Experimental).

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† CCDC reference numbers 725955–725958 for compounds **8**, **11a**, **13** and **18**. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b906450h

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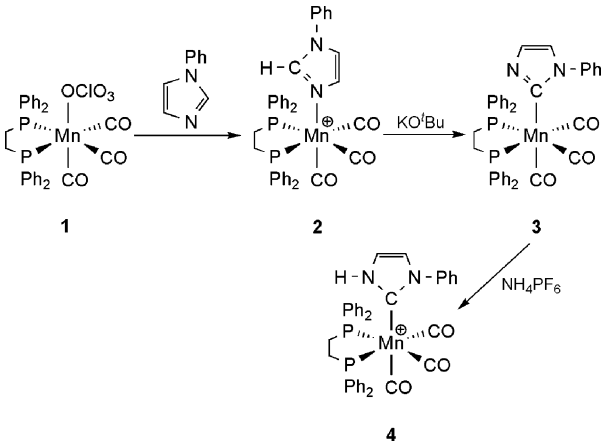
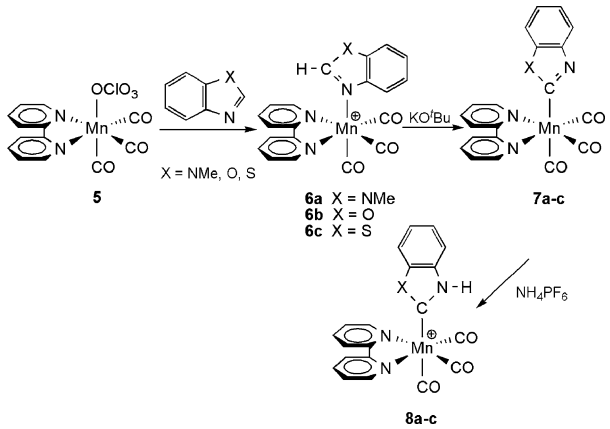


Scheme 2 Synthesis of the imidazolin-2-ylidene carbene complex **4**.



Scheme 3 Synthesis of benzannulated azolin-2-ylidene complexes **8a–c**.

Reaction of **6a–c** with KO^{t}Bu followed by treatment with NH_4PF_6 yields the carbene complexes **8a–c** (Scheme 3). Formation of the carbene complexes **4** and **8a–c** appears to be based on the preferential C-binding *versus* N-binding (or occasionally S-binding) in the azolyl intermediate species **3** and **7a–c**. It is worth noting that the tautomerization reaction is highly selective, even in the case of **6c**, which indicates that both the *N*- and *S*-coordinated isomers undergo the same tautomerization process. The two step generation of carbene complexes **4** and **8a–c** was monitored by IR spectroscopy (Table 1); a strong shift to lower frequencies in the ν(CO) bands of the carbonyl ligands is observed on passing from **2** and **6a–c** to the azolyl intermediates **3** and **7a–c**, and a new change to higher frequencies when forming the NHC complexes **4** and **8a–c** on protonation. The lower ν(CO) frequencies of **4** and

Table 1 Selected spectroscopic data (IR and NMR) for compounds **2–18**

Compound	IR (CH_2Cl_2/cm^{-1}) ν(CO)[a]	^{1}H NMR[b] δ	^{13}C {^{1}H} NMR,[bc] δ	^{31}P {^{1}H} NMR[b] δ
2	2031 vs, 1959 s, 1941 s	6.99 (1 H, s, =CH), 6.93 (1 H, s, =CH), 6.04 (1 H, s, =CH)	—	74.6 (s, dppe)
3	2002 vs, 1922 s, 1911 sh	6.73 (1 H, d, $^3J_{HH}$ = 1.0 Hz, =CH), 6.21 (1 H, d, $^3J_{HH}$ = 1.0 Hz, =CH)	169.2 (t, $^2J_{CP}$ = 20 Hz)	84.2 (s, dppe)
4	2022 vs, 1946 s	8.10 (1 H, s, NH), 6.80 (1 H, s, =CH), 6.58 (1 H, s, NH)	180.6 (t, $^2J_{CP}$ = 19 Hz)	75.9 (s, dppe)
6a	2038 vs, 1947 s, 1937 s	3.67 (3 H, s, NCH_3)	—	—
6b	2044 vs, 1958 s, 1943 s	7.45 (1 H, s, N=CH)	—	—
6c	2042 vs, 1956 s, 1942 s	8.06 (1 H, s, N=CH)	—	—
7a	2009 vs, 1918 s, 1901 s	—	—	—
7b	2018 vs, 1921 s	—	—	—
7c	2014 vs, 1922 s	—	—	—
8a	2033 vs, 1952 s, 1924 s	4.11 (3 H, s, NCH_3), 9.00 (1 H, s, NH)	197.2 (s)	—
8b	2040 vs, 1963 s, 1939 s	11.84 (1 H, s, NH)	235.2 (s)	—
8c	2037 vs, 1960 s, 1936 s	11.47 (1 H, s, NH)	236.2 (s)	—
9a	2028 vs, 1944 s, 1925 s	9.76 (1 H, s, NH), 6.94 (1 H, s, =CH), 1.74 (3 H, s, CH_3)	184.7 (s)	—
9b	2029 vs, 1945 s, 1923 s	10.02 (1H, s, NH), 7.02 (1H, s, =CH), 1.79 (3H, s, CH_3)	184.7 (s)	—
11a	2030 vs, 1936 s, 1927 s	5.84 (1 H, s, =CH), 1.78 (3 H, s, CH_3)	190.4 (s)	41.0 (s, PPh_3)
11b	2030 vs, 1937 s, 1926 s	5.89 (1 H, s, =CH), 1.82 (3 H, s, CH_3)	191.4 (s)	40.9 (s, PPh_3)
11c	2030 vs, 1933 s, 2217 w ν(CN),	5.88 (1 H, s, =CH), 1.78 (3 H, s, CH_3)	—	—
11d	2030 vs, 1939 s, 1928 s, 2207 w ν(CN)	5.86 (1 H, s, =CH), 1.83 (3 H, s, CH_3)	—	—
12a	—	11.40 (1 H, s, NH), 7.23 (1 H, s, =CH), 2.18 (3 H, d, $^4J_{HH}$ = 0.6 Hz, CH_3)	184.4 (d, $^2J_{CP}$ = 184 Hz)	40.6 (s, PPh_3)
12b	—	11.37 (1 H, s, NH), 2.17 (3 H, s, CH_3)	—	40.5 (s, PPh_3)
12d	2218 w ν(CN)	11.54 (1 H, s, NH), 2.16 (3 H, s, CH_3)	—	—
13	2023 vs, 1950 s, 1927 s	6.25 (1 H, s, =CH), 5.14 (1 H, s, =CH)	192.2 (d, $^2J_{CP}$ = 135 Hz)	75.0 (s, dppe), 40.5 (s, PPh_3)
15a	2023 vs, 1939 s, 1913 s	4.12 (3 H, s, NCH_3)	—	30.7 (s, PPh_3)
15b	2030 vs, 1949 s, 1917 s	—	—	31.2 (s, PPh_3)
16a	2031 vs, 1938 s, 1928 sh	3.92 (3 H, s, NCH_3)	—	40.7 (s, PPh_3)
16b	2037 vs, 1947 s, 1938 sh	—	—	39.1 (s, PPh_3)
17	2029 vs, 1937 s, 1925 s	5.81 (1 H, s, =CH), 1.80 (3 H, d, $^4J_{HH}$ = 1.0 Hz, CH_3)	—	12.4 (s, PPh_3)
18	2030 vs, 1939 s, 1928 s	7.16 (1 H, d, $^3J_{HH}$ = 1.1 Hz, N=CH), 6.18 (1 H, s, =CH), 1.94 (3 H, s, CH_3)	—	—

[a] Abbreviations: vs = very strong, s = strong, w = weak, sh = shoulder. [b] NMR spectra recorded in CD_2Cl_2. [c] $C_{carbene}$.

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8a–c with respect to those of **2** and **6a–c** reflect the stronger donor capability of the NHC ligands in comparison with their corresponding azole ligands. It must be pointed out that, though the azolyl species **3** and **7a–c** where spectroscopically detected, only compound **3** is stable enough to be isolated as a pure sample. The NMR data are in agreement with the proposed carbene nature of compounds **4** and **8a–c** (Table 1), specially the appearance of a low field singlet signal in the $^{13}C\{^1H\}$ NMR spectra assigned to the carbene carbon atom, together with the presence of a low field N–H signal in the ^1H NMR spectra. Additionally, for **8a** an X-ray diffraction study has been carried out (Fig. 1).

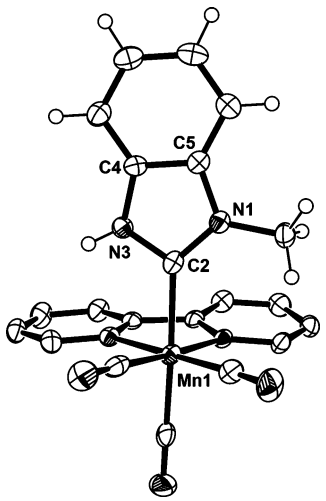
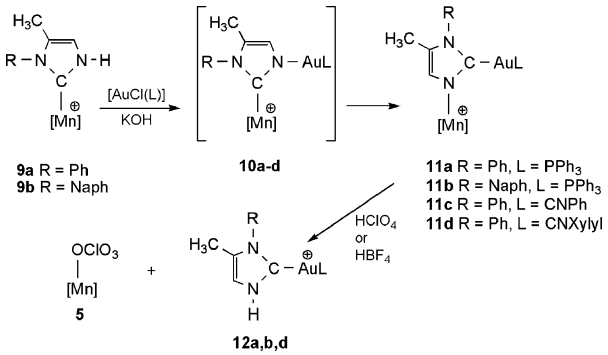


Fig. 1 Molecular structure of the complex **8a**, shown with 50% thermal ellipsoids. Hydrogen atoms of the bipy ligand are omitted for clarity. Selected interatomic distances (Å) and angles (°): Mn1–C2 = 2.060(4), N1–C2 = 1.358(4), C2–N3 = 1.358(4), N3–C4 = 1.388(4), C4–C5 = 1.384(5), C5–N1 = 1.395(4); Mn1–C2–N1 = 132.7(3), Mn1–C2–N3 = 122.8(3), N1–C2–N3 = 104.3(3), C2–N3–C4 = 112.4(3), N3–C4–C5 = 105.4(3), C4–C5–N1 = 106.4(3), C5–N1–C2 = 111.5(3).

In preliminary results we have shown that NHC complexes of Mn(I) can be used as carbene transfer agents to Au(I). We have now found that the designed transmetallation route can be applied, with some limitations that we will comment below, to any NHC–Mn(I) complex bearing a N–H residue in the carbene ligand, and that this transferring process involves translocation of Mn(I) and Au(I) metal ions in heterometallic intermediate species. Reaction of **9a**,**b** with the gold(I) triphenylphosphine or isocyanide complexes [AuCl(L)] (L = PPh_3 or CNR) in the presence of KOH leads to the formation of the heterometallic derivatives **11a–d** (Scheme 4). As shown in the scheme, apart from the target substitution of the proton by the isolobal $[Au(L)]^+$ fragment, which would afford complexes **10a–d**, an additional structural change has occurred so that the nitrogen atom of the imidazolyl ligand is now coordinated to manganese, whereas the carbon atom is bonded to gold.

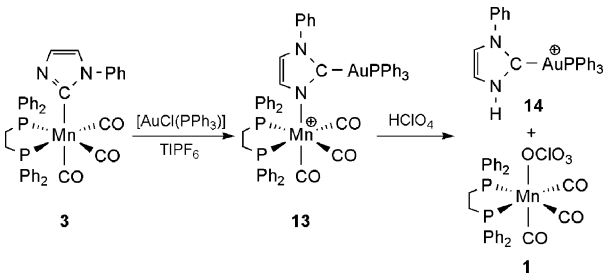
Considering the soft and hard character of carbon and nitrogen atoms in the heterocyclic ligand, respectively, this translocation process of the metal ions appears to be promoted by the softer character of Au(I) with respect to Mn(I). The assumed intermediate species **10a–d** were not detected during the reaction course, even by performing the reaction at low temperature. Note that **11a–d** are Mn(I)/Au(I) heterometallic complexes containing



Scheme 4 Transmetallation process of NHC ligands to obtain the gold(I) carbene complexes **12a**,**b**,**d**. [Mn] = *fac*-[Mn(CO)$_3$(bipy)].

imidazolyl bridging ligands, but alternatively can be considered as *N*-metalated NHC complexes of gold(I).

The heterometallic derivative **13**, analogous to **11a–d** but containing the diphosphine dppe as chelating ligand, was prepared in a slightly different way, involving direct reaction of **3** with [AuCl(PPh_3)] in the presence of $TlPF_6$ (Scheme 5). The need of the Tl(I) salt as chloride abstractor for the reaction to take place is probably due to the high steric hindrance of the dppe ligand, which diminishes the nucleophilicity of the deprotonated complex **3** with respect to the bipy counterpart.



Scheme 5 Formation of the NHC–Au(I) complex **14** through transmetallation reaction from complex **3**.

The new heterometallic compounds **11a–d** and **13** where fully analytically and spectroscopically characterized (Table 1). The $^{13}C\{^1H\}$ NMR spectra show a low field doublet signal (at about 190 ppm) for the carbene carbon atom, which is coupled with the PPh_3 phosphorus atom. The PPh_3 ligand gives rise to a characteristic singlet signal in the $^{31}P\{^1H\}$ NMR spectra at about 40 ppm. An X-ray diffraction study has been carried out for complexes **11a** (Fig. 2) and **13** (Fig. 3). Both structures are similar, the main differences arising from the distinct steric requirements of the chelating ligand, which lead to a different orientation of the gold fragment with respect to the manganese coordination sphere in each complex. In particular, the bulky dppe ligand forces the plain of the imidazolyl ligand to be locked between the two diphenylphosphine groups in complex **13**.

The treatment of **11a**,**b**,**d** and **13** with HBF_4 or $HClO_4$ in CH_2Cl_2 leads to the cleavage of the Mn–N linkage affording a mixture of the gold(I) carbene complexes **12a**,**b**,**d** and **14**, and the starting manganese(I) complexes **5** and **1**, respectively, (see Schemes 4 and 5). The low solubility of compound **5** allows separation and purification of the NHC–Au(I) complexes **12a**,**b**,**d**, which were

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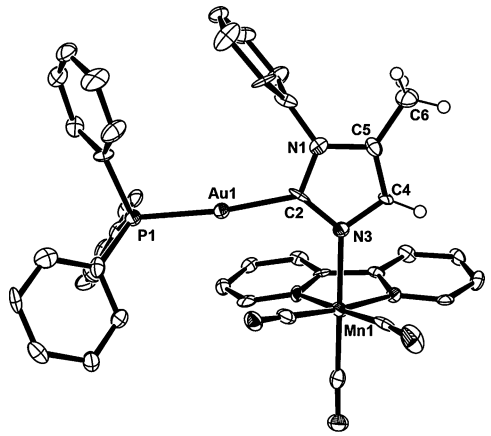


Fig. 2 Molecular structure of the complex **11a**, shown with 50% thermal ellipsoids. Hydrogen atoms of the bipy and Ph groups are omitted for clarity. Selected interatomic distances (Å) and angles (°): Mn1–N3 = 2.060(7), N1–C2 = 1.339(10), C2–N3 = 1.386(10), N3–C4 = 1.366(10), C4–C5 = 1.352(11), C5–N1 = 1.390(11), C5–C6 = 1.508(12), Au1–C2 = 2.027(9), Au1–P1 = 2.286(2); Mn1–N3–C2 = 128.4(6), Mn1–N3–C4 = 125.9(6), N1–C2–N3 = 107.8(8), C2–N3–C4 = 105.6(7), N3–C4–C5 = 111.9(8), C4–C5–N1 = 104.0(8), C5–N1–C2 = 110.7(8), N1–C2–Au1 = 123.2(7), N3–C2–Au1 = 129.0(7), C2–Au1–P1 = 172.9(3).

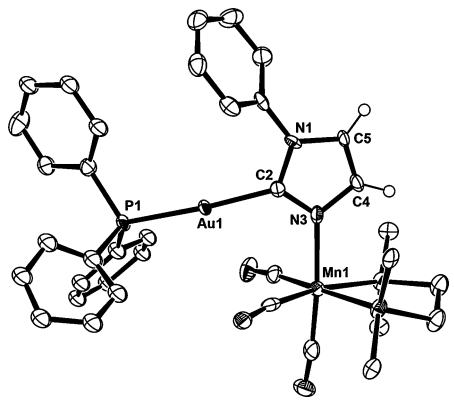
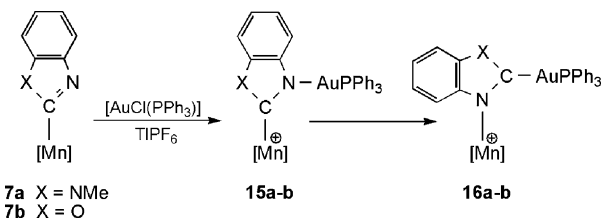


Fig. 3 Molecular structure of the complex **13**, shown with 50% thermal ellipsoids. Hydrogen atoms of the bipy and Ph groups are omitted for clarity. Ph groups of the dppe ligand are reduced to their C_{ipso} for clarity too. Selected interatomic distances (Å) and angles (°): Mn1–N3 = 2.101(6), N1–C2 = 1.372(9), C2–N3 = 1.334(9), N3–C4 = 1.387(9), C4–C5 = 1.318(10), C5–N1 = 1.380(9), Au1–C2 = 2.038(7), Au1–P1 = 2.292(2); Mn1–N3–C2 = 125.1(5), Mn1–N3–C4 = 127.8(5), N1–C2–N3 = 107.8(6), C2–N3–C4 = 106.9(6), N3–C4–C5 = 110.4(7), C4–C5–N1 = 106.2(7), C5–N1–C2 = 108.6(6), N1–C2–Au1 = 121.9(5), N3–C2–Au1 = 129.9(6), C2–Au1–P1 = 174.9(2).

isolated as white solids. This is not the case for compounds **1** and **14**, which show a similar solubility in most organic solvents, precluding isolation of the NHC–Au(I) complex **14** by this way. This result highlights the importance of the ancillary ligands in the starting manganese(I) complex for the synthetic viability of the present experimental approach to obtain NHC–Au(I) derivatives. This observation has also been pointed out by other authors when using group 6 metal complexes in NHC transfer reactions between transition metal ions.[9] NHC gold complexes have recently attracted renewed attention due to their applications in catalysis[10] and medicine.[11] For the preparation of NHC–Au(I) complexes transmetallation reactions from NHC–Ag(I) complexes have been extensively used.[3,12] This method, requiring deprotonation of imidazolium salts by Ag_2O, can only be applied when both nitrogen atoms in the carbene are substituted. In this sense, the transmetallation route from NHC–Mn(I) derivatives described herein can be an option for obtaining NHC–Au(I) complexes bearing N–H residues. An alternative method consisting of treatment of lithiated azoles with chloro-gold(I) complexes and subsequent protonation of the azolyl derivatives has been described in the literature.[13]

Benzannulated azolin-2-ylidene carbene complexes **8a**,**b** were also tested as carbene transfer agents. No reaction was found by following the one-pot procedure involving treatment of **8a**,**b** with [AuCl(PPh$_3$)]/KOH, so the alternative route consisting of the reaction of azolyl derivatives **7a**,**b** with [AuCl(PPh$_3$)] in the presence of $TlPF_6$ was used (Scheme 6). The reaction was performed at 0 °C, allowing in this case the spectroscopic detection of the intermediate species **15a**,**b** previous to the translocation process of the metal ions to afford **16a**,**b** occurring at room temperature, thus clarifying the full reaction pathway for the formation of these heterometallic species. Compounds **15a**,**b** and **16a**,**b** are easily distinguished by IR and $^{31}P\{^1H\}$ NMR spectroscopy (Table 1). The ν(CO) bands of the benzimidazolyl derivative **16a** are almost identical with those of the analogous imidazolyl complexes **11a**,**b**, whereas the bands corresponding to **15a** appear at lower frequencies (7 cm^{-1} on average), which reflects the stronger donor capability of the carbon atom in comparison with the nitrogen atom in the benzimidazolyl ligand. Similarly, the ν(CO) frequencies for the benzoxazolyl complex **15b** are lower than for **16b**. On the other hand, the $^{31}P\{^1H\}$ NMR spectra of **16a**,**b** show a singlet close to 40 ppm, that is in the expected region for a PPh$_3$ ligand located *trans* to the carbene carbon atom (see data of **11a**,**b** in Table 1), whereas those of **15a**,**b** reveal the presence of a singlet near to 30 ppm for the PPh$_3$ ligand, which has now a nitrogen atom in the *trans* position.[14] Unfortunately compounds **16a**,**b** slowly decompose during the work-up, precluding either the isolation of these species as pure samples or the proper hydrolysis reaction to complete the transmetallationn process of the carbene ligands to gold.



Scheme 6 Translocation process of Mn(I) and Au(I) ions in benzannulated azolyl bridging ligands. [Mn] = *fac*-[Mn(CO)$_3$(bipy)].

Assuming that the translocation process of the metal ions that allows transformation of the NHC–Mn(I) complexes into NHC–Au(I) complexes is favored with soft metal centers, we performed the reaction of complex **9a**, previously transformed into its deprotonated form by treatment with KO^{t}Bu, with [Ag(OClO$_3$)(PPh$_3$)] (Scheme 7). Formation of the expected Mn(I)/Ag(I) heterometallic derivative **17** readily takes place, as confirmed by the spectroscopic data of the complex (see Table 1).

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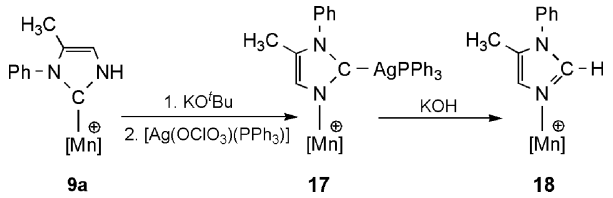


Scheme 7 "Inverse" tautomerization of NHC ligand to N-coordinated imidazole through the Mn(I)/Ag(I) heterometallic intermediate **17**. [Mn] = *fac*-[Mn(CO)$_3$(bipy)].

Compound **17** slowly undergoes spontaneous hydrolysis by standing in solution, probably due to the presence of traces of water. The hydrolysis of **17** is fully completed by addition of KOH. This process did not result in the formation of the target silver(I) carbene complex, but instead the N-coordinated imidazole manganese(I) complex **18** was obtained (Scheme 7). This means that in **17** the scission of the C–Ag bond is easier than the scission of the N–Mn bond, in contrast to that occurring in the analogous Mn(I)/Au(I) heterometallic species. The structure of **18** was confirmed by X-ray diffraction analysis (Fig. 4). Note that in overall, the reaction depicted in Scheme 7 supposes tautomerization of an *N*-heterocyclic carbene to the corresponding imidazole ligand, which is the inverse process to that drawn in Schemes 2 and 3. To our knowledge, such a process has only been observed once in the literature.[15]

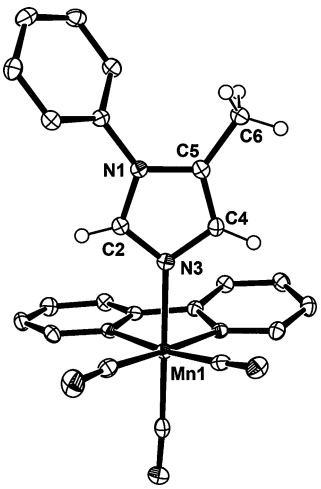


Fig. 4 Molecular structure of the complex **18**, shown with 50% thermal ellipsoids. Hydrogen atoms of the bipy and Ph groups are omitted for clarity. Selected interatomic distances (Å) and angles (°): Mn1–N3 = 2.067(1), N1–C2 = 1.358(2), C2–N3 = 1.318(2), N3–C4 = 1.386(2), C4–C5 = 1.356(2), C5–N1 = 1.391(2), C5–C6 = 1.489(2); Mn1–N3–C2 = 127.9(1), Mn1–N3–C4 = 126.2(1), N1–C2–N3 = 110.9(2), C2–N3–C4 = 105.8(1), N3–C4–C5 = 110.5(2), C4–C5–N1 = 105.1(1), C5–N1–C2 = 107.7(1).

Conclusions

In this paper we have shown that azole molecules (L) *N*-coordinated in the manganese(I) complexes *fac*-[Mn(L)(CO)$_3$(dppe)]$^+$ (L = *N*-phenylimidazole) and *fac*-[Mn(L)(CO)$_3$(bipy)]$^+$ (L = *N*-methylbenzimidazole, benzoxazole, benzothiazole) can be transformed into their corresponding NHC tautomers by means of acid–base treatments. We have also shown herein that NHC–Mn(I) complexes bearing an N–H residue in the carbene ligand can be used as carbene transfer agents, allowing the isolation of several NHC–Au(I) complexes by this way. The mechanism of the transmetallation process, which includes a key step involving translocation of Mn(I) and Au(I) metal ions, has been elucidated by spectroscopic detection and/or isolation of Mn(I)/Au(I) heterometallic intermediates containing azolyl bridging ligands. When trying to use silver(I) ion as carbene acceptor the transmetallation process was not completed but instead inverse tautomerization of the NHC to the corresponding imidazole ligand occurred.

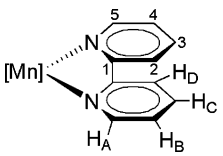
Experimental

General

All reactions and manipulations were carried out under a nitrogen atmosphere using standard Schlenk techniques. Solvents were distilled over appropriate drying agents under dry nitrogen prior to use. Compounds *fac*-[Mn(OClO$_3$)(CO)$_3$(dppe)] (**1**),[16] *fac*-[Mn(OClO$_3$)(CO)$_3$(bipy)] (**5**),[17] [**9a**]ClO$_4$[6] and [**9b**]ClO$_4$[6] were prepared according to reported protocols. NMR spectra were recorded on Bruker 300 and 400 MHz spectrometers. NMR multiplicities are abbreviated as follows: s = singlet, d = doublet, ddd = doublet of doublet of doublets, t = triplet, td = triplet of doublets, m = multiplet. Coupling constants *J* are given in Hz.

Safety note. Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of such materials should be prepared and these should be handled with great caution.

For the NMR spectra the atom labelling in 2,2′-bipyridine ligands is as follows:



Synthesis of [2]ClO$_4$. To a solution of **1** (0.10 g, 0.16 mmol) in CH_2Cl_2 (10 mL) 1-phenylimidazole (0.030 mL, d = 1.14 g mL^{-1}, 0.24 mmol) was added and the solution stirred for 12 h. After this period of time the solution was concentrated to 4 mL. Slow addition of hexane (10 mL) gave a yellow solid, which was filtered off and dried under vacuum (0.11 g, 90%). (Found: C 58.2, H 4.2, N 3.7 $C_{38}H_{32}ClMnN_2O_7P_2$ requires C 58.4, H 4.1, N 3.6%). IR ν_{max}/cm^{-1} 2031 vs, 1959 s, 1941 s (CO). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ/ppm: 74.6 (s, dppe). ^{1}H NMR (CD_2Cl_2) δ/ppm: 7.66–7.52 (23 H, m, H$_{arom}$ Ph), 6.52–6.50 (2 H, m, H$_{arom}$ Ph), 6.99 (1 H, s, =CH), 6.93 (1 H, s, =CH), 6.04 (1 H, s, =CH), 3.37–3.28 (4 H, m, CH_2).

Synthesis of 3. To a solution of [**2**]ClO$_4$ (0.10 g, 0.13 mmol) in CH_2Cl_2 (10 mL) KO^{t}Bu (0.029 g, 0.26 mmol) was added. The mixture was stirred for 15 min and then filtered off to give a yellow solution, which was concentrated to 3 mL. Addition of hexane (15 mL) afforded a pale yellow solid, which was filtered off and dried under vacuum (0.070 g, 80%). (Found: C 66.8, H 4.3, N 3.85 $C_{38}H_{31}MnN_2O_3P_2$ requires C 67.1, H 4.6, N 4.1%). IR ν_{max}/cm^{-1} 2022 vs, 1946 s (CO). ^{31}P{^{1}H} NMR (CD_2Cl_2) δ/ppm:

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84.2 (s, dppe). ^{1}H NMR (CD_2Cl_2) δ/ppm: 7.46–7.25 (25 H, m, Ph), 6.73 (1 H, d, $^{3}J_{HH}$ = 1.0 Hz, =CH), 6.21 (1 H, d, $^{3}J_{HH}$ = 1.0 Hz, =CH), 3.76 (2 H, m, CH_2), 2.79 (2 H, m, CH_2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ/ppm: 223.4 (s, CO), 216.6 (s, CO), 169.2 (t, $^{2}J_{CP}$ = 20 Hz, $C_{carbene}$), 143.2–127.7 (m, C_{arom} Ph), 127.3 (s, =CH), 123.6 (s, =CH), 27.1 (t, $^{2}J_{CP}$ = 19 Hz, CH_2).

Synthesis of [4]PF_6. To a solution of [**2**]ClO_4 (0.10 g, 0.13 mmol) in CH_2Cl_2 (10 mL) KO^{t}Bu (0.029 g, 0.26 mmol) was added. The mixture was stirred for 15 min, after which complex **3** was formed, as detected by IR spectroscopy. Then the solution was filtered off and NH_4PF_6 (0.042 g, 0.26 mmol) added. The resulting suspension was stirred for 2 h. Then the solution was filtered off and concentrated to 5 mL. Hexane (15 mL) was added dropwise affording a white solid, which was filtered off and dried under vacuum (0.051 g, 48%). (Found: C 54.9, H 3.6, N 3.5 $C_{38}H_{32}F_6MnN_2O_3P_3$ requires C 55.2, H 3.9, N 3.4%). IR ν_{max}/cm^{-1} 2022 vs, 1946 s (CO). $^{31}P\{^{1}H\}$ NMR (CD_2Cl_2) δ/ppm: 75.9 (s, dppe). ^{1}H NMR (CD_2Cl_2) δ/ppm: 8.10 (1 H, s, NH), 7.61–7.41 (23 H, m, H_{arom} Ph), 7.21 (2 H, d, $^{3}J_{HH}$ = 6.7 Hz, H_o Ph), 6.80 (1 H, s, =CH), 6.58 (1 H, s, =CH), 3.35 (2 H, m, CH_2), 3.03 (2 H, m, CH_2). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2): 220.1 (s, CO), 216.4 (s, CO), 180.6 (t, $^{2}J_{CP}$ = 19 Hz, $C_{carbene}$), 140.2 (s, C_{ipso} NPh), 134.4–128.4 (m, C_{arom} Ph), 125.8 (s, =CH), 120.9 (s, =CH), 26.2 (t, $^{1}J_{CP}$ = 20 Hz, CH_2).

Synthesis of [6a]ClO_4. To a solution of **5** (0.10 g, 0.24 mmol) in acetone (10 mL) 1-methylbenzimidazole (0.038 g, 0.28 mmol) was added and the resulting mixture stirred for 2 h. The solution was concentrated to 5 mL. Addition of hexane (15 mL) gave a yellow solid, which was filtered off and dried under vacuum (0.113 g, 91%). (Found: C 47.8, H 3.1, N 10.7 $C_{21}H_{16}ClMnN_4O_7$ requires C 47.9, H 3.1, 10.6%). IR ν_{max}/cm^{-1} 2038 vs, 1947 s, 1937 s (CO). ^{1}H NMR (CD_2Cl_2) δ/ppm: 9.18 (2 H, d, $^{3}J_{HH}$ = 5.5 Hz, H_A bipy), 8.47 (2 H, d, $^{3}J_{HH}$ = 7.7 Hz, H_D bipy), 8.20 (2 H, td, $^{3}J_{HH}$ = 7.7 Hz, $^{4}J_{HH}$ = 1.4 Hz, H_C bipy), 8.00 (1 H, m, H_{arom} C_6H_4), 7.67 (2 H, ddd, $^{3}J_{HH}$ = 7.7 Hz, $^{3}J_{HH}$ = 5.0 Hz,$^{4}J_{HH}$ = 1.4 Hz, H_B bipy), 7.46–7.40 (3 H, m, H_{arom} C_6H_4), 6.98 (1 H, s, =CH), 3.67 (3 H, s, CH_3).

Synthesis of [6b]ClO_4. The procedure was completely analogous to that described above, using **5** (0.10 g, 0.24 mmol) and benzoxazole (0.034 g, 0.28 mmol). Reaction time: 3 h (0.089 g, 71%). (Found: C 46.6, H 2.7, N 8.1 $C_{20}H_{13}ClMnN_3O_8$ requires C 46.8, H 2.55, N 8.2). IR ν_{max}/cm^{-1} 2044 vs, 1958 s, 1943 s (CO). ^{1}H NMR (CD_2Cl_2) δ/ppm: 9.20 (2 H, d, $^{3}J_{HH}$ = 5.4 Hz, H_A bipy), 8.51 (2 H, d, $^{3}J_{HH}$ = 8.0 Hz, H_D bipy), 8.23 (2 H, t, $^{3}J_{HH}$ = 7.2 Hz, H_C bipy), 8.06–8.03 (1 H, m, H_{arom} C_6H_4), 7.72 (2 H, t, $^{3}J_{HH}$ = 6.4 Hz, H_B bipy), 7.67–7.55 (3 H, m, H_{arom} C_6H_4), 7.45 (1 H, s, =CH).

Synthesis of [6c]ClO_4. This compound was prepared in a similar way to [**6a**]ClO_4, using **5** (0.10 g, 0.24 mmol) and benzothiazole (0.031 mL, d = 1.246 g mL^{-1}, 0.28 mmol). Reaction time: 3 h (0.111 g, 89%). (Found: C 45.6, H 2.7, N 7.75 $C_{20}H_{13}ClMnN_3O_7S$ requires C 45.3, H 2.5, N 7.9%). IR ν_{max}/cm^{-1} 2042 vs, 1956 s, 1942 s (CO). ^{1}H NMR (CD_2Cl_2) *N*-coordinated isomer (80%) δ/ppm: 9.17 (2 H, d, $^{3}J_{HH}$ = 4.8 Hz, H_A bipy), 8.56 (2 H, d, $^{3}J_{HH}$ = 8.5 Hz, H_D bipy), 8.29 (2 H, t, $^{3}J_{HH}$ = 6.7 Hz, H_C bipy), 8.06 (1 H, s, =CH), 8.02–7.99 (2 H, m, H_{arom} C_6H_4), 7.79–7.59 (4 H, m, H_B bipy y H_{arom} C_6H_4) *S*-coordinated isomer (20%) δ/ppm: 9.27 (2H, d, $^{3}J_{HH}$ = 5.7 Hz, H_A bipy), the rest of the signal are not distinguished from those of the corresponding *N*-coordinated isomer.

Synthesis of [8a]PF_6. To a solution of [**6a**]ClO_4 (0.10 g, 0.19 mmol) in CH_2Cl_2 (10 mL) KO^{t}Bu (0.043 g, 0.40 mmol) was added. The mixture was stirred for 45 min and then filtered off to give an orange solution corresponding to **7a**. Then, NH_4PF_6 (0.062 g, 0.40 mmol) was added and the resulting suspension stirred for 1 h. The solution was then filtered off and concentrated to 5 mL. Addition of hexane (15 mL) gave a yellow solid, which was filtered off and dried under vacuum (0.081 g, 75%). (Found: C 43.9, H 2.6, N 9.7 $C_{21}H_{16}F_6MnN_4O_3P$ requires C 44.05, H 2.8, N 9.8%). IR ν_{max}/cm^{-1} 2033 vs, 1952 s, 1924 s (CO). ^{1}H NMR (CD_2Cl_2) δ/ppm: 9.07 (2 H, d, $^{3}J_{HH}$ = 5.7 Hz, H_A bipy), 9.00 (1 H, s, NH), 8.42 (2 H, d, $^{3}J_{HH}$ = 8.0 Hz, H_D bipy), 8.19 (2 H, t, $^{3}J_{HH}$ = 7.5 Hz, H_C bipy), 7.65 (2 H, t, $^{3}J_{HH}$ = 6.6 Hz, H_B bipy), 7.52 (1 H, d, $^{3}J_{HH}$ = 7.7 Hz, H_{arom} C_6H_4), 7.41 (1 H, d, $^{3}J_{HH}$ = 7.7 Hz, H_{arom} C_6H_4), 7.32 (1 H, d, $^{3}J_{HH}$ = 7.4 Hz, H_{arom} C_6H_4), 7.25 (1 H, d, $^{3}J_{HH}$ = 7.4 Hz, H_{arom} C_6H_4), 4.11 (3 H, s, NCH_3). $^{13}C\{^{1}H\}$ NMR δ/ppm: 221.6 (s, CO), 212.9 (s, CO), 197.2 (s, $C_{carbene}$), 155.3 (s, C_1 bipy), 153.9 (s, C_2 bipy), 139.9 (s, C_3 bipy), 135.6 (s, C_{arom} C_6H_4), 133.8 (s, C_{arom} C_6H_4), 127.9 (s, C_4 bipy), 124.8 (s, C_5 bipy), 124.6 (s, C_{arom} C_6H_4), 124.0 (s, C_{arom} C_6H_4), 112.9 (s, C_{arom} C_6H_4), 110.0 (s, C_{arom} C_6H_4), 34.9 (s, NCH_3).

Synthesis of [8b]PF_6. The procedure was analogous to that described above, using [**6b**]ClO_4 (0.10 g, 0.19 mmol), KO^{t}Bu (0.044 g, 0.39 mmol) (30 min of stirring) and NH_4PF_6 (0.127 g, 0.78 mmol) (12 h of stirring) (0.075 g, 69%). (Found: C 42.75, H 2.4, N 7.4 $C_{20}H_{13}F_6MnN_3O_4P$ requires C 42.95, H 2.3, N 7.5%). IR ν_{max}/cm^{-1} 2040 vs, 1963 s, 1939 s (CO). ^{1}H NMR (CD_2Cl_2) δ/ppm: 11.84 (1 H, s, NH), 9.30 (2 H, d, $^{3}J_{HH}$ = 5.4 Hz, H_A bipy), 8.22 (2 H, d, $^{3}J_{HH}$ = 8.0 Hz, H_D bipy), 8.14 (2 H, td, $^{3}J_{HH}$ = 7.4 Hz, $^{4}J_{HH}$ = 1.0 Hz, H_C bipy), 8.06–8.01 (1 H, m, H_{arom} C_6H_4), 7.76–7.63 (3 H, m, H_B bipy y H_{arom} C_6H_4), 7.53–7.46 (1 H, m, H_{arom} C_6H_4), 7.41–7.34 (1 H, m, H_{arom} C_6H_4). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ/ppm: 235.2 (s, $C_{carbene}$), 220.3 (s, CO), 213.8 (s, CO), 155.3 (s, C_1 bipy), 154.4 (s, C_2 bipy), 146.1 (s, O*C*=C), 139.8 (s, C_3 bipy), 134.1 (s, N*C*=C), 128.1 (s, C_4 bipy), 127.8 (s, C_{arom} C_6H_4), 125.6 (s, C_{arom} C_6H_4), 123.6 (s, C_5 bipy), 121.4 (s, C_{arom} C_6H_4), 116.2 (s, C_{arom} C_6H_4).

Synthesis of [8c]PF_6. The procedure was similar that the synthesis of [**8a**]PF_6, using [**6c**]ClO_4 (0.10 g, 0.19 mmol), KO^{t}Bu (0.042 g, 0.37 mmol) (30 min of stirring) and NH_4PF_6 (0.123 g, 0.75 mmol) (12 h of stirring) (0.076 g, 70%). (Found: C 42.0, H 2.4, N 7.5 $C_{20}H_{13}F_6MnN_3O_3PS$ requires C 41.8, H 2.3, N 7.3). IR ν_{max}/cm^{-1} 2037 vs, 1960 s, 1936 s (CO). ^{1}H NMR (CD_2Cl_2) δ/ppm: 11.47 (1 H, s, NH), 9.18 (2 H, d, $^{3}J_{HH}$ = 5.1 Hz, H_A bipy), 8.21 (2 H, d, $^{3}J_{HH}$ = 7.7 Hz, H_D bipy), 8.10 (2 H, t, $^{3}J_{HH}$ = 7.7 Hz, H_C bipy), 7.67–7.59 (3 H, m, H_B bipy and H_{arom} C_6H_4), 7.47–7.29 (3 H, m, H_{arom} C_6H_4). $^{13}C\{^{1}H\}$ NMR (CD_2Cl_2) δ/ppm: 236.2 (s, $C_{carbene}$), 220.1 (s, CO), 213.8 (s, CO), 155.3 (s, C_1 bipy), 154.4 (s, C_2 bipy), 145.4 (s, S*C*=C), 139.9 (s, C_3 bipy), 133.9 (s, N*C*=C), 128.2 (s, C_4 bipy), 128.0 (s, C_{arom} C_6H_4), 125.8 (s, C_{arom} C_6H_4), 123.6 (s, C_5 bipy), 121.4 (s, C_{arom} C_6H_4), 116.0 (s, C_{arom} C_6H_4).

Synthesis of [11a]ClO_4. To a solution of [**9a**]ClO_4 (0.10 g, 0.18 mmol) in CH_2Cl_2 (20 mL), [AuCl(PPh_3)] (0.107 g, 0.22 mmol) and KOH (0.20 g, 3.56 mmol) were added and the mixture stirred for 10 min. The solution was then filtered off and concentrated to 3 mL. Addition of diethyl ether (15 mL) gave a yellow solid, which

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was filtered off and dried under vacuum (0.142 g, 78%). (Found: C 48.9, H 2.9, N 5.4 $C_{41}H_{32}AuClMnN_4O_7P$ requires C 48.7, H 3.2, N 5.5%). IR ν_{max}/cm^{-1} 2030 vs, 1936 s, 1927 s (CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ/ppm: 41.0 (s, PPh_3). ^1H NMR (CD_2Cl_2) δ/ppm: 9.15 (2 H, d, $^3J_{HH} = 4.6$ Hz, H_A bipy), 8.33 (2 H, d, $^3J_{HH} = 6.8$ Hz, H_D bipy), 8.07 (2 H, t, $^3J_{HH} = 7.5$ Hz, H_C bipy), 7.56–7.22 (20 H, m, H_{arom} C_6H_5), 7.13 (2 H, t, $^3J_{HH} = 5.8$ Hz, H_B bipy), 5.84 (1 H, s, =CH), 1.78 (3 H, s, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ/ppm: 221.0 (s, CO), 217.4 (s, CO), 190.6 (s, $C_{carbene}$), 155.8 (s, C_1 bipy), 153.4 (s, C_2 bipy), 139.9 (s, C_3 bipy), 139.4 (s, C_{ipso} Ph), 134.1–128.0 (m, C_{arom} C_6H_5), 126.8 (s, C_4 bipy), 126.4 (s, =CH), 123.7 (s, C_5 bipy), 9.9 (s, CH_3).

Synthesis of [11b]ClO_4. The procedure was completely analogous to that described above, using [**9b**]ClO_4 (0.10 g, 0.17 mmol), [AuCl(PPh_3)] (0.090 g, 0.18 mmol) and KOH (0.20 g, 3.56 mmol). Reaction time: 30 min (0.140 g, 80%). (Found: C 51.2, H 3.0, N 5.1 $C_{45}H_{34}AuClMnN_4O_7P$ requires C 51.0, H 3.2, N 5.3%). IR ν_{max}/cm^{-1} 2030 vs, 1937 s, 1926 s (CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ/ppm: 40.9 (s, PPh_3). ^1H NMR (CD_2Cl_2) δ/ppm: 9.17 (2 H, d, $^3J_{HH} = 5.1$ Hz, H_A bipy), 8.37 (2 H, d, $^3J_{HH} = 7.3$ Hz, H_D bipy), 8.09 (2 H, t, $^3J_{HH} = 6.7$ Hz, H_C bipy), 7.88–7.78 (3 H, m, H_{arom} $C_{10}H_7$), 7.68 (1 H, d, $^3J_{HH} = 7.8$ Hz, H_{arom} $C_{10}H_7$), 7.51–7.46 (4 H, m, H_B bipy H_{arom} $C_{10}H_7$), 7.34–7.11 (16 H, m, H_{arom} Ph and $C_{10}H_7$), 5.89 (1 H, s, =CH), 1.82 (3 H, s, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ/ppm: 221.0 (s, CO), 217.4 (s, CO), 191.4 (s, $C_{carbene}$), 155.8 (s, C_1 bipy), 153.4 (s, C_2 bipy), 139.8 (s, C_3 bipy), 136.8 (s, C_{ipso} $C_{10}H_7$), 133.9–127.0 (m, C_{arom} Ph and $C_{10}H_7$), 126.8 (s, C_4 bipy), 125.9 (s, =CH), 123.7 (s, C_5 bipy), 9.9 (s, CH_3).

Synthesis of [11c]ClO_4. To a solution of [**9a**]ClO_4 (0.10 g, 0.18 mmol) in CH_2Cl_2 (20 mL) [AuCl(CNPh)] (0.067 g, 0.20 mmol) and KOH (0.20 g, 3.56 mmol) were added and the mixture stirred for 1 h. Then the solution was filtered off and concentrated to 4 mL. Addition of a hexane/diethyl ether (1 : 1) (15 mL) gave a yellow solid, which was filtered off and dried under vacuum (0.114 g, 74%). (Found: C 42.1, H 2.55, N 8.0 $C_{30}H_{22}AuClMnN_5O_7$ requires C 42.3, H 2.6, N 8.2%). IR ν_{max}/cm^{-1} 2217 w (CN), 2030 vs, 1933 s (CO). ^1H NMR (CD_2Cl_2) δ/ppm: 9.38 (2 H, d, $^3J_{HH} =$ 5.1 Hz, H_A bipy), 8.36 (2 H, d, $^3J_{HH} = 8.3$ Hz, H_D bipy), 8.19 (2 H, t, $^3J_{HH} = 7.1$ Hz, H_C bipy), 7.62–7.51 (4 H, m, H_{arom} Ph H_B bipy), 7.41–7.18 (8H, m, H_{arom} Ph), 5.88 (1 H, s, =CH), 1.78 (3H, s, CH_3).

Synthesis of [11d]ClO_4. This was similarly prepared starting from [**9a**]ClO_4 (0.10 g, 0.18 mmol), KOH (0.20 g, 3.56 mmol) and [AuCl(CNXylyl)] (0.072 g, 0.20 mmol) (0.100 g, 63%). (Found: C 43.6, H 2.8, N 7.9 $C_{32}H_{26}AuClMnN_5O_7$ requires C 43.7, H 3.0, N 8.0%). IR ν_{max}/cm^{-1} 2207 w (CN), 2030 vs, 1939 s, 1928 s (CO). ^1H NMR (CD_2Cl_2) δ/ppm: 9.42 (2 H, d, $^3J_{HH} = 5.3$ Hz, H_A bipy), 8.44 (2 H, d, $^3J_{HH} = 7.8$ Hz, H_D bipy), 8.25 (2 H, t, $^3J_{HH} = 7.6$ Hz, H_C bipy), 7.70 (2 H, t, $^3J_{HH} = 5.9$ Hz, H_C bipy), 7.52–7.40 (4 H, m, H_{arom} Ph Xylyl), 7.28–7.25 (4 H, m, H_{arom} Ph Xylyl), 5.86 (1 H, s, =CH), 2.47 (6 H, s, Xylyl), 1.83 (3 H, s, CH_3).

Synthesis of [12a]BF_4. To a solution of [**11a**]ClO_4 (0.10 g, 0.10 mmol) in CH_2Cl_2 (10 mL) HBF_4 (0.027 mL, $d = 1.18$ g mL^{-1}, 54% in diethyl ether, 0.20 mmol) was added and the mixture stirred for 15 min. The solvent was removed under vacuum and the remaining yellow dissolved in CH_2Cl_2 (10 mL). Addition of hexane (10 mL) gave a yellow solid corresponding to **5**, which was eliminated by filtration. The remaining solution was concentrated to 3 mL and hexane (10 mL) added to obtain a white solid, which was filtered off and dried under vacuum (0.050 g, 71%). (Found: C 47.95, H 3.5, N 3.8 $C_{28}H_{25}AuBF_4N_2P$ requires C 47.75, H 3.6, N 4.0%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ/ppm: 40.6 (s, PPh_3). ^1H NMR (CD_2Cl_2) δ/ppm: 11.40 (1 H, s, NH), 7.63–7.43 (20 H, m, H_{arom} Ph), 7.23 (1 H, s, =CH), 2.18 (3 H, d, $^4J_{HH} = 0.6$ Hz, CH_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) δ/ppm: 184.4 (d, $^2J_{CP} = 184$ Hz, $C_{carbene}$), 138.1 (s, C_{ipso} Ph), 134.7–129.7 (m, C_{arom} Ph), 129.3 (s, C_{ipso} Ph), 128.5 (s, C_1), 127.8 (s, C_{arom} Ph), 117.4 (s, =CH), 10.4 (s, CH_3).

Synthesis of [12b]BF_4. This was similarly prepared from [**11b**]ClO_4 (0.10 g, 0.09 mmol) and HBF_4 (0.026 mL, 0.19 mmol). (0.052 g, 73%). (Found: C 50.8, H 3.7, N 3.5 $C_{32}H_{27}AuBF_4N_2P$ requires C 50.95, H 3.6, N 3.7%). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ/ppm: 40.5 (s, PPh_3). ^1H NMR (CD_2Cl_2) δ/ppm: 11.37 (1 H, s, NH), 8.01–7.97 (3 H, m, H_{arom} $C_{10}H_7$), 7.87 (1 H, d, $^3J_{HH} = 7.4$ Hz, H_{arom} $C_{10}H_7$), 7.67–7.41 (7 H, m, H_{arom} Ph, $C_{10}H_7$), 7.27–7.23 (13 H, m, H_{arom} Ph, =CH), 2.17 (3 H, s, CH_3).

Synthesis of [12d]BF_4. The procedure was analogous to the synthesis of [**12a**]BF_4, using [**11d**]ClO_4 (0.10 g, 0.11 mmol) and HBF_4 (0.024 mL, 0.17 mmol) (0.050 g, 77%). (Found: C 40.1, H 3.3, N 7.55 $C_{19}H_{18}AuBF_4N_3$ requires C 39.9, H 3.2, N 7.3%). IR ν_{max}/cm^{-1} 2218 w (CN). ^1H NMR (CD_2Cl_2) δ/ppm: 11.54 (1 H, s, NH), 7.62–7.60 (3 H, m, H_{arom} Ph), 7.49–7.47 (2 H, m, H_{arom} Ph), 7.38 (1 H, t, $^3J_{HH} = 8$ Hz, H_p Xylyl), 7.24–7.20 (3 H, m, H_{arom} Xylyl, =CH), 2.44 (6 H, s, CH_3 Xylyl), 2.16 (3 H, s, CH_3).

Synthesis of [13]PF_6. To a solution of **3** (0.10 g, 0.15 mmol) in CH_2Cl_2 (10 mL), [AuCl(PPh_3)] (0.073 g, 0.15 mmol) and $TlPF_6$ (0.103 g, 0.29 mmol) were added and the resulting suspension stirred for 45 min. Then the mixture was filtered off and concentrated to 3 mL. Addition of hexane (10 mL) gave a pale yellow solid which was filtered off and dried under vacuum. Recrystallization from CH_2Cl_2/hexane afforded colourless crystals of the compound suitable for X-ray crystallography (0.089 g, 47%). (Found: C 52.1, H 3.8, N 2.0 $C_{56}H_{46}AuF_6MnN_2O_3P_4$ requires C 52.35, H 3.6, N 2.2%). IR ν_{max}/cm^{-1} 2023 vs, 1950 s, 1927 s (CO). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ/ppm: 75.0 (s, dppe), 40.5 (s, PPh_3). ^1H NMR (CD_2Cl_2) δ/ppm: 7.59–7.33 (40 H, m, H_{arom} Ph), 6.25 (1 H, s, =CH), 5.14 (1 H, s, =CH), 3.26–3.22 (4 H, m, CH_2). $^{13}C\{^1H\}$ NMR δ/ppm: 220.1 (s, CO), 216.2 (s, CO), 192.2 (d, $^2J_{CP} = 134.8$ Hz, $C_{carbene}$), 140.0–126.1 (m, C_{arom} Ph), 125.9 (s, =CH), 120.0 (s, =CH), 27.0 (t, $^1J_{CP} = 19.3$ Hz, CH_2).

Synthesis of 18. To a solution of [**9a**]ClO_4 (0.10 g, 0.18 mmol) in CH_2Cl_2 (10 mL) KO^{t}Bu (0.041 g, 0.18 mmol) was added and the mixture stirred for 30 min. Then the solution was filtered off and [Ag($OClO_3$)(PPh_3)] (0.085 g, 0.18 mmol) added producing an immediate change in the colour of the solution from red to yellow owing to the formation of complex **17**. Then KOH (0.20 g, 3.56 mmol) was added and the mixture stirred for 1 h. The solution was then filtered off and concentrated to 3 mL. Addition of diethyl ether (15 mL) gave a yellow solid, which was filtered off and dried under vacuum (0.056 g, 56%). (Found: C 49.8, H 3.25, N 10.2 $C_{23}H_{18}ClMnN_4O_7$ requires C 50.0, H 3.3, N 10.1%). IR ν_{max}/cm^{-1} 2030 vs, 1939 s, 1928 s (CO). ^1H NMR (CD_2Cl_2) δ/ppm: 9.21 (2 H, d, $^3J_{HH} = 5.1$ Hz, H_A bipy), 8.47 (2 H, d, $^3J_{HH} = 8.0$ Hz, H_D bipy), 8.24 (2 H, t, $^3J_{HH} = 7.4$ Hz, H_C bipy), 7.71 (2 H, t, $^3J_{HH} =$ 6.6 Hz, H_C bipy), 7.48–7.46 (3 H, m, H_{arom} Ph), 7.16 (1 H, d,

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Table 2 Crystallographic data for **8a**, **11a**, **13** and **18**

	8a	**11a**	**13**	**18**
Formula	$C_{21}H_{16}F_6MnN_4O_3P$	$C_{41}H_{32}AuClMnN_4O_7P$	$4(C_{56}H_{46}AuF_6MnN_2O_3P_4)$, $3(CH_2Cl_2)$, $4(H_2O)$	$C_{23}H_{18}ClMnN_4O_7$
FW/g mol^{-1}	572.29	1011.04	5465.79	552.80
Colour/habit	Colourless	Yellow	Yellow	Yellow
Crystal dimensions/mm^3	$0.28 \times 0.20 \times 0.02$	$0.11 \times 0.07 \times 0.03$	$0.36 \times 0.32 \times 0.25$	$0.23 \times 0.08 \times 0.08$
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Triclinic
Space group	*Pccn*	$P2_1/c$	$P2_1/c$	$P\bar{1}$
a/Å	17.9823(7)	13.6998(3)	19.1731(8)	8.9537(2)
b/Å	20.1857(9)	16.4964(2)	34.8321(17)	10.4298(2)
c/Å	12.4699(5)	34.3632(8)	17.7003(9)	13.1270(3)
α/°	90	90	90	79.323(2)
β/°	90	95.510(2)	106.796(2)	80.763(1)
γ/°	90	90	90	73.754(1)
V/Å^3	4526.4(3)	7730.1(3)	11 316.7(9)	11 48.84(4)
Z	8	8	2	2
T/K	100(2)	100(2)	100(2)	100(2)
D_{calcd}/g cm^{-3}	1.680	1.737	1.639	1.598
μ/mm^{-1}	0.736	4.285	3.091	0.745
F(000)	2304.0	3984.0	5526.0	564.0
θ range/°	1.52–26.41	1.37–26.03	1.17–26.02	1.59–27.1
No. of reflections collected	61 187	69 647	101 972	35 256
No. of independent reflections/R_{int}	4653/0.1034	15 238/0.1049	22 254/0.1591	5040/0.0755
No. of observed reflections ($I > 2\sigma(I)$)	2859	10 969	15 792	4476
No. of data/restraints/parameters	4653/0/330	15 238/928/873	22 254/70/1221	5040/0/334
R_1/wR_2 ($I > 2\sigma(I)$)[a]	0.0434/0.083	0.0634/0.1026	0.0586/0.1486	0.0301/0.0734
R_1/wR_2 (all data)[a]	0.1034/0.1073	0.0931/0.1049	0.0940/0.1591	0.035/0.0755
GOF (on F^2)[a]	1.016	1.989	1.579	1.055
Largest diffraction peak and hole (e Å^{-3})	+0.542/−0.38	+2.884/−1.830	+4.207/−2.895	+0.607/−0.494

[a] $R^1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $wR_2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{1/2}$; GOF $= \{\sum[w(F_o^2 - F_c^2)^2]/(n-p)\}^{1/2}$.

$^3J_{HH}$ = 1.1 Hz, N=CH), 7.13–7.10 (2 H, m, H_{arom} Ph), 6.18 (1 H, s, =CH), 1.94 (3 H, s, CH_3).

X-Ray crystallography

Suitable single crystals of **8a** (yellow), **11a** (yellow), **13** (colourless) and 1**8** (yellow) for the X-ray diffraction study were selected. The data collection was carried out at 100(2) K. The crystals were mounted on a Smart-CCD-1000 BRUKER single crystal diffractometer equipped with a graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Multi-scan[18] absorption correction procedures were applied to the data. The structures were solved, using the WINGX package.[19] by direct methods (DIRDIF-99)[20] and refined by using full-matrix least-squared against F^2 (SHELXL-97).[21] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were geometrically placed and left riding on their parent atoms except for the hydrogen atoms on: N3 in compound **8a**, C2 and C4 in compound **18**. Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at shift/error < 0.001. The final residual electron density maps showed no remarkable features. (Table 2)

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