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Studies on gold–nitrone systems†

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A series of novel Au(I)–nitrone complexes with specific catalytic properties were prepared. Furthermore, Au(I)– and Au(III)–oxadiazole complexes were formed by a novel Au-generated nitrile–nitrone [3 + 2] cycloaddition, and the crystal structures of Au(I)–nitrones as well as the Au(I)– and Au(III)–oxadiazole complexes were studied (X-ray). A useful one-pot Au(III)-mediated cycloaddition method was developed for the formation of a number of dihydro-1,2,4-oxadiazoles, involving *in situ* formation of Au(III)–oxadiazole complexes. The observed Au(I) and Au(III) dual selective reactivity gives new understanding about the Au(I)– and Au(III)–nitrone chemistry.

Introduction

The chemistry of gold–nitrone systems is little explored.[1a,b] Realizing the promising potential of this field of gold chemistry, we have studied the complexation ability and synthetic utility of gold–nitrone based systems.[2,3] Terminal propargyl acetals and nitrones afforded 1,2-oxazine derivatives in the presence of a gold (I) catalyst (Scheme 1a)[2] by an uncommon [3 + 3] cycloaddition pathway. Moreover, we discovered that phosphane–gold–nitrone complexes were catalytically active in a unique regio-/chemoselective [2 + 2 + 2] cyclotrimerization of 1,3-diarylpropargyl acetals (**1**) to afford cyclohexylidene products (**3**, Scheme 1b).[3] The presence of a catalytic amount of Au–nitrone, prepared *in situ*, was essential for successful selective cyclotrimerization, as a Au(I) catalyst alone (**I** or **II**, Scheme 1d) was unable to afford the target product, and complex product mixtures were obtained.

X-ray analysis of crystalline JohnPhos Au(I)–nitrone complex **I-2a**, formed from Au(I)-JohnPhos **I** and nitrone **2a** (equimolar mixtures in DCM, Scheme 1c), confirmed for the first time the O-binding of the nitrone ligand to the Au(I) centre with a linear nitrone–O–Au(I)–P coordination mode. The crystalline Au(I)-JohnPhos–nitrone complex **I-2a** showed similar catalytic activity (60–74% yield of **3**) as the catalysts prepared *in situ* from Au(I)–phosphane **I** and nitrone **2a**. Au–NHC catalysts **III** or $AuCl_3$ **IV** (with or without nitrones) gave full conversion into unidentified product mixtures but failed to give trimerization.

We hereby report further investigations of the chemistry of Au/nitrone based systems, which allow formation of new Au complexes with specific properties.

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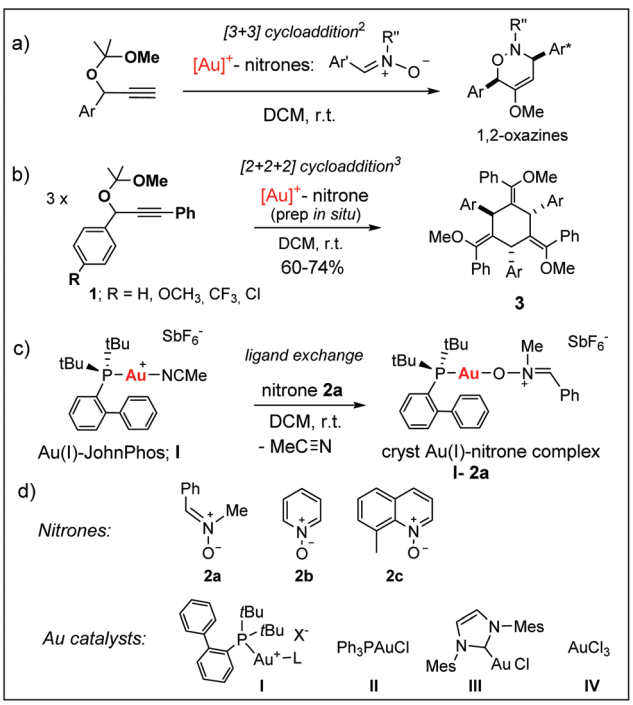
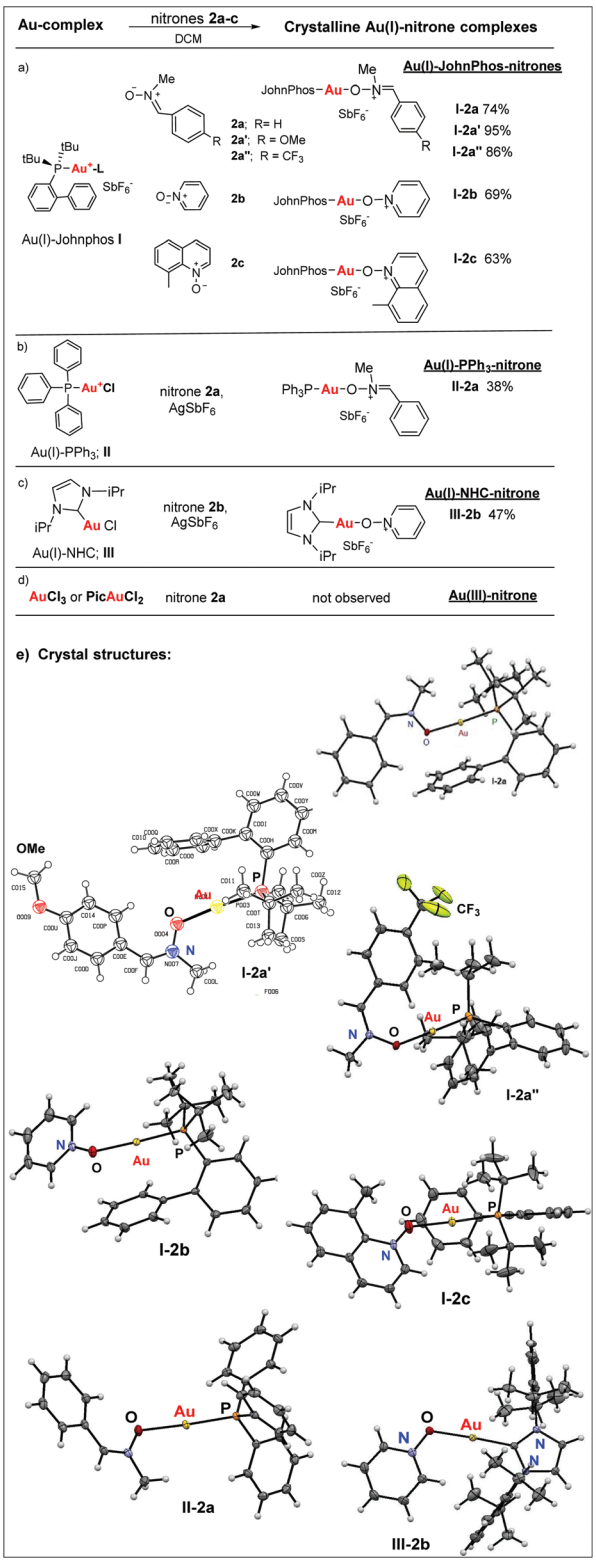
Results and discussion

Au(I)–nitrone complexes

Several additional crystalline Au(I)–nitrone complexes were prepared in moderate to high yields (38–95%) from Au(I)–phosphane or Au(I)–NHC (pre)catalysts **I–III** and nitrones **2a–c** Scheme 2.



Scheme 1 (a) Au(I) catalysed [3 + 3] cycloaddition[2] of terminal propargyl acetals and nitrones; (b) Au(I)–nitrone catalysed [2 + 2 + 2] cyclotrimerization[3] of 1,3-diarylpropargyl acetals; (c) formation of the Au(I)–nitrone complex **I-2a** (X-ray); (d) nitrones **2a–c** and Au complexes **I–IV** included in the present study.



Scheme 2 (a)–(d) Preparation of crystalline Au(I)–nitrone complexes; (e) crystal structures of Au–nitrone complexes **I-2a**, **I-2a′**, **I-2a″**, **I-2b**, **I-2c**, **II-2a** and **III-2b**.

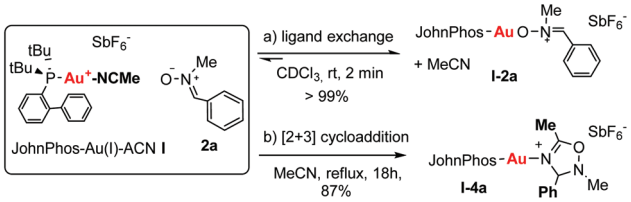
When tested in the original cyclotrimerization reaction (Scheme 1a), the catalytic activity of all the phosphane-based crystalline complexes (**I-2a**, **I-2a′**, **I-2a″**, **I-2b**, **I-2c**, **II-2a**; Scheme 2a and b) was similar to catalysts prepared *in situ* (Scheme 1b).[3] The crystalline Au(I)NHC-ligated nitrone complex (**III-2b**) afforded a complex product mixture and no trimerization, similar to the results by the *in situ* preparation method.[3] Nitrones did not coordinate to Au(III), as attempts to coordinate the Au(III) complexes $AuCl_3$ and $PicAuCl_2$ (dichloro-2-pyridinecarboxylato-gold) with nitrone **2a** failed (NMR) and only the parent compounds were recovered (Scheme 2d).

Au(I)–oxadiazoles

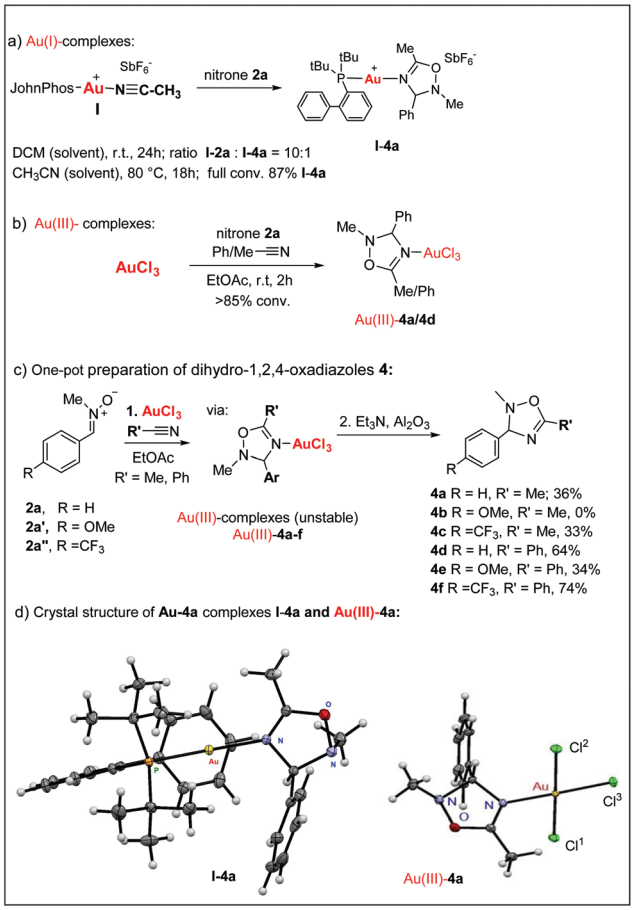
During the studies of the JohnPhos Au(I)–nitrone **I-2a** complex (Schemes 2a and 3a), an additional crystalline Au(I) heterocyclic complex, the Au(I)-dihydro-1,2,4-oxadiazole, **I-4a**, was identified (Scheme 3b and 4a, X-ray). The product is apparently formed by a transformation of JohnPhos-Au(I)–nitrile complex **I** in a [3 + 2] cycloaddition of the Au-ligated acetonitrile ligand with the present nitrone **2a**. This is indicated by the oxadiazole product coordination to Au(I) through the N(4)imine atom in the Au(I) complex. The reaction of the acetonitrile (ACN) ligand was slow in dichloromethane (9%, 24 h), but the product was selectively formed (87%, 18 h) in refluxing acetonitrile. In the absence of Au, the nitrone **2a** in refluxing acetonitrile failed to give the heterocyclic oxadiazole by cycloaddition in a possible thermal reaction (48 h). Hence, the reaction is mediated by gold.

In the ^{1}H NMR spectrum of gold(I)–nitrone complexes **I-2a, a′,a″**, the two *t*Bu(JohnPhos) groups appear as one doublet (1.36 ppm J = 16.0 Hz), due to ^{1}H–^{31}P coupling. In complex Au(I)-**I-4a**, the two *t*Bu groups are diastereotopic, shown as two doublets, separated by approx. 0.25 ppm (1.07/1.31, J = 16.2 Hz), due to the oxadiazoline chiral centre.

The formation of both Au(I)-complex **I-2a** and Au(I) **I-4a** indicates that the reaction between JohnPhosAu(I)–ACN **I** and nitrone **2a** has two possible competing outcomes (Scheme 3a and b). Either nitrone **2a** replaces the acetonitrile ligand to give complex **I-2a** or, alternatively, nitrone **2a** reacts with the ligated acetonitrile to form Au(I)–oxadiazole complex **I-4a**. According to NMR spectroscopy, the nitrile/nitrone ligand exchange was both rapid and quantitative in $CDCl_3$, while no Au(I)-complex **I-4a** was seen after several hours. This indicates a slow reaction and that a possible equilibrium between co-ordinated and non-coordinated nitrone (**2a**/**I-2a**, Scheme 3) is



Scheme 3 Competing dual reaction pathways of nitrone **2a** with Au(I)–ACN complex **I**.



Scheme 4 Formation of dihydro-1,2,4-oxadiazoles **4** by Au-mediated [2 + 3] cycloaddition of nitrones and nitriles; (a) Au(I)-**I-4a** complex; (b) Au(III)-**4a/4d** complexes; (c) one-pot process for the preparation and release of products **4**; (d) crystal structures of **I-4a** and Au(III)-**4a** complexes.

strongly in favour of gold(I)–nitrone complex **I-2a**. A large excess of nitrile, using acetonitrile as a solvent, indeed pushed the equilibrium toward Au(I)–ligated nitrile and speeded up the conversion into the desired cycloaddition product **I-4a**.

Au(III)–oxadiazoles

As Au(III) did not coordinate to nitrones (Scheme 2d), the possible formation of a Au(III)-**2a** complex could be excluded. As desired, a rapid conversion of equimolar amounts of nitrone **2a** and $AuCl_3$ in CD_3CN into Au(III)-d_3-oxadiazole (Au(III)-d_3-**4a**) was observed (NMR; >75%, 30 min, r.t.). The formation of Au(III)-**4a**/-**4d** complexes from $AuCl_3$, nitrone **2a** and Me-/Ph-nitriles was tested in a number of alternative reactivity of solvents. Most solvents were unsuccessful ($CHCl_3$, DCM, Et_2O, THF, acetone, MeOH) as either $AuCl_3$ did not dissolve, the formed Au(III)-complex or $AuCl_3$ decomposed during reaction, or a very slow reaction took place. However, the transformation of $AuCl_3$ and nitrone **2a** with the respective Me/Ph-nitriles in EtOAc readily gave >85% conversion (NMR) into the Au(III)-**4a**/-**4d** complexes in 2 hours at r.t. (Scheme 4b, Au(III)-**4a** X-ray).

Since the Au(III) mediated reaction was faster than that with Au(I), and the nitrile was not used as a solvent and would enable the preparation of modified products **4** from different nitriles, this procedure represented a convenient and versatile method for nitrile–nitrone [2 + 3] cycloaddition.

One-pot preparation of dihydro-oxadiazoles

The initially formed Au(III)-**4a**/**4d** complexes were only stable in EtOAc solutions for few hours, and attempts to isolate more those minor samples for X-ray were not successful. Aiming at the direct one-pot preparation of the target cycloaddition products **4** *via* Au(III)-**4** complexes, a number of methods were tested for cleavage of the Au(III)-**4** intermediates. Treatment with pyridine[4e] gave incomplete cleavage and the oxadiazole products **4** partly decomposed. However, a method based on treatment of the EtOAc reaction mixture with a combination of Et_3N and Al_2O_3 was successful. The complex was initially cleaved by the addition of minor amounts of Et_3N and subsequent alumina adsorption decomposed the released $AuCl_3$ and eliminated the problem of oxadiazole reattachment to gold(III) during purification. The released stable dihydro-1,2,4-oxadiazoles **4** were readily purified by silica flash chromatography.

A number of oxadiazole products **4a,c–f** (33–74%) were prepared from nitrones **2a–a″** and Me/Ph-nitriles by this one-pot procedure *via* the corresponding Au(III)**4** complexes (Scheme 4c). Electronic factors both from the nitrile and nitrone affected the outcome of the reactions. Much higher yields of the target products were formed from benzonitrile (64–34–74%; **4d,e,f**), than from acetonitrile (33–0–36%, **4a,b,c**), in accordance with other studies.[5a,b] This observation may be explained by the fact that aromatic conjugation would increase the rate of reaction by stabilization of the transition state. Replacing the *N*-Me-nitrone **2a** with the corresponding *N*-Ph-nitrone failed to give any cycloaddition, indicating that steric hindrance in the transition state dramatically lowers the reaction rate.

Au-Catalysed nitrile–nitrone [3 + 2] cycloaddition

In general, [3 + 2] cycloaddition reactions are concerted, pericyclic processes controlled by the frontier molecular orbitals on *e.g.* a nitrone 1,3-dipole and a dipolarophile.[5] Nitrone–nitrile cycloadditions are normal type II cycloadditions and seem to be controlled by $HOMO_{nitrone}$–$LUMO_{nitrile}$ interactions, as the large HOMO coefficient of the nitrone–oxygen center is expected to favor oxadiazole formation by $HOMO_{1,3\text{-dipole}}$–$LUMO_{dipolarophile}$ interaction in [3 + 2] cycloadditions.[5c] However, a crossover in the orbital control is observed. Thus, both possible interactions, $HOMO_{1,3\text{-dipole}}$–$LUMO_{dipolarophile}$ and $HOMO_{dipolarophile}$–$LUMO_{1,3\text{-dipole}}$, are reported to lead to the actual target oxadiazole products by overlap of orbitals with comparable terminal coefficients, *e.g.* orbitals of nitrone-C and -O atoms with, respectively, nitrile-N and -C atoms for the preparation of oxadiazoles **4**.[5a]

It is also known that 1,3-dipolar cycloaddition reactions of nitrones with both e-deficient and e-rich alkenes allow for

efficient syntheses of isoxazolidines by Cu-catalysis and have shown that the frontier orbitals may be affected by coordination to a Lewis acid.[5b,d,e] Similarly, the scope of nitrileoxide–nitrile cycloadditions to give the corresponding aromatic 1,2,4-oxadiazole derivatives[5f] is limited to benzonitrile oxides and e-deficient nitriles, unless in the presence of Lewis acids, *e.g.* for relatively unreactive alkylnitriles.[5b] Modified carbamoyl-nitrile oxides cause, however, inverse electron-demand 1,3-dipolar cycloaddition $LUMO_{nitrile\ oxide}$–$HOMO_{nitrile}$ with electron-rich aliphatic or aromatic nitriles to afford 3-functionalized 1,2,4-oxadiazoles.[5h]

In our study, the electron-deficient *p*-CF_3-substituted aromatic nitrone (**2a″**) indicates that decreased HOMO/LUMO levels of the nitrone affords high reactivity, as shown by high product yields (*e.g.* 74% of **4f** from **2a″**). The nitrone with a non-substituted phenyl group (**2a**) showed similar reactivity (*e.g.* 64% of **4d**). The fact that ERG (*p*-OMe-phenyl) deactivated for cycloaddition supports this theory, as nitrone **2a′** with an electron rich phenyl group afforded no or low product yields (0–34% of **4b** and **4e** from **2a′**). Thus, the outcome of the presently reported nitrone/Au–nitrile [2 + 3] cycloadditions seems to be controlled by the reverse $LUMO_{nitrone}$–$HOMO_{nitrile}$ interaction, even if a reduced nucleophilicity of the nitrile–nitrogen is expected, being coordinated to the gold centre.

Au(I) and Au(III) complexes; crystal structures

The crystal structures of the Au(I)–nitrone complexes (Table 1, X-ray) showed the expected approximate linear nitrone–O–Au(I)–P-coordination mode for Au(I)–phosphanes (**I-2a**, **I-2a′**, **I-2a″**, **I-2b**, **I-2c**, **II-2a**; Scheme 2a and b) and, analogously, O–Au–C(carbene) nearly linear complexation for the Au(I)–NHC complex **III-2b** (Scheme 2c). The largest deviation from linearity was observed for the most bulky non-aromatic nitrones **I-2a″**, as shown by O–Au–P bond angles < 176° (Table 1, entries 1–3). Both the nature of the Au(I)-ligand and the coordinated nitrone affected the O–Au(I) bond lengths. The pyridine-*N*-oxide O–Au bond length of complexes **I-2b** is 0.03 Å longer than that in complex **III-2b** (Table 1, JohnPhos and NHC ligands, respectively; entries 4 and 7), indicating that the nitrone is stronger bonded to gold(I)–NHC than to gold(I)–phosphane. Similarly, the shorter O–Au(I) bond length in complex **II-2a** than in **I-2a** (Ph_3P and JohnPhos ligands, respectively; entries 6 and 1) may be caused by steric effects,

Table 1 Bond lengths (Å) and angles in gold(I)–nitrone complexes (Scheme 2e)

Entry	Complex	O–Au	Au–L	N–O	O–Au–L
1	**I-2a**	2.096	2.2429	1.340	174.87°
2	**I-2a′**	2.087	2.239	1.343	175.83°
3	**I-2a″**	2.090	2.2363	1.340	175.85°
4	**I-2b**	2.074	2.2296	1.349	177.38°
5	**I-2c**	2.085	2.2358	1.326	178.20°
6	**II-2a**	2.068	2.222	1.344	177.14°
7	**III-2b**	2.045	1.959	1.348	177.51°

Table 2 Bond lengths (Å) and angles in Au(I) and Au(III) oxadiazole **4a** complexes (Scheme 4d)

Complex	N–Au	Au–X	N–O	N/Cl–Au–X
Au(I)-**I-4a**	2.066	Au–P 2.250	1.487	N–Au–P 172.16°
Au(III)-**4a**	2.0289	Au–Cl^1 2.2751 Au–Cl^2 2.2843 Au–Cl^3 2.2573	1.485	N–Au–Cl^3 178.65° Cl^1–Au–Cl^2 178.56°

allowing the nitrone to bind closer to the gold(I) centre attached to the less bulky Ph_3P ligand.

The deviation from linearity increases going from Au(I)–nitrone complexes **I-2a** (O–Au–P bond angles 174.8–176°, Table 1) to the more rigid highly substituted oxadiazole cyclic structure Au(I)-**I-4a** (N–Au–P bond angle 172.16°, Table 2). The N–O bond lengths in the nitrone and oxadiazole gold complexes indicate a N–O double bond character in all the nitrone complexes (1.326–1.349 Å; Table 1, entries 1–7) in contrast to a weaker single bond in the oxadiazole complexes Au(I)- and Au(III)-**4a** (approx. 1.48 Å, Table 2).

As expected, the Au(III)-**4a** complex was shown to have a nearly square planar structure. Interestingly, in the Au(III)-**4a** complex (Table 2), the oxadiazole Au–Cl^{trans} bond (Au–Cl^3 2.2573 Å) is shorter than the Au–Cl^{cis}. bonds (Au–Cl^1/–Cl^2: 2.2751 and 2.2843 Å). This has been observed in other $AuCl_3$ complexes with nitrogen ligands, *e.g.* with ammonia,[4a] pyridine[4b] and an aromatic nitrile.[4c] This suggests that the oxadiazole coordination strengthens the Au–Cl^{trans} bond, in contrast to that commonly observed in Pt(II) complexes.[4d]

Dihydro-1,2,4-oxadiazoles

Transition metal Pd(II)[6a–d] and Pt(II)/(IV)[7a–f] nitrile complexes are known to undergo similar [2 + 3] cycloaddition reactions with nitrones to give dihydro-1,2,4-oxadiazole-Pd/-Pt complexes. The Pd and Pt(II)/(IV)-oxadiazole methods require a separate step for cleavage of the isolated metal intermediate complexes to release the heterocyclic products. The obtained yields of released oxadiazoles by the Pt complex method are comparable to the obtained isolated yields in the one-step reaction *via* the Au(III)-oxadiazole complex (Scheme 4c) with respect to organic substrates. But two steps are required for product isolation from the Pd/Pt complexes. Nevertheless, Pd and Pt(IV) may coordinate two nitrile substrates to give two product units. None of the methods has been developed into catalytic processes.

Dihydro-1,2,4-oxadiazoles **4** represent a group of heterocyclic compounds with interesting bioactive properties[8a–c] The suitability of mixed ligand Pt(II) oxadiazoline complexes as anticancer agents has also been screened; and *in vitro* cytotoxicity has been studied.[8d–f] There are a limited number of non-metal-based preparation methods to afford the dihydro-1,2,4-oxadiazole heterocycle, in general obtained in moderate yields. Direct 1,3-dipolar cycloadditions of nitrones with nitriles are reported to take place by vigorous reaction conditions, such as thermal[9a] or at high pressure.[5a,9b] 2,3-Dihydro-

1,2,4-oxadiazoles have also been prepared in two steps from imines *via* oxaziridine and subsequent [3 + 2] cycloaddition with nitriles.[8f,9c] Some methods for the preparation of the corresponding aromatic 1,2,4-oxadiazole products are reported[9d–g] in addition to cycloadditions.[5b,f,g,h] However, no access to dihydro-1,2,4-oxadiazoles **4** by reduction of the aromatic oxadiazole compounds is known, as C–O or N–O ring cleavage mostly takes place.

Conclusions

In summary, crystalline Au(I)–nitrone complexes (**I-2a′**, **I-2a″**, **I-2b**, **I-2c**, **II-2a**, **III-2b**) were prepared from Au(I)–phosphane or Au(I)–NHC (pre)catalysts **I–III** and nitrones **2a–c** (*e.g.* 63–95% cryst. JohnPhos-Au(I)–nitrones). The Au(I)–phosphane–nitrones were catalytically active. All crystal structures (X-ray) showed a nearly linear nitrone–O–Au(I)/–P(phosphane)/–C(NHC) coordination mode.

Further studies on the gold–nitrone chemistry lead us to the discovery of a crystalline Au(I)-dihydro-1,2,4-oxadiazole complex **I-4a** (87%, 18 h, ACN, reflux), formed by a [3 + 2] cycloaddition of JohnPhos-Au(I)-ligated acetonitrile with nitrone **2a**. Corresponding Au(III)-**4a** complexes were more readily formed by conversion of $AuCl_3$, Me/Ph-nitriles and nitrone **2a** (>85%, 2 h, EtOAc, r.t.). The 1,2,4-oxadiazole heterocycles coordinated to Au(I)/(III) through the N(4)imine atom (X-ray), indicating a Au–nitrile origin. A convenient one-pot preparation method for dihydro-1,2,4-oxadiazoles **4** (up to 74%) by Au(III) mediated [2 + 3] nitrone–nitrile cycloaddition and final product release from the Au(III) complex was developed.

The present study contributes to a new understanding of Au(I)–/Au(III)–nitrone chemistry, as shown by the dual selective reactivity of such systems. The results demonstrate the versatility of gold–nitrone systems by the controlled ability to undergo complexation into (catalytic active) species and their selective synthetic utility.

Experimental

General

All reactions were performed under a normal atmosphere. Commercial grade reagents were used without any additional purification. Dry solvents were collected from a MB SPS-800 solvent purification system. All reactions were monitored by NMR and/or thin-layer chromatography (TLC) using silica gel 60 F254 (0.25 mm thickness). TLC plates were developed using UV-light and/or *p*-anisaldehyde stain. Flash chromatography was performed with Merck silica gel 60 (0.040–0.063 mm). ^{1}H and ^{13}C NMR spectra were recorded with either a Bruker Avance DPX 400 MHz or a Bruker Avance III 600 MHz spectrometer. Chemical shifts are reported in ppm (δ) downfield from tetramethylsilane (TMS) as an internal standard. Melting points (mp) were determined using a Stuart SMP40 apparatus and are uncorrected. Accurate mass determination was performed on a "Synapt G2-S" Q-TOF instrument from Waters. Samples were ionized with an ASAP probe with no chromatography separation performed before mass analysis. IR spectra were recorded with a Nicolet 20SXC FT-IR spectrometer using EZ OMNIC software to analyse the spectra and a Bruker Alpha FT-IR spectrometer using OPUS V7 software to analyse the spectra. Single crystal X-ray data were acquired using a Bruker D8 Venture diffractometer with the APEX3 suit, integrated with SAINT V9.32B, solved with XT and refined with XL using Olex2 as GUI. The cif files were edited with encipher 1.4 and molecular graphics were produced with Mercury 3.8. ORTEP plots are shown in the thesis and all metric data, including reflection data, are contained in the respective cif files.

General procedure for the synthesis of Au(I)–nitrone complexes

A solution of the appropriate nitrone (1.5 eq.) and gold complex (1 eq.) in 0.2 mL (DCM) was shaken and left at room temperature for 30 min. If applicable, anion exchange was performed by adding 1.5 eq. $AgSbF_6$ to the solution and the resulting AgCl was filtered after 30 min. Crystalline Au(I)–nitrone complexes were obtained by adding Et_2O (1 : 1 Et_2O : pentane for **I-2a′**) until the solution became cloudy and left at r.t. until full crystallisation (1–3 hours). Finally, the crystals were washed with Et_2O, re-dissolved in DCM and transferred to a round bottom flask. Removal of the solvent *in vacuo* yielded the pure Au(I)–nitrone complexes.

Complex I-2a. The title compound was prepared according to the general procedure, using nitrone **2a** (6 mg, 0.045 mmol) and Au(I) complex **I** (23 mg, 0.030 mmol), yielding Au(I)–nitrone complex **I-2a** (20 mg, 74%) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.15–8.16 (m, 2H, Ar), 8.01 (s, 1H, HC═N), 7.85–7.88 (m, 1H, Ar), 7.61–7.64 (m, 1H, Ar), 7.54–7.59 (m, 4H, Ar), 7.42–7.48 (b, 2H, Ar), 7.30–7.32 (m, 1H, Ar), 7.20–7.21 (m, 2H, Ar), 3.87 (s, 3H, CH_3N), 1.36 (d, 18H, J = 16.0 Hz, $(CH_3)_3C$). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.3 (d, J = 12.6 Hz, C_{Ar}), 147.7 (C═N), 142.3 (d, J = 8.0 Hz, C_{Ar}), 134.0 (CH_{Ar}), 133.3 (d, J = 6.9 Hz, CH_{Ar}), 133.9 (d, J = 3.6 Hz, CH_{Ar}), 132.6 (CH_{Ar}), 131.3 (d, J = 2.2 Hz, CH_{Ar}), 129.6 (CH_{Ar}), 128.8 (CH_{Ar}), 128.4 (d, J = 2.6 Hz, CH_{Ar}), 127.6 (C_{Ar}), 127.3 (d, J = 9.4 Hz, CH_{Ar}), 123.8 (d, J = 50.5 Hz, PC_{Ar}), 54.2 (CH_3N), 38.0 (d, J = 27.0 Hz, PC), 30.7 (d, J = 6.4 Hz, $(CH_3)_3C$). m.p: 160–162 °C (decomp.). IR (thin film, cm^{-1}) 3065, 2950, 1480, 1145, 924, 660. HRMS (ASAP) calcd for $C_{20}H_{27}AuP$ $[M^{\bullet} - \text{nitrone}]^+$ 495.1516, obsd 495.1715. X-Ray: CCDC 1531556.†

Complex I-2a′. The title compound was prepared according to the general procedure, using nitrone **2a′** (7 mg, 0.040 mmol) and gold complex **I** (21 mg, 0.027 mmol), yielding Au(I)–nitrone complex **I-2a′** (23 mg, 95%) as white crystals. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.15 (d, J = 8.8 Hz, 2H, Ar), 7.85–7.88 (m, 1H, Ar), 7.81 (s, 1H, CH═N), 7.53–7.58 (m, 2H, Ar), 7.41–7.44 (m, 2H, Ar), 7.29–7.31 (m, 2H, Ar), 7.20–7.21 (m, 2H, Ar), 7.02 (d, J = 8.8 Hz, 2H, Ar), 3.91 (s, 3H, CH_3O), 3.80 (s, 3H, CH_3N), 1.37 (d, J = 16.1 Hz, 18H, $(CH_3)_3C$). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 163.8 (C_{Ar}), 149.3 (d, J = 12.1 Hz, C_{Ar}), 142.3 (d, J = 6.7 Hz, C_{Ar}), 134.8 (b, C═N), 133.3 (d, J = 7.7 Hz, CH_{Ar}), 133.0 (d, J = 3.5 Hz, CH_{Ar}), 131.3 (d, J = 2.1 Hz,

CH_{Ar}), 129.5 (CH_{Ar}), 128.4 (CH_{Ar}), 127.3 (d, J = 7.6 Hz, CH_{Ar}), 123.8 (d, J = 49.6 Hz, PC_{Ar}), 120.7 (b, C_{Ar}), 114.3 (CH_{Ar}), 55.6 (CH_3O), 53.5 (CH_3N), 38.0 (d, J = 27.4 Hz, PC), 30.7 (d, J = 6.6 Hz, $(CH_3)_3C$). IR (thin film, cm^{-1}) 3061, 2959, 1600, 1510, 1265, 1177, 1142, 1022, 759. X-Ray: CCDC 1579660.†

Complex I-2a″. The title compound was prepared according to the general procedure, using nitrone **2a″** (10 mg, 0.048 mmol) and gold complex **I** (19 mg, 0.024 mmol), yielding Au(I)–nitrone complex **I-2a″** (19 mg, 86%) as white crystals. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.29 (d, J = 8.3 Hz, 2H, Ar), 8.11 (s, 1H, CH═N), 7.88–7.85 (m, 1H, Ar), 7.79 (d, J = 8.3 Hz), 7.54–7.60 (m, 2H, Ar), 7.44–7.46 (m, 2H, Ar), 7.33–7.28 (m, 2H, Ar), 7.21 (d, J = 7.5 Hz, 2H, Ar), 3.92 (s, 3H, CH_3), 1.37 (d, J = 16.2 Hz, 18H, $(CH_3)_3C$). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 149.2 (d, J = 12.2 Hz, C_{Ar}), 146.0 (b, CH═N), 142.3 (d, J = 6.7 Hz), 134.5 (q, J = 35.2 Hz, C_{Ar}), 133.3 (d, J = 7.7 Hz, CH_{Ar}), 132.9 (d, J = 4.4 Hz, CH_{Ar}), 132.6 (b, CH_{Ar}), 131.4 (d, J = 2.2 Hz, CH_{Ar}), 130.7 (b, C_{Ar}), 129.6 (CH_{Ar}), 128.5 (CH_{Ar}), 128.4 (CH_{Ar}), 127.4 (d, J = 7.7 Hz, CH_{Ar}), 125.6 (q, J = 4.1 Hz, CH_{Ar}), 123.7 (d, J = 50.4 Hz, PC), 123.3 (q, J = 273.2 Hz, CF_3), 54.7 (CH_3N), 38.1 (d, J = 27.5 Hz, PC), 38.7 (d, J = 5.9 Hz, $(CH_3)_3C$). m.p.: 160–165 °C (decomp.). IR (thin film, cm^{-1}) 3061, 2959, 2903, 1600, 1510, 1462, 1265, 1177, 1142. X-Ray: CCDC 1548791.†

Complex I-2b. The title compound was prepared according to the general procedure, using nitrone **2b** (5 mg, 0.054 mmol) and gold complex **I** (28 mg, 0.036 mmol) yielding Au(I)–nitrone complex **I-2b** (20 mg, 69%) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.38–8.40 (m, 2H, Ar), 7.86–7.90 (m, 2H, Ar), 7.77–7.80 (m, 2H, Ar), 7.54–7.57 (m, 2H, Ar), 7.20–7.36 (m, 6H, Ar), 1.44 (d, 18H, J = 16.4 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 149.4 (d, J = 11.8 Hz, C_{Ar}), 142.5 (d, J = 6.6 Hz, C_{Ar}), 139.1 (CH_{Ar}), 133.3 (d, J = 7.5 Hz, CH_{Ar}), 133.0 (d, J = 3.8 Hz, CH_{Ar}), 131.4 (d, J = 2.8 Hz, CH_{Ar}), 129.7 (CH_{Ar}), 128.6 (CH_{Ar}), 128.0 (CH_{Ar}), 127.8 (CH_{Ar}), 127.5 (CH_{Ar}), 127.4 (d, J = 7.4 Hz, CH_{Ar}), 124.0 (d, J = 50.7 Hz, PC_{Ar}), 38.2 (d, J = 28.0 Hz, PC), 31.0 (d, J = 6.0 Hz, CH_3).

m.p.: 179–181 °C (decomp.). IR (thin film, cm^{-1}) 3122, 2963, 2900, 1469, 1201, 1175, 765. X-Ray: CCDC 1548784.†

Complex I-2c. The title compound was prepared according to the general procedure, using nitrone **2c** (4 mg, 0.026 mmol) and gold complex **I** (14 mg, 0.018 mmol), yielding Au(I)–nitrone complex **I-2c** (10 mg, 63%) as yellow crystals. ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 8.75–8.77 (m, 1H, Ar), 8.26–8.28 (m, 1H, Ar), 7.87–7.91 (m, 2H, Ar), 7.80–7.83 (m, 1H, Ar), 7.65–7.69 (m, 2H, Ar), 7.54–7.57 (m, 2H, Ar), 7.14–7.28 (m, 6H, Ar), 6.56–6.60 (m, 1H, Ar), 3.06 (s, 3H, CH_3), 1.46 (d, 18H, J = 16.2 Hz, $(CH_3)_3C$). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 149.3 (d, J = 12.1 Hz, C_{Ar}), 142.5 (d, J = 5.8 Hz, C_{Ar}), 139.8 (CH_{Ar}), 139.0 (C_{Ar}), 136.4 (CH_{Ar}), 133.3 (d, J = 7.9 Hz, CH_{Ar}), 132.9 (d, J = 3.5 Hz, CH_{Ar}), 132.3 (C_{Ar}), 132.1 (C_{Ar}), 131.3 (d, J = 2.4 Hz, CH_{Ar}), 129.7 (CH_{Ar}), 129.5 (CH_{Ar}), 128.2 (CH_{Ar}), 127.7 (CH_{Ar}), 127.4 (CH_{Ar}), 127.3 (CH_{Ar}), 127.2 (CH_{Ar}), 123.6 (d, J = 49.8 Hz, PC_{Ar}), 121.3 (CH_{Ar}), 38.2 (d, J = 27.4 Hz, PC), 30.9 (d, J = 6.3 Hz, $(CH_3)_3C$), 25.6 (CH_3). m.p.: 178–183 °C (decomp.). IR (thin film, cm^{-1}) 3059, 2961, 2902, 1584, 1462, 1201, 1160, 821.7. X-Ray: CCDC 1548787.†

Complex II-2a. The title compound was prepared according to the general procedure, using nitrone **2a** (9 mg, 0.066 mmol), gold complex **II** (22 mg, 0.044 mmol) and $AgSbF_6$ (15 mg, 0.044 mmol) yielding Au(I)–nitrone complex **II-2a** (14 mg, 38%) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 8.25–8.27 (m, 2H, Ar), 8.09 (s, 1H, N═CH), 7.54–7.60 (m, 4H, Ar), 7.48–7.52 (m, 8H, Ar), 7.38–7.44 (m, 6H, Ar), 4.13 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm) 147.8 (C═N), 134.0 (d, J = 13.7 Hz, CH_{Ar}), 132.7 (d, J = 3.2 Hz, CH_{Ar}), 132.1 (CH_{Ar}), 129.6 (d, J = 12.5 Hz, CH_{Ar}), 128.9 (CH_{Ar}), 127.6 (C_{Ar}), 126.9 (d, J = 66.5 Hz, PC_{Ar}), 54.1 (CH_3). m.p.: 152–156 °C (decomp.). IR (thin film, cm^{-1}) 3059, 3021, 2926, 1697, 1438, 1143, 1102, 751. HRMS (ASAP) calcd for $C_{18}H_{15}AuP$ $[M^{\bullet} - \text{nitrone}]^+$ 459.0577 obsd 459.0576. X-Ray: CCDC 1548788.†

Complex III-2b. The title compound was prepared according to the general procedure, using nitrone **2b** (5 mg, 0.056 mmol), gold complex **III** (23 mg, 0.037 mmol) and $AgSbF_6$ (13 mg, 0.037 mmol) yielding Au(I)–nitrone complex **III-2b** (34 mg, 47%) as white crystals. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.90 (b, 2H, Ar), 7.62–7.68 (m, 4H, Ar), 7.59 (b, 2H, Ar), 7.39–7.40 (m, 4H, Ar), 7.37 (s, 2H, NHC═CHN), 2.41 (sept, 2H, J = 6.9 Hz, CH), 1.27 (d, 12H, J = 6.8 Hz, CH_3), 1.25–1.27 (d, 12H, J = 7.0 Hz, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm), the signals belonging to pyridine N-oxide cannot be seen for some unknown reason. 162.4 (C–Au), 145.8 (C_{Ar}), 133.5 (C_{Ar}), 131.4 (CH_{Ar}), 124.6 (CH_{Ar}), 124.3 (NHC═CHN), 28.9 (CH), 24.5 ($(CH_3)_2$), 24.0 ($(CH_3)_2$). m.p.: 174–176 °C (decomp.). IR (thin film, cm^{-1}) 3171, 2964, 2928, 2871, 1469, 1387, 1175, 1060, 761. HRMS (ASAP) calcd for $C_{27}H_{37}N_2$ $[M^{\bullet} - (\text{Au–nitrone})]^+$ 389.2957 obsd 389.2950. X-Ray: CCDC 1548789.†

Synthesis of Au(I)–oxadiazole complex I-4a

A solution of nitrone **2a** (9 mg, 0.064 mmol) and gold complex **I** (25 mg, 0.032 mmol) in 2 mL dry CH_3CN was heated to 80 °C and stirred for 18 hours. The solvent was removed *in vacuo* and the product was re-dissolved in 0.2 mL DCM. The product complex was crystallised by adding Et_2O to the solution. The resulting white crystals were washed with Et_2O, which yielded the pure Au(I)–oxadiazole complex **20** (29 mg, 87%). ^{1}H NMR (600 MHz, $CDCl_3$) δ (ppm) 7.77–7.82 (m, 1H, Ar), 7.60–7.64 (m, 1H, Ar), 7.46–7.56 (m, 3H, Ar), 7.37–7.43 (m, 6H, Ar), 7.20–7.25 (m, 2H, Ar), 7.11–7.14 (m, 1H, Ar), 5.40 (s, 1H, CH), 3.06 (s, 3H, CH_3N), 2.13 (d, 3H, J = 0.5 Hz, CH_3C═N), 1.31 (d, 9H, J = 16.2 Hz, $(CH_3)_3C$), 1.07 (d, 9H, J = 16.0 Hz, $(CH_3)_3C$). ^{13}C NMR (150 MHz, $CDCl_3$) δ (ppm) 169.7 (C═N), 149.0 (d, J = 12.3 Hz, C_{Ar}), 143.1 (d, J = 6.5 Hz, C_{Ar}), 135.7 (C_{Ar}), 133.3 (CH_{Ar}), 133.2 (d, J = 4.7 Hz, CH_{Ar}), 131.1 (d, J = 2.2 Hz), 130.3 (CH_{Ar}), 129.9 (CH_{Ar}), 129.8 (CH_{Ar}), 129.2 (CH_{Ar}), 128.9 (CH_{Ar}), 128.6 (CH_{Ar}), 128.1 (CH_{Ar}), 127.7 (CH_{Ar}), 127.4 (d, J = 6.5 Hz, CH_{Ar}), 123.8 (d, J = 49.5 Hz, PC_{Ar}), 92.0 (CH), 45.9 (CH_3–N), 37.9 (d, J = 26.4 Hz, PC). 37.8 (d, J = 27.5 Hz, PC), 30.8 (d, J = 5.6 Hz, $(CH_3)_3C$), 30.4 (d, J = 6.6 Hz, $(CH_3)_3C$), 14.0 (CH_3C═N). IR (thin film, cm^{-1}) 2961, 2927, 1647, 1460, 1260, 1173, 1020, 764. HRMS (ASAP) calcd for $C_{30}H_{39}AuN_2OP$ $[M^{\bullet}]^+$ 671.2466, obsd 671.2474. Not enough compound remained for m.p. determination. X-Ray: CCDC 1548790.†

Synthesis of Au(III)–oxadiazole complex Au(III)-4a

A solution of nitrone **2a** (6 mg, 0.043 mmol) and $AuCl_3$ (13 mg, 0.043 mmol) in $CDCl_3$ (0.6 mL) was added to acetonitrile (8 mg, 0.19 mmol), shaken well and left for 90 min. The solvent was evaporated and the product was re-dissolved in 0.2 mL acetonitrile. The product complex Au(III)-**4a** was crystallised as yellow crystals by addition of 1 : 1 Et_2O : pentane to the solution. The complex could only be isolated in amounts sufficient for X-ray analysis, and the reaction yield could not be determined. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) Crude reaction mixture: 7.45–7.58 (m, 5H, Ar), 5.94 (s, b, 1H, CH), 3.05 (s, 3H, CH_3N), 2.56 (d, J = 0.6 Hz, 3H, CH_3). X-Ray: CCDC 1548801.†

General one-pot procedure for the synthesis of 1,2,4-dihydro-oxadiazoles (4)

A solution of $AuCl_3$ (1 eq.) and acetonitrile/benzonitrile (5 eq.) in EtOAc (1 mL) was stirred for 10 min before adding the appropriate nitrone (1 eq.) and stirred for 2 hours. The reaction was quenched by addition of a few drops of Et_3N, followed by adsorption of the reaction mixture on alumina. The mixture was left for 16 hours, followed by filtration with DCM (50–100 mL). Concentration of the filtrate *in vacuo* followed by flash column chromatography (4 : 1 pentane : DCM) yielded the pure oxadiazoles.

2,5-Dimethyl-3-phenyl-2,3-dihydro-1,2,4-oxadiazole, 4a.[7f] The title compound was prepared according to the general procedure from $AuCl_3$ (24 mg, 0.079 mmol), acetonitrile (16 mg, 0.38 mmol), and nitrone **2a** (11 mg, 0.079 mmol) to give oxadiazole **4a** (5 mg, 36%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.29–7.40 (m, 5H, Ar), 5.53 (s, 1H, CH), 2.88 (s, 3H, CH_3N), 2.10 (s, 3H, CH_3). ^{1}H NMR corresponds to previously reported data.[7f]

2,5-Dimethyl-3-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1,2,4-oxadiazole 4c. The title compound was prepared according to the general procedure from $AuCl_3$ (31 mg, 0.10 mmol), acetonitrile (21 mg, 0. 52 mmol), and nitrone **2a″** (21 mg, 0.10 mmol) to give oxadiazole **4c** (8 mg, 33%) as a yellow oil. R_f = 0.29 (DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.60–7.62 (d, 2H, J = 8.5 Hz, Ar), 7.52–7.54 (d, 2H, J = 8.4 Hz, Ar), 5.58 (s, 1H, CH), 2.88 (s, 3H, CH_3N), 2.09 (s, 3H, CH_3). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.6 (C=N), 143.8 (C_{Ar}), 130.1–130.8 (q, J = 32.2 Hz, C_{Ar}), 126.7 (CH_{Ar}), 125.4–125.5 (q, J = 4.4 Hz, CH_{Ar}), 121.3–126.7 (q, J = 272.4 Hz, CF_3), 92.7 (CH), 47.1 (CH_3N), 12.0 (CH_3). IR (thin film, cm^{-1}) 2965, 2916, 1621, 1325, 1066, 804. HRMS (ASAP) calcd for $C_{16}H_{14}F_3N_2O$ $[M^{\bullet}]^+$ 307.1058 obsd 307.1055.

2-Methyl-3,5-diphenyl-2,3-dihydro-1,2,4-oxadiazole 4d.[7f] The title compound was prepared according to the general procedure from $AuCl_3$ (22 mg, 0.073 mmol), benzonitrile (38 mg, 0.37 mmol) and nitrone **2a** (10 mg, 0.073 mmol) to give oxadiazole **4d** (11 mg, 64%) as a yellow oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.98–7.99 (m, 2H, CH_{Ar}), 7.51–7.53 (m, 1H, CH_{Ar}), 7.42–7.45 (m, 4H, CH_{Ar}), 7.34–7.37 (m, 2H, CH_{Ar}), 7.30–7.32 (m, 1H, CH_{Ar}), 5.75 (s, 1H, CH), 2.98 (s, 3H, CH_3N). ^{1}H NMR corresponds to previously reported data.[7f]

3-(4-Methoxyphenyl)-2-methyl-5-phenyl-2,3-dihydro-1,2,4-oxadiazole 4e.[7f] The title compound was prepared according to the general procedure from $AuCl_3$ (22 mg, 0.073 mmol), benzonitrile (37 mg, 0.36 mmol), and nitrone **2a′** (12 mg, 0.072 mmol) to give oxadiazole **4e** (7 mg, 34%) as a colourless oil. ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.97–7.99 (m, 2H, Ar), 7.51–7.53 (m, 1H, Ar), 7.43–7.45 (m, 2H, Ar), 7.35–7.37 (m, 2H, Ar), 6.88–6.90 (m, 2H, Ar), 5.70 (s, 1H, CH), 3.79 (s, 3H, CH_3O), 2.96 (s, 3H, CH_3N). ^{1}H NMR corresponds to previously reported data.[7f]

2-Methyl-5-phenyl-3-(4-(trifluoromethyl)phenyl)-2,3-dihydro-1,2,4-oxadiazole 4f. The title compound was prepared according to the general procedure from $AuCl_3$ (12 mg, 0.038 mmol), benzonitrile (20 mg, 0.19 mmol), and nitrone **2a″** (8 mg, 0.038 mmol) to give oxadiazole **4f** (9 mg, 74%) as a colourless oil. R_f = 0.32 (DCM). ^{1}H NMR (400 MHz, $CDCl_3$) δ (ppm) 7.96–7.98 (m, 2H, Ar), 7.59–7.63 (m, 4H, Ar), 7.52–7.55 (m, 1H, Ar), 7.43–7.46 (m, 2H, Ar), 5.80 (s, 1H, CH), 2.99 (s, 3H, CH_3N). ^{13}C NMR (100 MHz, $CDCl_3$) δ (ppm): 161.0 (C=N), 143.7 (C_{Ar}), 132.2 (CH_{Ar}), 130.2–130.9 (q, J = 32.9 Hz, C_{Ar}), 128.7 (CH_{Ar}), 128.6 (CH_{Ar}), 127.0 (CH_{Ar}), 125.5–125.6 (q, J = 4.3 Hz, CH_{Ar}), 125.3 (C_{Ar}), 121.1–126.8 (q, J = 272.2 Hz, CF_3), 93.1 (CH), 47.1 (CH_3N). IR (thin film, cm^{-1}) 3064, 2964, 2992, 1777, 1325, 1165, 1124, 771. HRMS (ASAP) calcd for $C_{11}H_{12}F_3N_2O$ $[M + H]^+$ 245.0902 obsd 245.0898.

Conflicts of interest

There are no conflicts to declare.

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