Dalton Transactions

PAPER

View Article Online
View Journal | View Issue

Cite this: *Dalton Trans.*, 2014, **43**, 11059

Received 14th March 2014, Accepted 23rd May 2014

DOI: 10.1039/c4dt00778f

www.rsc.org/dalton

Gold(III) compounds containing a chelating, dicarbanionic ligand derived from 4,4′-di-*tert*-butylbiphenyl†

B. David,[a] U. Monkowius,[b] J. Rust,[c] C. W. Lehmann,[c] L. Hyzak[a] and F. Mohr*[c]

An oligomeric gold(III) compound containing dicarbanionic chelating 4,4′-di-*tert*-butylbiphenyl was prepared *via* transmetallation using the corresponding organotin(IV) compound. The reactivity of the chloro-bridged oligomer with various species including neutral N-, P-, and C-donor ligands as well as monoanionic S- and Se-ligands was investigated. Some of the products were characterised by X-ray crystallography. The photophysical properties of two derivatives were studied.

Introduction

The transfer of an organic group to a gold centre is traditionally carried out using organolithium compounds, Grignard reagents or organomercurials.[1,2] There are however alternative transmetallation agents, which are particularly attractive because of their insensitivity to air and moisture, their mild reaction conditions and simple work-up. These include organotin(IV) compounds and boronic acids.[3–9] Whilst the former have been used in the preparation of both gold(I) and gold(III) compounds, the latter are so far limited to gold(I). Gold(III) compounds represent interesting alternatives to other metal-based luminescent compounds with a d^8 electron configuration.[10,11] For Pd(II) and Pt(II) complexes (in the absence of metal–metal interactions) the emissive excited state is either a metal-to-ligand charge transfer (MLCT) or an intra-ligand (IL) transition (or a mixture of both) and of triplet-character (phosphorescence).[12] Their metal-centred transitions are usually at high energy and do not strongly influence the luminescence properties, which is important as these dd-states usually lead to a very efficient radiationless deactivation of the excited state. Au(III) complexes are much less investigated due to some preconditions which have to be fulfilled for an emissive behaviour: because of the high oxidation potential of gold in the oxidation state +3 a MLCT is not favoured. For these complexes containing ligands with an extended π-system an emissive IL excited state is feasible, but the energetically low lying dd-states quench potential emissive states of most Au(III) complexes. However, these dd-states can be destabilized by strong field ligands diminishing the radiationless deactivation. Consequently, several cyclometallated complexes of the general formula $[Au(C–N)L_2]^{n+}$ (C–N = 2-phenylpyridine type ligand; L = acetylide, NHC; n = 0 or 2) and similar complexes bearing pincer type ligands including 2,6-diphenylpyridine or 6-phenyl-2,2′-bipyridine were reported to feature luminescence even in fluid solution at room temperature. The emissions are mostly assignable to an ^{3}IL-transition and sometimes these complexes also show a dual emission of both ^{1}IL and ^{3}IL character.[13] Luminescent cyclometallated Au(III) complexes were reviewed in 2011[11] and since then, several new examples of this type were published.[14–22] To the best of our knowledge, there is only one report on a luminescent Au(III) complex bearing a biphenyl moiety: [Au(Ppy)(Bip)] (Ppy = 2-phenylpyridine; Bip = biphenyl).[23] However, the second chromophore (Ppy) complicates the precise assignment of the transition. Indeed, according to TD-DFT calculations, both a ligand-to-ligand charge transfer (^{3}LLCT) [π(Bip) → π*(Ppy)] and ^{3}IL [π(Bip) → π*(Bip)] contribute to the excited state. For this reason, the complexes presented below are particularly valuable, because they allow the investigation of the discrete chromophoric Au(III)-biphenyl moiety.

In continuation of our work on the design of organogold(I) compounds and their applications,[8,24–28] we now wished to extend this to gold(III) and report here the preparation of an auracycle derived from 2,2′-dibromo-4,4′-di-*tert*-butylbiphenyl and its derivatives as well as detailed photophysical studies of some compounds.

---

[a] *Fachbereich C, Anorganische Chemie, Bergische Universität Wuppertal, Gaußstr. 20, 42119 Wuppertal, Germany. E-mail: fmohr@uni-wuppertal.de*

[b] *Institut für Anorganische Chemie, Johannes Kepler University Linz, Altenbergerstr. 69, 4040 Linz, Austria*

[c] *Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany*

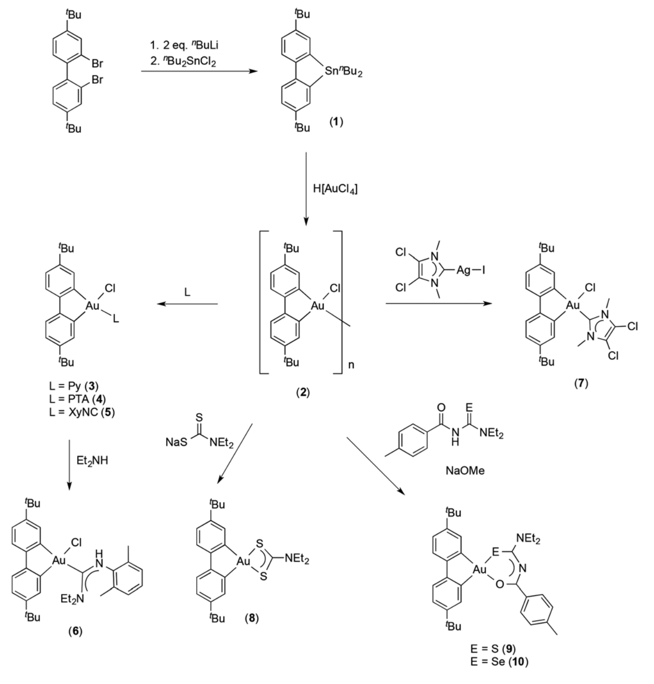
† CCDC 973049, 973050, 973052 and 973053. For crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00778f

Results and discussion

Synthesis and reactivity

The organotin(IV) heterocycle $[Sn(^tBu_2Bip)(^nBu)_2]$ (**1**) ($^tBu_2Bip$ = 4,4′-di-*tert*-butylbiphenyl-2,2′-diyl) was prepared in good yield from the reaction of 2,2′-dibromo-4,4′-di-*tert*-butylbiphenyl with two equivalents of ^nBuLi and subsequent addition of one equivalent of $^nBu_2SnCl_2$ according to a modified literature procedure (Scheme 1). An improved method for the preparation of 2,2′-dibromo-4,4′-di-*tert*-butylbiphenyl which uses CH_2Cl_2 instead of CCl_4 was also developed. The tin species $[Sn(^tBu_2Bip)(^nBu)_2]$ (**1**) reacts with $H[AuCl_4]$ in refluxing acetonitrile to give a cream coloured material in moderate yield (Scheme 1). The same compound could also be obtained (in similar yield) using $[AuCl_3(tht)]$. However, commercial $H[AuCl_4]$ was more convenient and also avoids use of malodorous tetrahydrothiophene.

Our hope that the presence of the two ^{t}Bu-groups on the biphenyl unit might improve the solubility of the compound was unfortunately not realised. The cream coloured compound which we formulate as the oligomer $[AuCl(^tBu_2Bip)]_n$ (**2**) could not be characterised by solution NMR spectroscopy due to its insolubility in common solvents. However, MALDI mass spectra, recorded using a solvent-free sample preparation technique and the dried-droplet technique, showed signals corresponding to the dimer $[AuCl(^tBu_2Bip)]_2{}^+$ as well as a fragment peak due to $[\{AuCl(^tBu_2Bip)\}_2–Cl]^+$. The fragment peak gives the most intense signal in all mass spectra recorded. The ionization in positive mode seems to favour the loss of one chloride ion towards the formation of a radical cation of the aromatic system. This mass spectroscopic data suggests that $n = 2$ *i.e.* compound **2** may be a chloro-bridged dimer. For the analogous unsubstituted biphenyl species $[AuCl(Bip)]_n$ it was also proposed that $n = 2$.[4] Furthermore, the formation of a halide bridged arylgold(III) dimer has been confirmed by a structural study of the mesityl gold compound $[AuCl(mes)]_2$.[29] Similarly to what was reported by Usón for the biphenyl derivative,[4] the addition of donor ligands including pyridine, PTA (1,3,5-triaza-7-phosphaadamantane) or xylyl isonitrile to a CH_2Cl_2 suspension of **2** results in rapid dissolution of the dimer. Out of these solutions the monomeric gold(III) complexes $[AuCl(^tBu_2Bip)(L)]$ [L = Py (**3**); PTA (**4**), XyNC (**5**)] were isolated as pale yellow solids in good yields. The Au(III) derivative containing the N-heterocyclic carbene donor ligand (**7**) was obtained by a transmetallation reaction of **2** with the NHC-silver complex Cl_2Me_2ImAgI. The chlorido ligands in **2** can also be replaced by monoanionic chelating ligands as exemplified by compounds **8–10** which were obtained by addition of NaS_2CNEt_2 or the acylthio- and selenoureas $4\text{-}MeC_6H_4C(O)NHC(E)NEt_2$ (E = S, Se) to a suspension of **2** in the presence of base (Scheme 1). These monomeric gold(III) compounds were characterized by solution NMR spectroscopy and elemental analysis. In the case of complexes **3–5**, **7** and **9–10**, there appear two sets of resonances for the ^{t}Bu-biphenyl groups in the ^1H NMR spectra due to the non-equivalence of the two aromatic rings. While it was easy to determine which signals belong to the same ring using 2D NMR experiments, it was not always possible to assign absolutely which proton belongs to which ring. However, in the case of the pyridine and NHC complexes (**3** and **7**), one set of doublets corresponding to H-3 of the biphenyl ring is shifted considerably upfield (to *ca.* 6.4 ppm). We attribute this shift to be caused by the close proximity of the aromatic ring (Py or NHC), the centre of which lies almost directly above this proton. With this information we could subsequently assign all proton and carbon signals unambiguously in these two compounds. In the carbene complex **7** the resonance of the carbene-carbon atom was observed at 186 ppm in the ^{13}C NMR spectrum.[30] For comparison, in NHC-$AuCl_3$ complexes the chemical shifts of the carbene-carbon atom fall within the range of 140 to 150 ppm. The gold(III) isonitrile complex (**5**) was reacted with Et_2NH at room temperature affording a gold(III) compound containing an N-acyclic carbene (NAC) ligand $[AuCl(^tBu_2Bip)\text{-}\{C(NEt_2)(NHXy)\}]$ (**6**) (Scheme 1). Whilst the proton NMR data for this compound is not very diagnostic, the ^{13}C NMR spectrum shows a resonance at 209 ppm due to the carbene-carbon atom. Similar addition reactions of secondary amines to chlorogold(I) isonitrile complexes giving chlorogold(I)-NAC derivatives have previously been described.[31] In these compounds the resonance for the carbene-carbon atoms are observed at around 190 ppm in the ^{13}C NMR spectra. Unfortunately, we were unable to obtain X-ray quality crystals of the NAC derivative **6** despite numerous attempts to unambiguously confirm the proposed structure.



Scheme 1

Structural studies

We were able to obtain X-ray quality crystals of several of the gold(III) compounds reported here. The molecular structures of compounds **3**, **5**, **8** and **10** are shown in Fig. 1–4. Selected bond lengths and angles are collected in Table 1.

In all of the compounds reported here, the gold atom is coordinated by two carbon atoms of the biphenyl unit as well as two other ligand atoms in a square planar arrangement, as expected for gold(III). The carbon–gold bond-lengths are typical for aromatic compounds bound to a gold(III) centre. Only one other crystal structure of a gold(III) complex containing a dicarbanionic, chelating biphenyl ligand has been reported so far.[12] The carbon–gold bond lengths show a narrow distribution centered at 2.05 Å. The carbon–gold–carbon angle is significantly smaller than 90° and comparable to the bite angle in phenylpyridyl ligands. The acylselenoureato complex (**10**) represents the only known example of a gold(III) compound containing a deprotonated acylselenourea ligand. Generally, attempts to react such organoselenium species with gold(III) precursors have resulted in reduction to gold(I) accompanied by oxidation of the selenium compound.[32,33] The dianionic chelating carbon ligand is likely to be stabilising this complex in the +3 oxidation state.

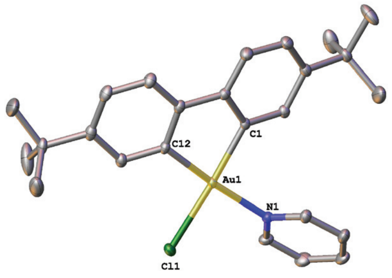


Fig. 1 Molecular structure of [Au(^{t}Bu$_2$Bip)(Py)] (**3**). Only one of the two independent molecules of the asymmetric unit is shown. Hydrogen atoms have been omitted for clarity.

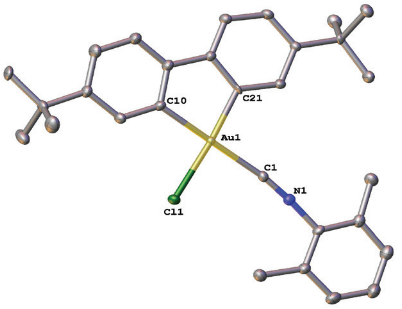


Fig. 2 Molecular structure of [Au(^{t}Bu$_2$Bip)(XyNC)] (**5**). Hydrogen atoms have been omitted for clarity.

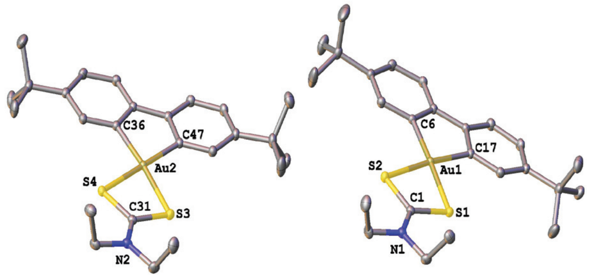


Fig. 3 Molecular structure of [Au(^{t}Bu$_2$Bip)(S$_2$CNEt$_2$)] (**8**). Hydrogen atoms have been omitted for clarity.

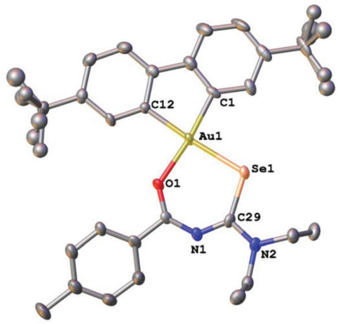


Fig. 4 Molecular structure of [Au(^{t}Bu$_2$Bip){4-MeC$_6$H$_4$C(O)NC(Se)NEt$_2$}] (**10**). Only one of the two independent molecules of the asymmetric unit is shown. Hydrogen atoms have been omitted for clarity. The disordered ^{t}Bu-groups are shown as spheres with arbitrary radii.

Table 1 Selected bond lengths and angles of the gold coordination sphere[a]

	(**3**)	(**5**)	(**8**)	(**10**)
Au–C$_1$	2.0233(1) 2.029(2)	2.038(3)	2.0328(11) 2.0277(12)	2.048(6) 2.043(5)
Au–C$_2$	2.024(2) 2.025(2)	2.036(3)	2.0267(11) 2.0386(11)	2.022(6) 2.027(5)
Au–L$_3$	2.3757(5) [Cl] 2.3686(5)	2.3762(7) [Cl]	2.3810(3) [S] 2.4077(3)	2.4551(10) [Se] 2.4599(9)
Au–L$_4$	2.1326(17) [N] 2.1500(17)	2.069(3) [C]	2.3947(3) [S] 2.3802(3)	2.099(4) [O] 2.084(4)
L$_3$–Au–L$_4$	88.68(5) 87.77(5)	85.95(8)	74.610(12) 74.315(13)	91.63(12) 93.30(11)
C$_1$–Au–L$_3$	176.81(6) 173.64(6)	179.31(12)	177.64(3) 174.08(3)	175.63(15) 176.28(15)
C$_2$–Au–L$_4$	172.85(7) 177.18(8)	175.85(8)	174.81(3) 178.26(3)	172.8(2) 171.19(19)
C$_1$–Au–C$_2$	80.85(8) 81.30(8)	81.27(12)	81.47(5) 81.29(5)	81.1(2) 81.2(2)

[a] Standard uncertainties are given in parentheses. For ligands L3 and L4 the atom type is given in square brackets. For those crystal structures with more than one molecule in the asymmetric unit, bond lengths and angles for both molecules are listed in separate rows.

Photophysical studies

The pyridyl and isonitrile complexes **3** and **5** displayed blue luminescence upon irradiation with a UV lamp, therefore more detailed photophysical studies were carried out with these two compounds. For both complexes, comparable photophysical behaviour typical for Au complexes bearing a ligand with an extended and rigid π-system could be observed.[13,34–36] The electronic absorption spectra exhibit features at ~250 nm and a band centred around 300 nm (Fig. 5).

The high energy signals are superimposable with the absorption of free biphenyl[37] and can be assigned to a π–π* transition. Frequently, IL bands are bathochromic shifted due

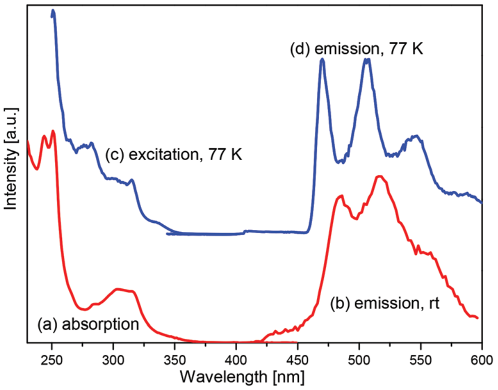


Fig. 5 Electronic spectra of **3**: (a) absorption spectrum, (b) emission spectrum at r.t. in CH_2Cl_2 ($c \approx 10^{-5}$ mol L^{-1}, degassed, λ_{exc} = 310 nm), and (c) excitation spectrum (λ_{det} = 520 nm), and emission spectrum at 77 K in MeTHF glass ($c \approx 10^{-5}$ mol L^{-1}, λ_{exc} = 310 nm).

to metal coordination, *i.e.* the low energy bands might result from further, metal perturbed IL transitions covering the Cl → Au ligand-to-metal-charge-transfer (LMCT) states, which are usually of lower intensity.[36,38–40] Interestingly, these low energy excited states are even further bathochromically shifted in the solid state. In the excitation spectra of neat **3** intensive bands reaching up to 400 nm (Fig. 6) are observed, clearly indicating a strong influence of the rigidity of the environment and/or of the supramolecular arrangement of the molecules.

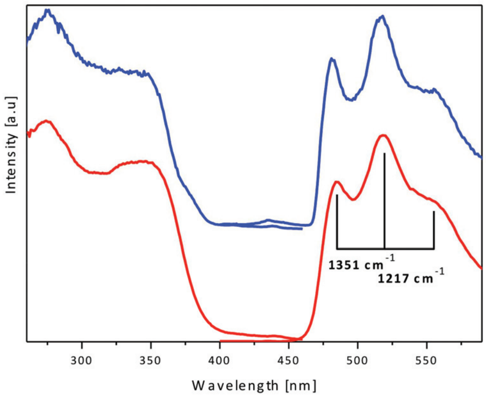


Fig. 6 Electronic spectra of neat **3**: excitation (left, λ_{det} = 480 nm) and emission spectra (right, λ_{exc} = 310 nm) at r.t. (red) and at 77 K (blue).

Formation of excimers can be ruled out due to the bulky *t*-butyl substituents of the ligand. In addition, we could not observe any evidence for excimer based absorption or emission bands in solution. A detailed investigation in solution is somewhat hampered by the photosensitivity of the compounds. In de-aerated solutions, the emission signals are very weak at room temperature. The low emission intensity of solutions of luminescent Au(III) complexes is well known and a result of the photoreductive elimination of *e.g.* the halide ligands and of low-energy non-radiative d–d LF states.[10,11,13,34,40] On the other hand, the luminescence of the complexes becomes more intense in a glass matrix at 77 K or as neat powders, where competing quenching processes are minimized. Both compounds feature structured emission bands both in solid state and solutions typical for an intraligand π–π* transition. Again, there is no evidence for excimer based emissions. A huge Stokes shift and a long emission decay time in the microsecond regime indicate phosphorescence from a ^{3}LC state (Table 2).

This assignment is further supported be the vibrational progressional spacing (*e.g.* 1351 and 1217 cm^{-1} for solid **3** at r.t.; Fig. 6), which are similar to biphenyl (1055 and 1274 cm^{-1}) and typical for vibrational stretching modes of aromatic ligands.[41] It should be noted, that the homologous Au(I) complex [Au(Bip)(PPh_3)] features a very similar luminescence behaviour with somewhat hypsochromic shifted emission bands.[42] It is instructive to compare these data with the isoelectronic [Pt(Bip)L_2] complexes (L = neutral ligands such as CO, phosphines, COD).[43] Whereas the wavelengths of the emission bands are similar, their emission decay times are almost one magnitude smaller. Due to the fact that the spin orbit coupling (SOC) is slightly higher for gold than for platinum, the spin-forbidden $T_1 \rightarrow S_0$ transition for the gold complexes should be at least as probable as for Pt(II) complexes. This fact shines light on the different nature of the emissive state: The d-orbitals of the highly oxidizing Au(III) ions do not directly participate in the electronic transition rendering the SOC rather low in spite of the high atomic number of the gold. This interpretation is further supported by the very similar photophysical behaviour of Au(I) complexes bearing ligands

Table 2 Photophysical data of compounds **3** and **5**

Compound	Absorption λ_{max} (lgε)	Medium	Emission λ_{max}	Excitation λ_{max}	τ [μs]
3	244 (4.36), 253 (4.38), 265 sh (3.75), 284 (3.75), 304 (3.77), 316 (3.76)	CH_2Cl_2 (r.t.)	485, 517, 554		—^{a}
		MeTHF (77 K)	470, 506, 545	250, 274, 283, 300, 315	220
		Solid (r.t.)	485, 519, 554	270, 330, 347	48
		Solid (77 K)	481, 517, 555	275, 326, 346	77
5	254 (4.90), 275 sh (4.43), 286 sh (4.29), 305 (3.99), 317 (4.01)	CH_2Cl_2 (r.t.)	501, 533, 576		—^{a}
		MeTHF (77 K)	483, 517, 553	315, 302, 283 sh, 276	150
		Solid (r.t.)	492, 529, 568, 615 sh	275, 331, 344	61
		Solid (77 K)	484, 496, 523, 566, 613 sh	275, 325, 344	92

[a] Due to the photosensitivity and low intensity of the emission, no reliable emission decay time could be measured in solution at r.t.

with an extended π-system and leads to the conclusion that the gold atom (regardless of its oxidation state) is modulating the electronic properties of the ligand according to the so called "external heavy atom effect".[44] In contrast, the metal character of the excited triplet states of the Pt(II) complexes are high even in cases where the transitions are dominantly ligand centred. Therefore, the SOC is more effective resulting in shorter emission decay time.

Conclusions

A family of gold(III) compounds containing dicarbanionic chelating ligands derived from 4,4′-di-*tert*-butylbiphenyl were prepared and fully characterised. The structures of several analogues were determined by X-ray crystallography. The pyridine and xylyl isonitrile compounds show interesting photophysical properties, which were studied both in solution and solid-state.

Experimental

General procedures

^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were recorded on a Bruker Avance ARX 400 (400 MHz) or a Bruker Avance III 600 (600 MHz) spectrometer. Chemical shifts are quoted relative to external $SiMe_4$ (^{1}H, ^{13}C), or H_3PO_4 (^{31}P). Elemental analyses were performed by staff of the microanalysis laboratory of the Technical University Dortmund. PTA, Cl_2Me_2ImAgI, 4,4′-di-*tert*-butylbiphenyl and 4-$MeC_6H_4C(O)NHC(Se)NEt_2$ were prepared according to literature methods.[45–48] All other chemicals and solvents (anhydrous grade) were sourced commercially and used as received. Reactions involving air- and moisture sensitive compounds were carried out under dry dinitrogen gas using standard Schlenk techniques. MALDI and LDI analyses were performed on a Shimadzu AXIMA-Performance MALDI instrument, equipped with a pulsed nitrogen laser (λ = 337 nm) delivering 3 ns laser pulses, a nominal energy of 100 μJ per laser shot and a laser ablation width of 100 μm. The laser flux was adjusted to be slightly above the threshold for the observation of MALDI ions. The instrument was adjusted to the positive-ion mode using the reflectron and an acceleration voltage of 20 kV. For the dried-droplet technique pyrene 10 mg mL^{-1} was solved in $CHCl_3$ and mixed with the solid sample to give a suspension. Aliquots (0.5 μL) of the suspension were spotted on the target and allowed to air-dry. For the solvent-free technique the sample was pressed with a spatula on a stainless steel target giving a thin film of sample on the target.

2,2′-Dibromo-4,4′-di-*tert*-butylbiphenyl. To a solution of 4,4′-di-*tert*-butylbiphenyl (2.5 g, 10.0 mmol) in CH_2Cl_2 (10 mL) was added Fe powder (few mg) and bromine (2.8 mL, 22.0 mmol). After *ca.* 2 h stirring at room temperature the stirrer bar with the adhering iron powder was removed and the deep orange solution was left to evaporate in the hood. The resulting orange solid was recrystallised from EtOH to afford yellow needles of 2,2′-dibromo-4,4′-di-*tert*-butylbiphenyl in 63% yield. GC-MS (*m/z*): 424 $[M]^+$, 409 $[M - CH_3]^+$, 313 $[M - 2\ ^{t}Bu]^+$. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.40 (s, 18 H, ^{t}Bu), 7.21 (d, J = 8.0 Hz, 2 H, H-6), 7.41 (dd, J = 8.8, 2.0 Hz, 2 H, H-5), 7.70 (d, J = 2.0 Hz, 2 H, H-3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 31.23 (^{t}Bu), 34.70 (^{t}Bu), 123.40 (C-2), 124.14 (C-5), 129.48 (C-6), 130.72 (C-3), 139.01 (C-1), 152.65 (C-4). Elemental analysis calcd (%) for $C_{20}H_{24}Br_2$: C 56.6, H 5.7; found: C 56.2, H 5.9.

[Sn(^{t}Bu$_2$Bip)(^{n}Bu)$_2$] (1). To a solution of 2,2′-dibromo-4,4′-di-*tert*-butylbiphenyl (1.9 g, 4.4 mmol) in Et_2O (20 mL) was slowly added ^{n}BuLi (3.7 mL of a 2.5 M solution in hexanes) at 0 °C. After complete addition the mixture was allowed to warm to room temperature and was subsequently stirred for 2 h. To the suspension of the dilithium salt was added a solution of $^{n}Bu_2SnCl_2$ (1.3 g, 4.2 mmol) in Et_2O (10 mL). After stirring overnight at room temperature the mixture was hydrolysed with water. The phases were allowed to separate and the organic phase was washed with water (3 × 20 mL). After drying ($MgSO_4$) and removal of the solvent, the resulting yellow oil was triturated with MeOH and cooled. The resulting yellow solid was isolated by filtration and was dried in air. The product was obtained in 85% yield. GC-MS (*m/z*): 498 $[M]^+$, 385 $[M - 2\ ^{n}Bu]^+$, 272 $[M - 2\ ^{t}Bu - 2\ ^{n}Bu]^+$. ^{1}H NMR (600 MHz, $CDCl_3$): δ = 0.96 (t, J = 7.5 Hz, 6 H, ^{n}Bu CH_3), 1.40 (m, 4 H, $SnCH_2$), 1.44 (s, 18 H, ^{t}Bu), 1.45 (m, 4 H, ^{n}Bu CH_2CH_3), 1.72 (quint., J = 7.5 Hz, 4 H, ^{n}Bu $CH_2CH_2CH_3$), 7.46 (dd, J = 2.3, 8.3 Hz, 2 H, H-4), 7.70 (d, J = 2.3 Hz, 2 H, H-6), 7.90 (d, J_{HH} = 8,3 Hz, 2 H, H-3). ^{13}C{^{1}H} NMR (151 MHz, $CDCl_3$): δ = 12.1 (J_{C-Sn} = 178.8 Hz, ^{n}Bu C-α), 13.6 (^{n}Bu C-δ), 27.1 (J_{C-Sn} = 26.9 Hz, ^{n}Bu C-γ), 29.1 (J_{C-Sn} = 12.1 Hz, ^{n}Bu C-β), 31.4 (^{t}Bu), 34.5 (^{t}Bu), 121.8 (J_{C-Sn} = 35.5 Hz, C-3), 125.9 (C-4), 133.2 (J_{C-Sn} = 42.9 Hz, C-6), 140.8 (C-5), 146.0 (J_{C-Sn} = 58.3 Hz, C-1), 149.7 (J_{C-Sn} = 37.4 Hz, C-2). Elemental analysis calcd (%) for $C_{28}H_{42}Sn$: C 67.6, H 8.5; found: C 67.4, H 8.4.

[AuCl(^{t}Bu$_2$Bip)]$_n$ (2). A solution containing $H[AuCl_4]\cdot 2H_2O$ (0.100 g, 0.27 mmol) and **1** (0.134 g, 0.27 mmol) in MeCN (25 mL) was heated to reflux for *ca.* 24 h. The resulting solid was isolated by filtration and was washed successively with H_2O, MeCN and Et_2O. A cream coloured solid was obtained in 38% yield (0.050 g). MALDI-MS (pyrene matrix, *m/z*): 461.2 $[M - Cl]^+$, 957.3 $[2M - Cl]^+$, 992.1 $[2M]^+$. LDI-MS (matrix-free sample, *m/z*): 461.3 $[M - Cl]^+$, 957.3 $[2M - Cl]^+$, 992.2 $[2M]^+$. Elemental analysis calcd (%) for $[C_{20}H_{24}AuCl]_2$: C 39.7, H 4.9; found: C 40.1, H 4.6.

Reactions of [AuCl(^{t}Bu$_2$Bip)]$_n$

To a suspension of **2** in CH_2Cl_2 (8 mL) was added one equivalent of the appropriate ligand (Py, PTA, XyNC, NaDTC, $Cl_2MeImAgI$). The mixture was left to stir at room temperature for *ca.* 2 h and subsequently passed through a pad of celite. The filtrate was taken to dryness and the resulting solids were washed with water and Et_2O and subsequently dried in air.

[AuCl(^{t}Bu$_2$Bip)(Py)] (3). 28.4 mg, 84% yellow solid from **2** (30.0 mg, 0.03 mmol) and pyridine (4.2 μL, 0.06 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.11 (s, 9 H, ^{t}Bu′), 1.39 (s, 9 H,

^{t}Bu), 6.34 (d, J = 1.5 Hz, 1 H, H-6′), 7.18 (dd, J = 7.9 Hz, 1.2 Hz, 1 H, H-4′), 7.22 (dd, J = 7.9, 1.5 Hz, 1 H, H-4), 7.24 (d, J = 7.9 Hz, 1 H, H-3), 7.29 (d, J = 7.9 Hz, 1 H, H-3′), 7.74 (t, J = 6.4 Hz, 2 H, *m*-Py), 8.11 (t, J = 7.9 Hz, 1 H, *p*-Py), 8.24 (d, J = 1.2 Hz, 1 H, H-6), 8.88 (d, 2 H, J = 4.9 Hz, *o*-Py). ^{13}C {^{1}H} NMR (151 MHz, $CDCl_3$): δ = 31.1 (^{t}Bu′); 31.4 (^{t}Bu), 34.73 (^{t}Bu′), 35.2 (^{t}Bu), 120.8 (C-3), 121.2 (C-3′), 124.7 (C-4, C-4′), 126.5 (*m*-Py, C-6′), 131.26 (C-6), 140.0 (*p*-Py), 149.2 (C-5′), 149.4 (C-2′), 149.6 (C-5), 149.8 (C-2), 150.0 (C-1), 150.3 (*o*-Py) 155.7 (C-1′). Elemental analysis calcd (%) for $C_{25}H_{29}NAuCl$: C 34.2, H 5.9, N 2.4; found: C 34.6, H 5.4, N 2.1.

[AuCl(^{t}Bu$_2$Bip)(PTA)] (4). 26.5 mg, 81% beige solid from **2** (30.0 mg, 0.03 mmol) and PTA (9.4 mg, 0.06 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.37 (s, 9 H, ^{t}Bu′), 1.41 (s, 9 H, ^{t}Bu), 4.64 (s, 6 H, NCH_2N), 4.66 (s, 6 H, PCH_2N), 7.19 (m, 2 H, H-4, H-6), 7.25 (m, 2 H, H-6′, H-3), 7.33 (d, 1 H, J = 8.3 Hz, H-3′), 8.24 (dd, 1 H, J = 9.8 Hz, 1.9 Hz, H-4′). ^{13}C {^{1}H} NMR (101 MHz, $CDCl_3$): δ = 31.4 (^{t}Bu), 31.8 (^{t}Bu′), 35.0 (^{t}Bu), 35.4 (^{t}Bu′), 51.1 (d, J_{CP} = 9.9 Hz, PCH_2N), 73.2 (d, J_{CP} = 6.6 Hz, NCH_2N), 120.7 (d, J_{CP} = 6.6 Hz, C-6′), 121.9 (C-3′), 124.7 (C-4), 124.9 (C-4′), 129.1 (C-3), 130.9 (d, J_{CP} = 11.0 Hz, C-6), 148.9 (C-2′), 149.9 (C-5′), 150.0 (C-5), 51.2 (d, J_{CP} = 4.4 Hz C-2), 154.4 (d, J_{CP} = 7.7 Hz, C-1′), 165.8 (C-1). ^{31}P{^{1}H} NMR (162 MHz, $CDCl_3$): δ = −54.41. Elemental analysis calcd (%) for $C_{26}H_{36}N_3PAuCl$: C 47.8, H 5.6, N 6.4; found: C 48.0, H 5.8, N 6.3.

[AuCl(^{t}Bu$_2$Bip)(XyNC)] (5). 36.1 mg, 95% colourless solid from **2** (30.0 mg, 0.03 mmol) and XyNC (7.8 mg, 0.06 mmol). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 1.35 (s, 9 H, ^{t}Bu′), 1.39 (s, 9 H, ^{t}Bu), 2.66 (s, 6 H, $\mathrm{C}H_3$-Xy), 7.22 (dd, J = 8.3 Hz, 1.9 Hz, 1 H, H-4), 7.26 (m, 4 H, H-3, H-4′, *m*-Xy), 7.31 (d, J = 8.3 Hz, 1 H, H-3′), 7.42 (t, J = 7.9 Hz, 1 H, *p*-Xy), 7.65 (d, J = 1.9 Hz, 1 H, H-6′), 8.27 (d, J = 1.9 Hz, 1 H, H-6). ^{13}C{^{1}H}-NMR (151 MHz, $CDCl_3$): δ = 19.0 (2 × $C\mathrm{H_3}$-Xy), 31.3 (^{t}Bu′), 31.4 (^{t}Bu), 34.9 (^{t}Bu), 35.3 (^{t}Bu′), 120.7 (C-3), 121.5 (C-3′), 124.2 (*ipso*-Xy), 124.9 (C-4′), 125.0 (C-4), 128.6 (*m*-Xy); 129.7 (C-6), 131.5 (*p*-Xy), 131.8 (C-6′), 136.71 (*o*-Xy), 149.7 (C-5), 150.1 (C-2′), 150.3 (C-2, C-5′), 156.0 (C-2′), 156.5 (C-1). The signal due to the carbon atom of the N≡C group was not observed. Elemental analysis calcd (%) for $C_{29}H_{34}NAuCl$: C 55.4, H 5.5, N 2.2; found: C 55.2, H 5.6, N 2.0.

[AuCl(^{t}Bu$_2$Bip){C(NEt$_2$)(NHXy)}] (6). To a solution of **5** (25.0 mg, 0.04 mmol) in CH_2Cl_2 (6 mL) was added Et_2NH (4.2 μL, 0.04 mmol). The solution was stirred at room temperature for *ca.* 24 h and worked up as above to give 13.0 mg (47%) yellow solid. ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.31 (s, 9 H, ^{t}Bu), 1.34 (s, 9 H, ^{t}Bu′), 1.43 (t, 3 H, $\mathrm{NCH_2C}H_3$), 1.59 (t, 3 H, $\mathrm{NCH_2C}H_3$), 2.14 (br. s, 1 H, Xy CH_3), 2.56 (br. s, 1 H, Xy CH_3), 3.63 (m, 1H, $\mathrm{NC}H_2\mathrm{CH_3}$), 3.76 (m, 2 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 4.33 (m, 1 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 6.92 (br. s, 1 H, *p*-Xy), 7.12 (m, 3 H, *m*-Xy, H-4), 7.20 (dd, J = 8.1, 2.3 Hz, 1 H, H-4′), 7.22 (d, J = 8.1 Hz, 1 H, H-3), 7.30 (m, 2 H, H-3′, H-6′); 8.04 (d, J = 2.0 Hz, 1 H, H-6). The NH proton signal could not be observed. ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 12.6 ($\mathrm{NCH_2}C\mathrm{H_3}$), 13.8 $\mathrm{NCH_2}C\mathrm{H_3}$), 19.9 (Xy CH_3), 20.1 (Xy CH_3), 31.4 (^{t}Bu), 34.8 (^{t}Bu′), 35.1 (^{t}Bu), 41.7 ($\mathrm{N}C\mathrm{H_2CH_3}$), 52.2 ($\mathrm{N}C\mathrm{H_2CH_3}$), 119.7 (C-3), 120.8 (C-3′), 123.6 (C-4′, C-4), 128.6 (*m*-Xy), 129.0 (*p*-Xy), 130.2 (C-6), 131.0 (C-6′), 149.9 (C-2), 151.1 (C-2′), 148.2 (C-5′), 148.9 (C-5), 151.7 (C-1′), 159.3 (C-1), 208.7 (C-7). Signals from the quaternary carbon atoms of the xylyl group were not observed. Elemental analysis calcd (%) for $C_{33}H_{45}N_2AuCl$: C 56.5, H 6.5, N 4.0; found: C 56.8, H 6.3, N 3.9.

[AuCl(^{t}Bu$_2$Bip)(Cl$_2$MeIm)] (7). 35.7 mg, 89% yellow solid from **2** (0.03 mg, 0.03 mmol) and Cl_2MeImAgI (23.9 mg, 0.06 mmol). ^{1}H NMR (400 MHz, $CDCl_3$): δ = 1.19 (s, 9 H, ^{t}Bu′), 1.39 (s, 9 H, ^{t}Bu), 3.90 (s, 6 H, CH_3), 6.40 (d, J = 2.0 Hz, 1 H, H-6′), 7.19 (dd, J = 8.1, 1 H, 1.8 Hz, H-4′), 7.22 (dd, J = 7.8, 1.8 Hz, 1 H, H-4), 7.30 (d, J = 8.1 Hz, 1 H, H-3), 7.34 (d, J = 7.8 Hz, 1 H, H-3′), 8.27 (d, J = 2.0 Hz, 1 H, H-6). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 31.2 (^{t}Bu′), 31.4 (^{t}Bu), 34.4 (^{t}Bu′), 35.2 (^{t}Bu), 36.2 (CH_3), 118.8 (CCl), 120.2 (C-3), 121.5 (C-3′), 124.3 (C-4′), 124.5 (C-4), 128.9 (C-6′), 129.9 (C-6), 149.5 (C-5′), 149.7 (C-5), 149.9 (C-2′), 151.4, (C-2) 151.5 (C-1), 158.8 (C-1′), 186.2 (C-Au). Elemental analysis calcd (%) for $C_{25}H_{31}N_2AuCl_3$: C 45.3, H 4.7, N 4.2; found: C 45.5, H 4.4, N 4.3.

[Au(^{t}Bu$_2$Bip)(SSCNEt$_2$)] (8). 27.1 mg, 74% yellow solid from **2** (30.0 mg, 0.03 mmol) and NaDTC (13.5 mg, 0.06 mmol). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.37 (s, 18 H, ^{t}Bu), 1.43 (t, J = 7.1 Hz, 6 H, $\mathrm{NCH_2C}H_3$), 3.84 (q, J = 7.1 Hz, 4 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 7.30 (d, J = 1,8 Hz, 2 H, H-6), 7.36 (d, J = 8.1 Hz, 2 H, H-3), 7.42 (dd, J = 7.8, 2.0 Hz, 2 H, H-4). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 12.4 ($\mathrm{NCH_2}C\mathrm{H_3}$), 31.4 (^{t}Bu), 34.9 (^{t}Bu), 46.4 ($\mathrm{N}C\mathrm{H_2CH_3}$), 120.9 (C-3), 124.0 (C-4), 127.9 (C-6), 149.1 (C-2), 150.1 (C-5), 153.4 (C-1), 203.4 (C-7). Elemental analysis calcd (%) for $C_{25}H_{34}NS_2Au$: C 49.3, H 5.6, N 2.3; found: C 49.0, H 5.7, N 2.1.

[Au(^{t}Bu$_2$Bip){4-MeC$_6$H$_4$C(O)NC(S)NEt$_2$}] (9). To a solution of 4-$MeC_6H_4C(O)NHC(S)NEt_2$ (11.3 mg, 0.05 mmol) in CH_2Cl_2 (8 mL) was added a solution of NaOMe (2.8 mg, 0.05 mmol) in MeOH (6 mL). The mixture was stirred at room temperature for *ca.* 15 min before solid **2** (25.0 mg, 0.05 mmol) was added. After stirring for 2 hours at room temperature, the solution was passed through celite and the filtrate was evaporated to dryness. The resulting solid was washed with water, Et_2O and subsequently dried in air. A yellow solid was obtained in 73% yield (26.1 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.35 (m, 3 H, $\mathrm{NCH_2C}H_3$), 1.37 (s, 9 H, ^{t}Bu), 1.45 (m, 3 $\mathrm{HNCH_2C}H_3$), 1.65 (s, 9 H, ^{t}Bu′), 2.47 (s, 3 H, Me), 3.96 (q, J = 7.0 Hz, 4 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 4.05 (q, J = 7.0 Hz, 4 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 7.20 (d, J = 7.8 Hz, 1 H, H-4), 7.27–7.35 (m, 5 H, MeC6H4, H4′, H3, H3′), 7.62 (d, J = 1.8 Hz, 1 H, H-6′), 8.17 (d, J = 1.8 Hz, 1 H, H-6), 8.25 (d, J = 8.3 Hz, 2 H, MeC_6H_4). ^{13}C{^{1}H}-NMR (101 MHz, $CDCl_3$): δ = 12.6 ($\mathrm{NCH_2}C\mathrm{H_3}$), 13.2 ($\mathrm{NCH_2}C\mathrm{H_3}$), 21.6 (Me), 31.4 (^{t}Bu), 31.5 (^{t}Bu′), 35.0 (^{t}Bu), 35.2 (^{t}Bu′), 46.2 ($\mathrm{N}C\mathrm{H_2CH_3}$), 47.4 ($\mathrm{N}C\mathrm{H_2CH_3}$), 120.5 (C-3), 121.0 (C-3′), 124.3 (C-4′), 124.4 (C-4), 125.0 (C-6), 128.5 (C-6′), 128.9 (*m*-MeC_6H_4), 129.9 (*o*-MeC_6H_4), 133.4 (C-1, C-1′), 145.4 (C-1, C-1′), 142.5 (*m*-MeC_6H_4), 148.3 (C-2′), 149.1 (C-5′), 150.6 (C-2), 162.1 (*ipso* MeC_6H_4), 170.8 (C–S), 171.2 (C–O). Elemental analysis calcd (%) for $C_{33}H_{41}N_2OSAu$: C 55.8, H 5.8, N 3.9; found: C 56.0, H 5.9, N 4.0.

[Au(^{t}Bu$_2$Bip){4-MeC$_6$H$_4$C(O)NC(Se)NEt$_2$}] (10). This was prepared as described above using 4-$MeC_6H_4C(O)NHC(Se)NEt_2$. A dark yellow solid was obtained in 87% yield (33.2 mg). ^{1}H-NMR (400 MHz, $CDCl_3$): δ = 1.30–1.57 (m, 24 H, $\mathrm{NCH_2C}H_3$, ^{t}Bu), 2.46 (s, 3 H, Me), 3.97 (q, J = 6.8 Hz, 4 H, $\mathrm{NC}H_2\mathrm{CH_3}$), 4.08

(q, J = 6.8 Hz, 4 H, NCH_2CH_3), 7.21 (d, J = 7.3 Hz, 1 H, H-4), 7.24–7.41 (m, 5 H, MeC6H4, H4′, H3, H3′), 7.53 (d, J = 1.8 Hz, 1 H, H-6′), 8.17 (d, J = 1.8 Hz, 1 H, H-6), 8.24 (d, J = 7.3 Hz, 2 H, MeC_6H_4). $^{13}C\{^1H\}$-NMR (101 MHz, $CDCl_3$): δ = 13.1 (NCH_2CH_3), 13.2 (NCH_2CH_3), 21.6 (Me), 31.4 (^{t}Bu), 31.5 (^{t}Bu′), 35.0 (^{t}Bu), 35.2 (^{t}Bu′), 46.2 (NCH_2CH_3), 49.3 (NCH_2CH_3), 120.5 (C-3), 121.2 (C-3′), 124.2 (C-4′), 124.3 (C-4), 124.7 (C-6), 128.9 (m-MeC_6H_4), 130.0 (o-MeC_6H_4), 130.1 (C-6′), 134.1 (C-1, C-1′), 145.1 (C-1, C-1′), 142.6 (p-MeC_6H_4), 148.1 (C-2′), 149.3 (C-5′), 150.7 (C-2), 163.9 (*ipso* MeC_6H_4), 166.9 (C–Se), 171.4 (C–O). Elemental analysis calcd (%) for $C_{33}H_{41}N_2OSeAu$: C 52.3, H 5.5, N 3.7; found: C 52.1, H 5.5, N 3.9.

Photophysical studies

Spectroscopic grade solvents were used throughout all measurements. Absorption spectra were recorded with a Varian Cary 300 double beam spectrometer. Emission spectra at 300 and at 77 K were measured with a steady-state fluorescence spectrometer (Jobin Yvon Fluorolog 3). Emission decay times were measured with a pulsed UV xenon flash tube using the R928P detector in the photon-counting mode implemented in the fluorescence spectrometer. Fluid solutions were degassed by three pump–freeze–thaw cycles.

X-Ray crystallography

Suitable single crystals were picked under inert oil and cooled to 100 K in a nitrogen cold gas stream using an Oxford Cryosystems cooler. Data were collected on a four circle diffractometer equipped with a CCD detector using Mo-Kα radiation generated by a rotating anode and a focussing graded multilayer mirror. Further details about the crystal structure determinations have been included in the CIF files, which have been deposited with the Cambridge Crystallographic Data Centre and can be retrieved quoting CCDC numbers 973049 (**8**), 973050 (**3**), 973052 (**5**) and 973053 (**10**). The figures were generated using OLEX2.[49]

Notes and references

1 *Gold. Progress in Chemistry, Biochemistry and Technology*, ed. H. Schmidbaur, John Wiley & Sons, Chichester, 1999.
2 *Gold chemistry. Applications and future directions in the life sciences*, ed. F. Mohr, Wiley-VCH, Weinheim, 2009.
3 R. Usón, J. Vicente and M. T. Chicote, *Inorg. Chim. Acta*, 1979, **35**, L305–L306.
4 A. Usón, J. Vicente and M. T. Chicote, *J. Organomet. Chem.*, 1980, **198**, 105–112.
5 R. Usón, J. Vicente and M. T. Chicote, *J. Organomet. Chem.*, 1981, **209**, 271–279.
6 R. Usón, J. Vicente, M. T. Chicote, P. G. Jones and G. M. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1983, 1131–1136.
7 N. Meyer, S. Sivanathan and F. Mohr, *J. Organomet. Chem.*, 2011, **696**, 1244–1247.
8 N. Meyer, C. W. Lehmann, T. K. M. Lee, J. Rust, V. W. W. Yam and F. Mohr, *Organometallics*, 2009, **28**, 2931–2934.
9 D. V. Partyka, M. Zeller, A. D. Hunter and T. G. Gray, *Angew. Chem., Int. Ed.*, 2006, **25**, 8188–8191.
10 V. W. W. Yam and K. M. C. Wong, *Chem. Commun.*, 2011, **47**, 11579–11592.
11 C. Bronner and O. S. Wenger, *Dalton Trans.*, 2011, **40**, 12409–12420.
12 H. Yersin, A. F. Rausch, R. Czerwieniec, T. Hofbeck and T. Fischer, *Coord. Chem. Rev.*, 2011, **255**, 2622–2652.
13 M. Kriechbaum, M. List, R. J. F. Berger, M. Patzschke and U. Monkowius, *Chem. – Eur. J.*, 2012, **18**, 5506–5509.
14 V. K. M. Au, N. Zhu and V. W. W. Yam, *Inorg. Chem.*, 2013, **52**, 558–567.
15 W. P. To, K. T. Chan, G. S. M. Tong, C. Ma, W. M. Kwok, X. Guan, K. H. Low and C. M. Che, *Angew. Chem., Int. Ed.*, 2013, **52**, 6648–6652.
16 A. Szentkuti, M. Bachman, J. A. Garg, O. Blacque and K. Venkatesan, *Chem. – Eur. J.*, 2014, **20**, 2585–2596.
17 Y. Tanaka, K. M. C. Wong and V. W. W. Yam, *Chem. Sci.*, 2012, **3**, 1185–1191.
18 W. P. To, G. S. M. Tong, W. Lu, C. Ma, J. Liu, A. L. F. Chow and C. M. Che, *Angew. Chem., Int. Ed.*, 2012, **51**, 2654–2657.
19 D. A. Smith, D. A. Roşca and M. Bochmann, *Organometallics*, 2012, **31**, 5998–6000.
20 R. Muñoz-Rodríguez, E. Buñuel, J. A. G. Williams and D. J. Cárdenas, *Chem. Commun.*, 2012, **48**, 5980–5982.
21 D. A. Roşca, D. A. Smith and M. Bochmann, *Chem. Commun.*, 2012, **48**, 7247–7249.
22 W. Lu, K. T. Chan, S. X. Wu, Y. Chen and C. M. Che, *Chem. Sci.*, 2012, **3**, 752–755.
23 J. A. Garg, O. Blacque, T. Fox and K. Venkatesan, *Inorg. Chem.*, 2010, **49**, 11463–11472.
24 F. Mohr, S. H. Privér, S. K. Bhargava and M. A. Bennett, *Coord. Chem. Rev.*, 2006, **250**, 1851–1888.
25 E. Schuh, S. M. Valiahdi, M. A. Jakupec, B. K. Keppler, P. Chiba and F. Mohr, *Dalton Trans.*, 2009, 10841–10845.
26 E. Schuh, C. Pflüger, A. Citta, A. Folda, M. P. Rigobello, A. Bindoli, A. Casini and F. Mohr, *J. Med. Chem.*, 2012, **55**, 5518–5528.
27 A. Molter, J. Rust, C. W. Lehmann and F. Mohr, *Tetrahedron*, 2012, **68**, 10586–10591.
28 A. Citta, E. Schuh, F. Mohr, A. Folda, M. L. Massimino, A. Bindoli, A. Casini and M. P. Rigobello, *Metallomics*, 2013, **5**, 1006–1015.
29 M. Contel, A. J. Edwards, J. Garrido, M. B. Hursthouse, M. Laguna and R. Terroba, *J. Organomet. Chem.*, 2000, **607**, 129–136.
30 S. Gaillard, A. M. Z. Slawin, A. T. Bonura, E. D. Stevens and S. P. Nolan, *Organometallics*, 2010, **29**, 394–402.
31 A. S. K. Hashmi, T. Hengst, C. Lothschütz and F. Rominger, *Adv. Synth. Catal.*, 2010, **352**, 1315–1337.
32 A. Bredenkamp, X. Zeng and F. Mohr, *Polyhedron*, 2012, **33**, 107–113.

33 A. Molter and F. Mohr, *Coord. Chem. Rev.*, 2010, **254**, 19–45.

34 V. K. M. Au, W. H. Lam, W. T. Wong and V. W. W. Yam, *Inorg. Chem.*, 2012, **51**, 7537–7545.

35 J. A. Garg, O. Blacque and K. Venkatesan, *Inorg. Chem.*, 2011, **50**, 5430–5441.

36 L. Gao, M. A. Peay, D. V. Partyka, J. B. Updegraff III, T. S. Teets, A. J. Esswein, M. Zeller, A. D. Hunter and T. G. Gray, *Organometallics*, 2009, **28**, 5669–5681.

37 I. B. Berlman, *Handbook of Flourescence Spectra of Aromatic Molecules*, Academic Press, New York, 1971.

38 H. Isci and W. R. Mason III, *Inorg. Chem.*, 1983, **22**, 2266–2272.

39 W. R. Mason III and H. B. Gray, *Inorg. Chem.*, 1968, **7**, 55–58.

40 C. Hirtenlehner, C. Krims, J. Hölbling, M. List, M. Zabel, M. Fleck, R. J. F. Berger, W. Schoefberger and U. Monkowius, *Dalton Trans.*, 2011, **40**, 9899–9910.

41 A. F. Rausch, U. Monkowius, M. Zabel and H. Yersin, *Inorg. Chem.*, 2010, **49**, 7818–7825.

42 M. Osawa, M. Hoshino and D. Hashizume, *Chem. Phys. Lett.*, 2007, **436**, 89–93.

43 H. Yersin, U. Monkowius and R. Czerwieniec, *WO* 2007/11867 A1, 2007.

44 C. W. Hsu, C. C. Lin, M. W. Chung, Y. Chi, G. H. Lee, P. T. Chou, C. H. Chang and P. Y. Chen, *J. Am. Chem. Soc.*, 2011, **133**, 12085–12099.

45 D. J. Daigle, *Inorg. Synth.*, 1998, **32**, 40–45.

46 K. M. Hindi, T. J. Siciliano, S. Durmus, M. J. Panzner, D. A. Medvetz, D. V. Reddy, L. A. Hogue, C. E. Hovis, J. K. Hilliard, R. J. Mallet, C. A. Tessier, C. L. Cannon and W. J. Youngs, *J. Med. Chem.*, 2008, **51**, 1577–1583.

47 R. Hohenadel and H. A. Brune, *J. Organomet. Chem.*, 1988, **350**, 101–108.

48 A. Molter, J. Rust, C. W. Lehmann and F. Mohr, *ARKIVOC*, 2011, **vi**, 10–17.

49 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *J. Appl. Crystallogr.*, 2009, **42**, 339–341.