Fischer-type tungsten acyl (carbeniate), carbene and carbyne complexes bearing C5-attached thiazolyl substituents: interaction with gold(I) fragments†

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2-(1-Piperidinyl)thiazole and 2-phenylthiazole were deprotonated at C5 of the thiazole rings and both reacted with $[W(CO)_6]$ to form Fischer-type tungsten carbeniate complexes **1a** and **1b** of the type $[(CO_5)WC(O)\{\overline{C=CHN=C(R)S}\}]$ (R = 1-piperidinyl for **1a** and phenyl for **1b**). Reaction of carbeniate **1b** with $[(Ph_3P)AuCl]$ afforded by acyl ligand transfer a tungstenoxycarbene complex of gold(I), $[(Ph_3P)Au{=}C\{OW(CO)_5\}\{\overline{C=CHN=C(Ph)S}\}]$ (**2**), in which the $W(CO)_5$ fragment remains coordinated to the acyl oxygen atom. Alkylation of **1a** and **1b** with $[Me_3O][BF_4]$ afforded the carbene complexes $[(CO)_5W{=}C(OMe)\{\overline{C=CHN=C(R)S}\}]$, **3a** and **3b**. A rare example of a hydroxycarbene complex of **1a** stabilised by a hydrogen bond to **1a**, $[NMe_4][\{\overline{S(R)C=NCH=C}\}C\{{=}W(CO)_5\}OH...(O)C\{W(CO)_5\}\{\overline{C=CHN=C(R)S}\}]$, **4**, (*R* = 1-piperidinyl) was crystallised while attempting to prepare **3a** by a different route. Reaction of **3b** with [ClAu(tht)] (tht = tetrahydrothiophene) furnished the corresponding alkoxycarbene gold(I) complex $[ClAu{=}C(OMe)\{\overline{C=CHN=C(Ph)S}\}]$, **5**. Subsequent reaction of **1a** and **1b** with bis(trichloromethyl)carbonate and pyridine yielded the carbyne complexes $[Cl(CO)_2(py)_2W{\equiv}C\{\overline{C=CHN=C(R)S}\}]$, **6a** and **6b**. Reaction of **6a** with [ClAu(tht)] afforded an unstable addition compound, **7**, in which the gold atom is coordinated to the formal carbyne triple bond. Interaction between gold and the proton of the thiazole ring in this complex was observed by variable temperature NMR. The crystal and molecular structures of complexes **1a**, **1b**, **2**, **3b**, **4**, **5**, **6a** and **6b** were all determined by single crystal X-ray diffraction.

Introduction

Fischer-type carbene complexes of chromium and tungsten bearing five-membered heterocyclic rings as the organic group R^1 in the general formula $[(CO)_5M{=}C(OR^2)R^1]$ have been prepared and characterised before. Some of them have been utilised as starting materials in the synthesis of more complex heteroaromatic systems.[1] Such complexes with side chains derived from thiophenes or polythiophenes[2–4] and those with 2- or 3-furyl groups[5,6] were prepared with an eye on possible application in non-linear optics, new materials, organic conductors and in fine-tuning of carbene reactivity. Using the Fischer-method, we have previously prepared 2-benzothiazolyl,[7] 5-pyrazolyl[8] and 4-methylthiazolyl carbene complexes of group 6 metals and could also show that the precursor acyl complex of the latter is an excellent ligand, well suited for coordination to mainly hard metal centres while affording complexes of complexes.[9] Related carbene syntheses, also using *N*-heterocyclic precursors, have been carried out by various other groups.[10–13]

Despite the fact that five-membered heterocyclic rings have been shown to stabilise the rather elusive Fischer-type carbene complexes of molybdenum,[14] rather few heterocyclic groups have found application in Fischer-type carbyne methodology and only 2-furyl[15] and 2-thienyl[15,16] have been utilised. Furthermore, we have established, in a preliminary investigation,[17] that decomposition occurs immediately when attempts are made to convert acylmetallate complexes obtained from 2-lithiobenzothiazole or 2-lithio-4-methylthiazole into carbyne complexes.

Recently, so-called "abnormal" *N*-heterocyclic carbene complexes and isomers of the more general Öfele-Wanzlick-type were discovered. They belong to a class of ligands with reduced heteroatom stabilisation[18] while simultaneously being excellent σ-donors. The carbene carbon in imidazolylidenes is C4/C5 whereas in thiazolylidenes, it is usually C5. In azoles, the precursors for such ligands, for example, the C2-position (normal), is more acidic than the other positions by as much as 9 pK_a units—a difference that could be rationalised in simple terms as being a result of much better charge delocalisation upon deprotonation in the 2-position than in the others. These results prompted us to investigate the use of 5-deprotonated thiazoles in the preparation of Fischer-type carbenes and carbynes.

Acyl ligand transfer from tungsten(0) to gold(I) has been investigated.[19] Despite the fact that a working mechanism has

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been proposed for such (so called aurolysis) reactions,[20] convincing confirmation for initial O-coordination to the liberated $W(CO)_5$ fragment is still lacking. Although carbene ligand transfer to gold fragments is also known,[21] Fischer-type carbene complexes of gold and structural data thereof remain rare.[22] Heterocyclic substituents on such carbene ligands could offer alternative coordination possibilities for the $W(CO)_5$ fragments during ligand transfer or to a gold(I) unit if ligand transfer does not occur.

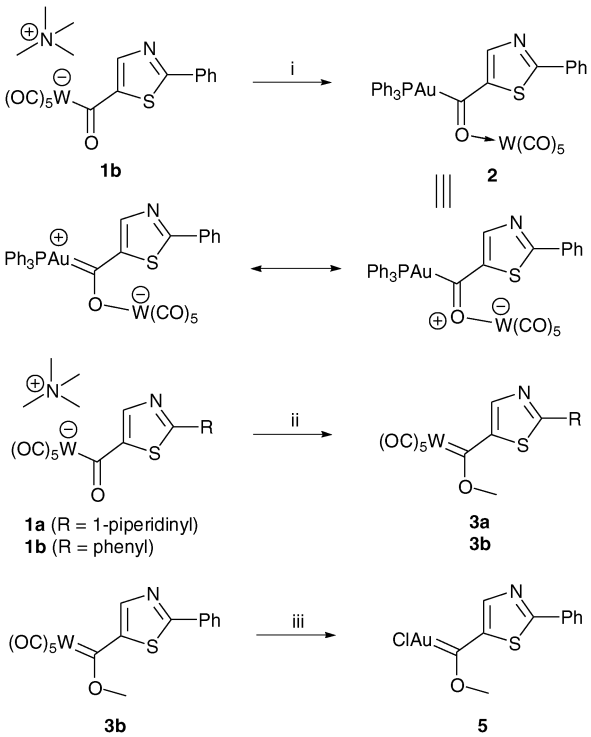
Here, we report the synthesis and physical characterisation of tungsten carbeniate, carbene, and carbyne complexes bearing not the normal 2-deprotonated, but rather the unusual 5-thiazolyl side chains, as well as the interaction of these products with Au^I fragments while focusing on the bonding mode of the $W(CO)_5$ fragment after the reactions. The role of an electron-donating piperidinyl group attached to the 5-membered ring in comparison to a phenyl group in the same position, is also assessed.

Results and discussion

Thiazoles can be readily lithiated at the 5-position if the 2-position is blocked by suitable substituents.[23] Furthermore, electron donating substituents could have a stabilising influence upon subsequent complex formation. As precursors, 2-(1-piperidinyl)thiazole, offering additional electron density at the 5-position in the thiazole ring and, for comparison, 2-phenylthiazole, a more rigid substituent that is electron attracting, were selected. The carbeniate complexes **1a** and **1b** (Scheme 1) were then synthesised in moderate to good yields by reacting the 5-lithiated azoles with $[W(CO)_6]$ followed by cation exchange to afford $[NMe_4]^+$ salts of the anionic complexes.

To establish whether the 5-thiazolyl carbeniate complex **1b** would react in the expected manner with $[(Ph_3P)AuCl]$ by transfer of the acyl ligand to gold and what then would happen to the liberated $W(CO)_5$ fragment, or whether coordination of a gold fragment to the imine nitrogen atom would simply occur, **1b** was reacted with the gold(I) starting material (Scheme 1). A gold acyl (carbeniate) complex formed and, unexpectedly, the extricated $W(CO)_5$ fragment remained bonded to the acyl oxygen yielding the complex, **2**, that could also be formulated as a zwitterionic tungstenoxycarbene complex of gold (Scheme 1). Why this unusual O-coordination of $W(CO)_5$ is preferred to potential N-coordination at the thiazole ring cannot readily be explained. It was nevertheless satisfying to see our previous assumption of weak acylgold coordination to $M(CO)_5$-fragments[19] in related products vindicated.

Since Fischer-type alkoxycarbene complexes bearing 5-thiazolyl side chains are unknown, preparation of **3a** and **3b** from the carbeniate complexes **1a** and **1b** was attempted (Scheme 1). To circumvent the problem of competing *N*-alkylation in the classic method, an indirect route that involves acetylation of the carbeniate and subsequent methanolysis was first followed.[24] Later, direct alkylation with $[Me_3O][BF_4]$ was found to be simpler and to give similar yields. The colour of **3b** is noteworthy in that it forms dark red solutions whilst the microcrystalline solid is purplish-black and the isolated



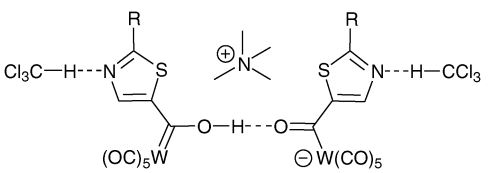
Scheme 1 Reagents and conditions: (i) $[(Ph_3P)AuCl]$, thf, −50 °C; (ii) $[Me_3O][BF_4]$, CH_2Cl_2–CH_3CN, 0 °C; (iii) [ClAu(tht)], thf, −5 °C.

single crystals dark orange. While attempting to crystallise crude **3a** prepared according to the former method, crystals of **4**, a rare hydroxycarbene complex, stabilised by a hydrogen bond to its carbeniate precursor, were isolated (Scheme 2).

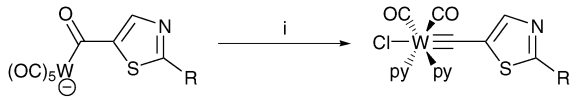
The gold alkoxycarbene complex, **5** (Scheme 1), was formed in fair yield by carbene transfer from **3b** using the labile complex [ClAu(tht)]. The crude product is readily soluble in CH_2Cl_2 whereas once crystallised, solubility of **5** is poor in most standard solvents.

The suitability of (a somewhat modified) protocol for the one developed by Mayr and coworkers[25] for conversion of oxycarbene complexes (carbeniates) into carbyne complexes, while replacing phosgene or oxalyl halides with solid bis(trichloromethyl)carbonate, was verified by the successful preparation of the known carbyne complex $[Cl(CO)_2(py)_2W{\equiv}CC_6H_4\text{-}4\text{-}Me]$.[26] The initial tetracarbonyl species was stabilised by substitution of a set of *cis*-CO ligands with pyridine (py).

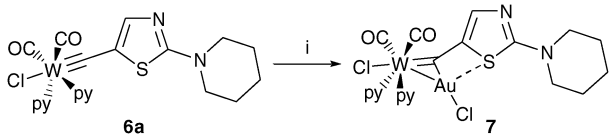
The same reactions worked well when starting with the 5-thiazolyl carbeniates **1a** and **1b** (Scheme 3). The carbyne complexes **6a** and **6b** were isolated in moderate yields (49 and 54%, respectively) after purification by flash



Scheme 2 Connectivity within compound **4**, R = 1-piperidinyl.



Scheme 3 Reagents and conditions: i: $(Cl_3CO)_2CO$, CH_2Cl_2, −78 °C, py, r.t.



Scheme 4 Reagent and conditions: i: [ClAu(tht)], thf, −10 °C.

chromatography under inert conditions. The compounds are stable as solids at low temperature. Stability at room temperature is somewhat lower and the products decompose slowly in solution even at temperatures below 0 °C.

Interaction of the new carbyne complexes **6a** and **6b** with Au^I reagents was then examined. Both compounds readily react with [ClAu(tht)] but, unfortunately, complex mixtures resulted and only intergrown crystals of the addition product **7** (Scheme 4) could eventually be obtained by crystallisation from thf–pentane. The molecular structure clearly indicated coordination of Au^I to the carbyne functionality as well as further stabilisation by Au···S intramolecular interaction.

Infrared spectroscopy

The complexes that contain a $W(CO)_5$ fragment (**1a**, **1b**, **2**, **3a** and **3b**) exhibit signals expected for a pentacarbonyl group. In most instances, the $A_1^{(2)}$ vibration is obscured by the E and/or acyl vibration. The wavenumbers of the $A_1^{(1)}$ vibrations of the piperidinyl-substituted complexes, which are readily assignable, always seem lower (by 2 and 12 cm^{-1} for pairs **1** and **3**) than those of the phenyl-substituted compounds showing the greater electron-donating effect of the former substituent. The $A_1^{(1)}$ vibration of $[(CO)_5W{=}C(OMe)Ph]$[27] is observed at 2068 cm^{-1} in CH_2Cl_2 solution and thus comparable to the value found for **3b** and **2**.

The carbyne complexes **6a** and **6b**, each comprising a pair of *cis*-CO ligands, show bands of A' and A'' symmetry in their infrared spectra, as expected for local C_s symmetry. Both bands of **6a** are observed at lower wavenumbers than those found for **6b**, highlighting the electron-donating influence of the piperidine substituent at the thiazole ring.

NMR spectroscopy

In the ^1H NMR spectra of all the products, only the single proton of the thiazole ring is of some use to gain information about the electronic situation within the heterocyclic ligand. The resonances for the complexes are found at *ca.* δ 8.7 with the exception of **6b** where it appears at a more shielded 7.79 ppm. A routine spectrum of the gold carbene complex **5** revealed an unusually broad signal for this proton at ambient temperature, indicating a potential Au···H interaction and thus prompting us to investigate its behaviour at lower temperatures. The signal half-width drastically decreases from

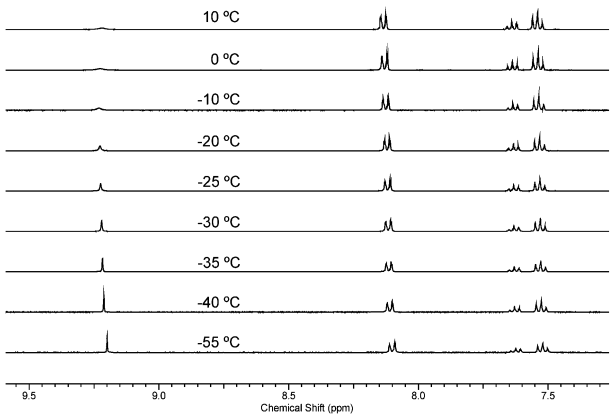


Fig. 1 Expansion of a segment of the ^1H NMR spectra of **5** at different temperatures.

10.5 Hz at 10 °C to 0.93 Hz at −55 °C which proved to be the solubility limit of **5** in CD_2Cl_2 (Fig. 1). This signal has its highest value at −10 °C and moves towards higher field both upon warming ($d\delta/dT \approx 7 \times 10^{-4}$ K^{-1}) or cooling (-6×10^{-4} K^{-1}). Concomitantly, the other signals experience only small and monotonic upfield changes on cooling.

The carbene carbon atoms in **3a** and **3b** resonate at δ 274.3 and 291.6, respectively. They appear at higher field compared to that of $[(CO)_5W{=}C(OMe)Ph]$ (δ 321.9)[28] which can be attributed to the more electron-rich 5-thiazolyl substituent compared to a phenyl group. Even the larger shielding effected by the piperidinyl substituent in the 2-position of the heterocyclic ring compared to phenyl substitution is obvious. The carbene resonance of compound **5** (δ 248.6) is observed at higher field than that of its precursor, **3b**, while the opposite is true for the thiazole resonances. The C-4 resonance at δ 160 is also broadened at room temperature. A similar decrease in the chemical shift of the carbene resonance of tungsten complexes when compared to the gold analogues has been observed for *r*NHC complexes as well.[29]

Notably, the carbyne carbon signal in complex **6a** (δ 245.1) appears at a somewhat lower field strength than that of the more electron-poor ligand in **6b** (δ 240.8).

Solid-state CP-MAS ^{13}C NMR spectroscopy

The acylmetallate **1b** crystallised with two unique molecules in the asymmetric unit (*vide infra*) and the question arose whether their different environments could cause separate ^{13}C NMR signals in the solid state.[30] A sample of the crystalline solid was measured with the cross-polarisation magic angle spinning (CP-MAS) technique utilising spinning frequencies of 5 to 11 kHz for identification of the strong spinning side bands. Data are summarised in Table 1 and Fig. 2 portrays an expansion of a measured spectrum.

The signals for the thiazole and *ipso*-phenyl carbon atoms are well resolved while the resonances for the other phenyl carbon signals do not allow identification of each unique carbon atom, owing to small chemical shift differences. The differences between the individual chemical shifts of the NCS carbon of the thiazole rings ($\Delta\delta$ 2.9, signals 6 in Fig. 2) and the *ipso*-C of the phenyl rings ($\Delta\delta$ 2.2, signals 3 in Fig. 2),

Table 1 ^{13}C NMR data (δ) of **1b**

	Solid-state CP-MAS (126 MHz, 11 kHz spinning)	Solution (101 MHz, CD_2Cl_2)
C(carbeniate)	Not detected	268.2 (s)
trans-CO	Not detected	207.2 (s, d, $^1J_{WC}$ 134.0)
cis-CO	202.8[a]	203.1 (s, d, $^1J_{WC}$ 127.4)
C-2 thiazole	171.0, 168.1 (Δ 367 Hz)	168.7 (s)
C-4 thiazole	160.7, 160.0 (Δ 82 Hz)	160.9 (s)
C-5 thiazole	148.3, 147.7 (Δ 82 Hz)	147.9 (s)
i-Ph	134.7, 132.5 (Δ 284 Hz)	135.1 (s)
p-, *m*-, *o*-Ph	130.2, 129.2, 128.6, 127.3, 125.7, 124.4	130.6 (s), 129.4 (s), 127.0 (s)
$[NMe_4]^+$	56.1, 54.4 (Δ 204 Hz)	56.9 (t, $^1J_{NC}$ 3.8)

[a] Observed only without cross-polarisation.

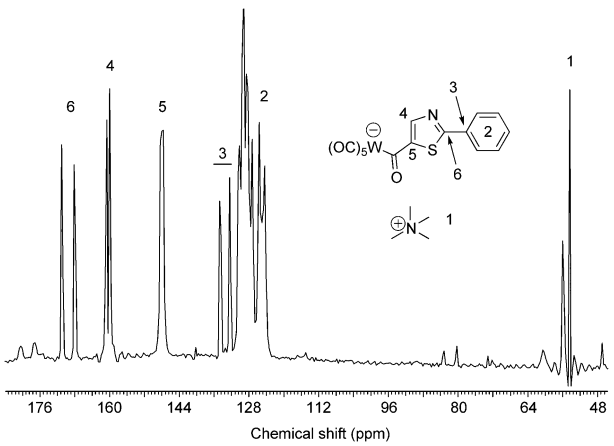


Fig. 2 Solid-state CP-MAS ^{13}C NMR (126 MHz) spectrum of **1b**; spinning frequency 11 kHz; unassigned peaks are spinning side-bands.

respectively, are much larger than the differences within the other signal groups. C-2 of the thiazole, as well as the *ipso*-carbon of the phenyl group, are affected the most by different interplanar angles of the benzene and thiazole rings, which is indeed one of the most significant differences between the asymmetric molecules in the solid state (*vide infra*). Two signals are observed for the $[NMe_4]^+$ counter ions which we believe stem from different carbons within the unique cations rather than being one each for two unique cations. Signals for the pentacarbonyl metal fragment could not be identified in the CP experiments. But in an experimental run without cross-polarisation, the *cis*-CO carbons appear as a broad resonance at δ 202.8 while the intensities of the thiazolyl and phenyl signals are much weaker. The carbeniate carbon and *trans*-CO, however, could not be identified in any spectrum.

Mass spectrometry

Except for compounds **2** and **5**, fast atom bombardment gave the best results and molecular peaks were observed for all the other complexes. Loss of the piperidinyl group of the carbene complex **3a**, but not of the carbyne complex **6a**, was observed. The gold complex, **5**, only afforded interpretable signals from the loss of chloride, a methyl group and the associated decarbonylation peak. Notably, the carbyne complexes **6a** and **6b** fragment *via* two pathways, either by loss of chloride, which seemingly precludes further fragmentation, or sequential loss of CO and pyridine. A number of fragment ions are observed both as protonated and radical cationic species.

Crystallography

The ease with which single crystals of the compounds were obtained varied considerably; while crystals of **1a**, **1b**, **3b** and **6a** suitable for X-ray diffraction formed readily, **3a** gave no crystals of sufficient quality and **6b** only crystallised as a dichloromethane solvate. Selected bond lengths and angles within the molecular structures determined, are summarised in Table 2.

Compound **1a** (Fig. 3) crystallises with only one molecule in the asymmetric unit. The relative position of the $[NMe_4]^+$ cation is similar in the two acyl complexes (**1a** and **1b**): it approaches the negatively charged carbeniate oxygen atom. The piperidine ring is in the chair conformation with the thiazole ring as an equatorial substituent. Bond lengths of **1a** and **1b** are comparable, indicating no appreciable influence of the 2-substituent at the thiazole ring, in contrast to the results obtained from the IR and ^{13}C NMR investigations.

Compound **1b** (Fig. 4) crystallises as two independent molecules (designated A and B) per unit cell. The main differences within the molecules are the respective interplanar angles of the essentially flat phenyl and thiazolyl groups [5.2(2) and 16.3(2)°]. The $[NMe_4]^+$ cations are located adjacent to the carbeniate oxygen atoms forming O···H contacts in the range of 2.27 to 2.40 Å. The C–O bond distances of the acyl groups in the anionic complexes **1a** and **1b** are somewhat longer [1.248(5) and 1.246(4) Å, respectively] than in the neutral complex [$(Ph_3P)AuC(O)Ph$] [1.200(7) Å].[19]

The product of an acyl (or anionic carbene) transfer to a Au^I fragment, **2**, was isolated as red crystals of a pentane solvate. The Ph_3PAu^+ group is coordinated to what essentially amounts to be an acyl carbon, while the displaced $W(CO)_5$ fragment is bonded to the acyl oxygen atom. Compound **2**·C_5H_{12}, shown in Fig. 5, confirms the existence of the proposed intermediate during the preparation of tungsten-free gold acyls.[19] As mentioned above, the $W(CO)_5$ unit surprisingly prefers O-coordination to imine bonding. When compared to **2**·C_5H_{12}, the Au–C bond in the free benzoyl-gold complex, [$(Ph_3P)AuC(O)Ph$],[19] is found to be shorter [1.200(7) Å] than the respective value of 1.247(8) Å for **2**·C_5H_{12}. The Au–C bonds are similar in both structures [2.085(5) Å in the free acyl and 2.053(7) Å in **2**], and both are longer than those found in the Fischer-type carbene

Table 2 Selected bond lengths (Å) and angles (°)

	1a	**1b** A/B	**2**·C_5H_{12}	**3b**	**4**	**5** A/B	**6a**	**6b**·CH_2Cl_2
M(1)–C(1)	2.251(5)	2.251(3)/2.248(3)	2.053(7)	2.195(5)	2.246(7)	1.976(4)/1.959(4)	1.841(4)	1.822(3)
W(1)–C(CO_{trans})	1.994(5)	1.994(4)/2.019(4)	1.953(7)	2.029(5)	2.012(7)	—	—	—
W(1)–C(CO_{cis})[a]	2.035	2.035/2.035	2.033	2.047	2.024	—	1.996(4)/ 1.990(4)	2.001(3)/ 1.993(3)
C(1)–O(1)	1.248(5)	1.245(5)/1.245(5)	1.247(8)	1.330(5)	1.284(8)	1.296(5)/1.302(5)	—	—
C(1)–C(10)	1.467(6)	1.495(5)/1.507(4)	1.460(9)	1.447(7)	1.437(9)	1.430(6)/1.433(6)	1.411(5)	1.418(5)
M(1)–Cl(1)	—	—	—	—	—	2.289(1)/2.279(2)	2.523(2)	2.5107(8)
C(1)–W(1)–C(2)	173.6(2)	177.7(2)/174.4(2)	175.0(2)[c]	175.2(2)	178.9(3)	174.8(2)/177.5(2)[d]	176.7(2)[e]	170.9(1)[e]
M(1)–C(1)–C(10)	125.0(3)		115.8(5)	124.6(3)	124.4(5)	119.9(3)/122.6(3)	175.1(3)	169.4(3)
M(1)–C(1)–O(1)	121.9(3)	122.9(2)/123.8(2)	127.1(5)	129.4(3)	125.2(5)	127.9(3)/125.9(3)	—	—
N(2)–ε[b]	0.185(5)	—	—	—	0.146(8)	—	0.074(5)	—
Interplanar angle C_3HNS–C_6H_5	—	5.2(2)/16.3(2)	5.2(4)	8.2(2)	—	1.9(3)/13.8(3)	—	21.9(2)
Others	—	—	Au(1)–P(1) 2.301(2) W(1)–O(1)–C(1) 132.1(4)	—	2.418(9) [O(1)···O(1)′] 3.09(1) [C(7)···N(1)]	3.3866(3) [Au(1A)···Au(1B)] 3.4871(4) [Au(1B)···Au(1B″)]	2.276(3) [W(1)–N(3)], 2.269(3) [W(1)–N(4)]	2.246(3) [W(1)–N(3)], 2.254(3) [W(1)–N(4)]

[a] Average values. [b] ε corresponds to the plane of C(12), C(13), C(17). [c] O(1)–W(1)–C(2) angle. [d] Cl(1)–Au(1)–C(1) angles. [e] Cl(1)–W(1)–C(1) angles. Symmetry operators: ′ $1-x, y, 3/2-z$; ″ $2-x, 1-y, -z$.

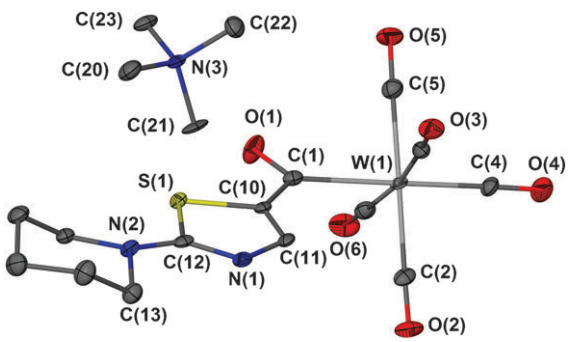


Fig. 3 Molecular structure of **1a**.

complexes of gold, such as the recently described chloro-(pyrazolin-3-ylidene)gold compounds [Au–C 1.981(6) and 1.991(5) Å].[31] Structurally related metaloxycarbene complexes include an acylgold complex coordinated to a dirhenium fragment with similar bond lengths in the acyl moiety[32] and a compound wherein $[BrW(CO)_5]^-$, diethyl ether and two [(Ph_3P)AuC(O)Ph] molecules are coordinated to one Li^+ ion, again with closely related geometry.[19] Complex **2**·C_5H_{12} is one of very few examples comprising a $W(CO)_5$ group coordinated to an oxygen donor. Such compounds are usually of very limited stability. $[(CO)_5W(OPPh_3)]$ is presently the only neutral example in the literature that has been crystallographically authenticated.[33] Its W–O bond [2.244(3) Å] is slightly longer than the one in **2**·C_5H_{12} [2.205(5) Å]. Both molecules, however, share a considerably shorter W–CO_{trans} distance [1.942(5) Å in the literature example and 1.953 Å in **2**·C_5H_{12}] compared to the corresponding values for the *cis*-CO ligands [2.048 *vs.* 2.033 Å on average]. The W–O–C angle of 132.1(4)° in **2**·C_5H_{12} indicates sp^2-hybridisation at the oxygen atom in contrast to group 4 bis(cyclopentadienyl)metal

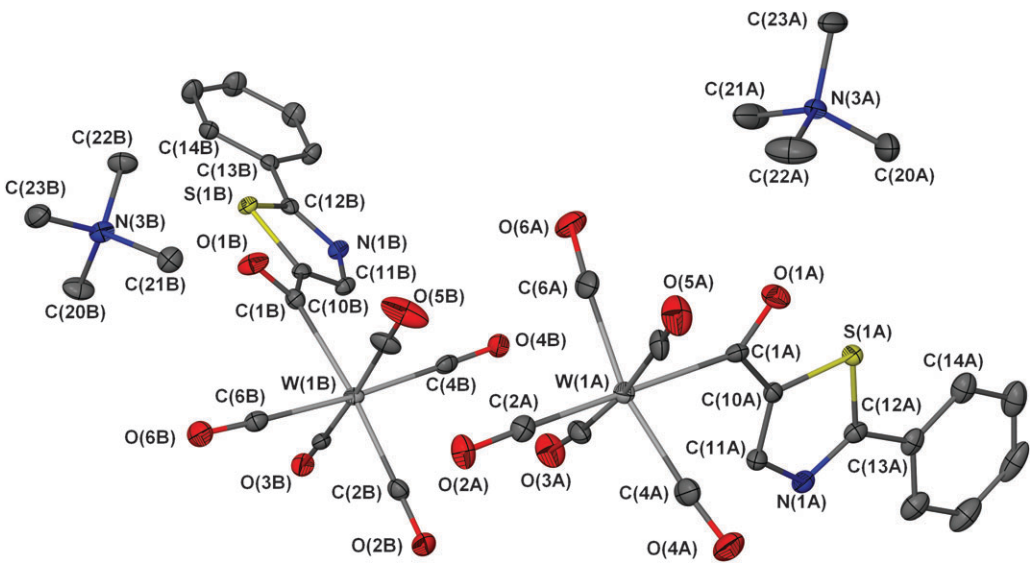


Fig. 4 Molecular structure of **1b**.

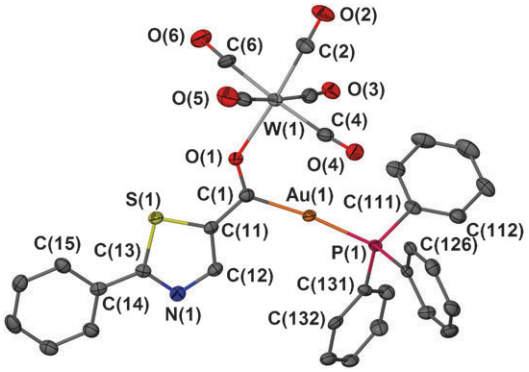


Fig. 5 Molecular structure of **2**·C_5H_{12}; the solvent molecule is omitted for clarity.

fragments that cause the M–O–C angle to approach linearity.[34] The thiazole ring in **2**·C_5H_{12} is oriented in such a way that the hydrogen atom is close to the gold centre [Au···H 2.84 Å] in what could amount to an attractive interaction, as was found for complex **5** (*vide infra*). In contrast to **5**, no evidence of such an interaction was found by NMR measurements in solution.

The structural effects of *O*-alkylation on the molecular structure of a carbeniate such as **1b** that contains a

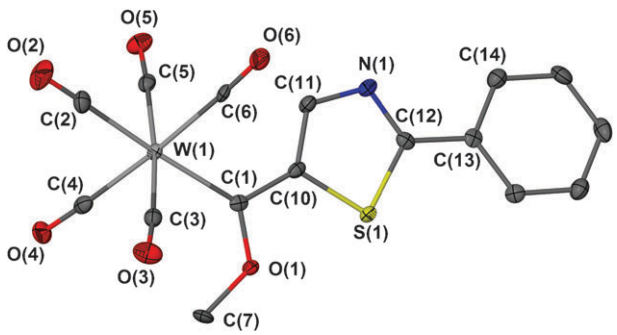


Fig. 6 Molecular structure of **3b**.

complicated *N*-heterocyclic azolyl as a substituent can be inferred from the structure of the carbene complex **3b** (Fig. 6). The bond lengths most influenced are W(1)–C(1)—which is shortened in view of the formal metal–carbene double bond formation [2.195(5) Å in **3b**, 2.251(3) and 2.248(3) Å in **1b**]—and, obviously, C(1)–C(10) [1.447(7) Å *vs.* 1.495(5) and 1.507(4) Å] is shortened owing to a participation of the heterocyclic ring in decreasing the carbocationic character of C(carbene). As expected, the C(1)–O(1) bond is elongated considerably [1.330(5) Å *vs.* 1.246(4) Å]. In the comparable phenylcarbene complex,[35] the C(carbene)–C(phenyl) bond of 1.59 Å is *ca.* 0.1 Å longer than C(1)–C(10) in **3b**.

As mentioned previously, a crystal of **4** (Scheme 2) was isolated during an attempt to purify crude **3a** by recrystallisation from $CHCl_3$–hexane. It represents only the second example of a tungsten hydroxycarbene complex that is stabilised by a carbeniate moiety; another example was previously reported by us.[36] Compound **4** (Fig. 7) crystallises in the monoclinic space group $C2/c$ and is ordered around a C_2 axis passing between the oxygen atoms of the carbene groups. The bridging proton is distributed evenly between the two molecules and stabilises the arrangement by a strong hydrogen bond [O···O′ 2.418(9) Å, ′ = $1-x, y, 3/2-z$]. The basicity of the imine nitrogen atom in the thiazole ring, enhanced by the piperidinyl substituent, is demonstrated by the $CHCl_3$ molecules engaging in weak hydrogen bonds. The piperidine nitrogen N(2) is essentially sp^2-hybridised. Comparison to the other example in the literature that contains a phenyl substituent reveals the same structural parameters except for the C(1)–C(10) bond, which is shorter in **4** than in the phenyl analogue [1.437(9) Å *vs.* 1.505(7) Å]; additional electron delocalisation from the heterocycles may be responsible for this observation.

The alkoxycarbene **5** (Fig. 8) crystallises as two asymmetric molecules (A and B) that form chains of four complex units linked by aurophilic interactions, two of them asymmetric and the others related by a centre of inversion. Molecule A forms one contact to molecule B of the crossed-sword type

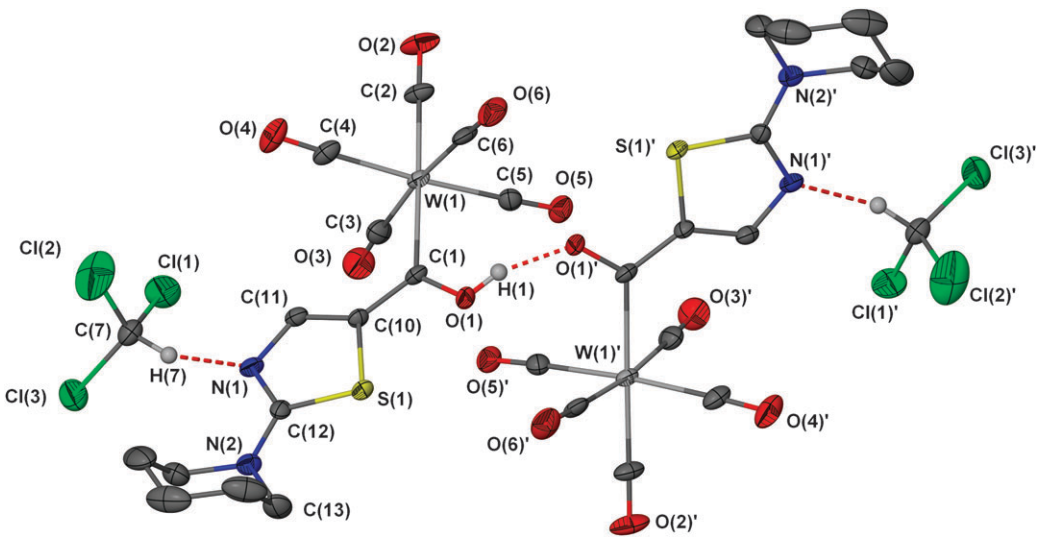


Fig. 7 Molecular structure of **4**; H(1) is arbitrarily located in one position; primed atoms are related by a C_2 rotation; disordered $[NMe_4]^+$ is not shown.

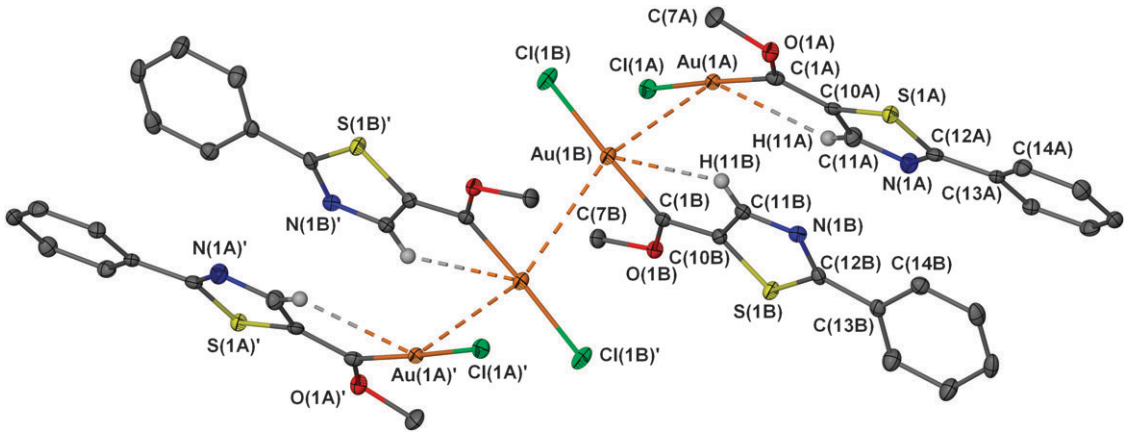


Fig. 8 Molecular structure of **5**; primed atoms are related by a centre of inversion located between Au(1B) and Au(1B)′.

[Cl(1A)–Au(1A)···Au(1B)–Cl(1B) 88.20(4)°] while B is further linked to its symmetry-generated image by a longer, antiparallel metallophilic bond [Cl(1B)–Au(1B)···Au(1B)″–Cl(1B)″ 180°; symmetry operator ″ = 2 − *x*, 1 − *y*, −*z*]. Only a few other examples are known in which four gold centres form a chain of intermolecular aurophilic interactions.[37] It is remarkable that by substituting $W(CO)_5$ in **3b** by isolobal AuCl in **5** only minor changes occur in the bond distances and angles of the carbene complex. The structures of [ClAu=C(NMe$_2$)Ph],[22] a cationic combined NHC/Fischer alkoxycarbene Au^{I} complex,[22] and a series of gold pyrazolin-3-ylidene complexes[31] have been reported. The Au–C distances in all of these are comparable to those in **5**; in the cationic alkoxycarbene complex, the Au–C may be longer, as was observed for neutral and cationic Au^{I} *r*NHC complexes.[29] Notably, the interplanar angle between the phenyl group and the heterocycle in **5** is much smaller [1.9(3)° and 13.8(3)°] than in the pyrazolinylidene complexes which show angles of 45.9° and 47.7°.[31] The thiazole in **5** is arranged to enable close Au···H contacts of 2.87 Å and 2.97 Å which can also be observed in the ^{1}H NMR spectrum of the compound (*vide supra*). Au···H interactions in the solid state have also been initially reported as ranging between 2.6 Å and 3.0 Å.[38] Later, it was found that in thione complexes, such Au···H distances could vary between 2.80–3.07 Å,[39] and in a recent study employing pyridinethiolates, distances between 2.83 Å and 2.88 Å were observed.[40]

The crystal structures of both tungsten carbyne complexes **6a** (Fig. 9) and **6b** (Fig. 10) were determined; they crystallise in rather similar triclinic lattices. Compound **6b** (Fig. 10) co-crystallises with a CH_2Cl_2 solvent molecule per formula unit. In complex **6a**, the piperidine nitrogen atom is essentially planar, possibly showing increased delocalisation of its lone pair compared to the situation in the structure of **1a** and in accordance with the increased electron-withdrawing power of the –C≡W$Cl(CO)_2(py)_2$ unit over the anionic –C(O)W$(CO)_5^-$ fragment. The effect of the piperidine lone pair can be observed in the elongated W(1)–Cl(1) bond in **6a** [2.523(2) Å] compared to **6b**·CH_2Cl_2 [2.5107(8) Å] (Scheme 5). Again, comparison to other tungsten carbyne complexes is complicated by the fact that only one complex exhibiting *cis*-bis(pyridine) substitution, [$Cl(CO)_2(\eta^2$-Ppyr$_3$)W≡CPh] (pyr = 2-pyridyl), has so far been structurally characterised.[41]

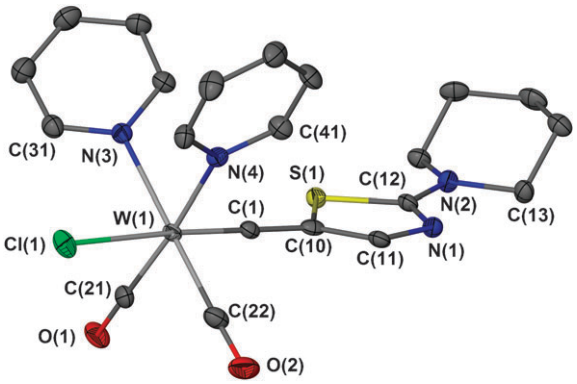


Fig. 9 Molecular structure of **6a**.

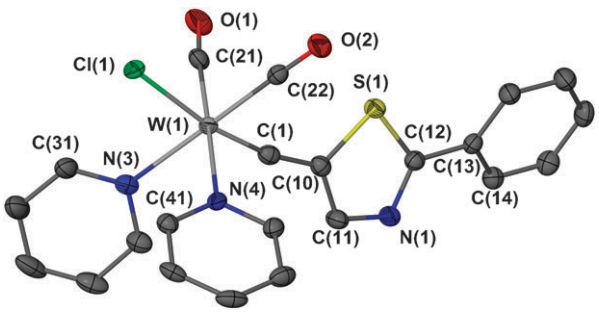
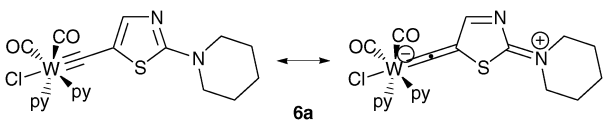


Fig. 10 Molecular structure of **6b**·CH_2Cl_2; the solvent molecule is omitted for clarity.



Scheme 5 Electron delocalisation in **6a** effects a longer W(1)–Cl(1) bond length than in the Ph-substituted analogue.

Its W(1)–C(1) bond length of 1.806(6) Å is similar to that in **6b**·CH_2Cl_2 but shorter than in **6a**. The W–N separations are similar. To supplement this example, the crystal and molecular structure of [$Cl(CO)_2(py)_2$W≡CC_6H_4-4-Me], **8**, was also determined and is included in the ESI† to this article. The angle at the carbyne carbon [169.4(3)°] as well as the

Cl(1)–W(1)–C(1) angle [170.9(1)°] in **6b**·CH_2Cl_2 deviate from linearity.

Conclusions

Although group 6 metalcarbonyl carbeniates from standard 2-lithiated thiazoles cannot be converted into carbyne complexes, the 'abnormal' 5-deprotonated analogs produce relatively stable carbene and carbyne complexes. No appreciable stability difference is effected by changing the substituent in the 2 position of such complexes. Nevertheless, a 1-piperidinyl substituent clearly transfers more electron density onto the rest of the carbene ligand than a phenyl group. Treatment of the carbeniate and corresponding carbene complexes with gold(I) fragments leads to ligand transfer reactions and, in the former example, the liberated $W(CO)_5$ group is trapped by the acyl ligand bonded to gold. The carbene transfer affords rare alkoxycarbene complexes of gold and while no tungsten carbonyl fragments remain in the products, agostic-type Au···H interactions may be studied by NMR spectroscopy and verified by crystal and molecular structure determination. One of the carbyne complexes forms an adduct with the gold AuCl fragment that is stabilised by an Au···S interaction.

Experimental

Crystallography

Data associated with the crystal structures are summarised in Table 3. Intensity data were collected at T = 100 K with a Bruker SMART Apex diffractometer[42] with graphite monochromated Mo Kα radiation (λ = 0.71073 Å). Intensities were measured using the ω-scan mode and were corrected for Lorentz and polarisation effects. The structures were solved by direct methods and refined by full-matrix least-squares on F^2 using the SHELXL-97 software package within the X-Seed environment.[43] All non-hydrogen atoms were refined with anisotropic displacement parameters and all hydrogens were placed in calculated positions. Ellipsoids were drawn at the 50% probability level throughout. Hydrogen atoms in Figures were omitted for clarity except when noted otherwise. In the crystal structure of **4**, H(1) was refined with an occupancy factor of 0.5 resembling the bulk average and the N–C bond distances involving C(21), C(22) and C(23) in the tetramethylammonium cation were restrained to have equal lengths.

Syntheses

All work was performed under an atmosphere of dry argon using standard Schlenk- and vacuum line techniques. All solvents were distilled under a dry dinitrogen atmosphere,[44] MeOH was distilled from $Mg(OMe)_2$, CH_2Cl_2 from CaH_2, pentane, hexane, hexanes (commercial mixture of isomers) and toluene from sodium and diethyl ether and thf from sodium wire and sodium benzophenone ketyl radical. Flash chromatographic separations were performed at low temperature with "flash grade" silica gel (230–400 mesh) under inert atmosphere. [ClAu(Me_2S)], [ClAu(tht)][45] and 2-(1-piperidinyl)-thiazole[46] were prepared according to literature procedures. 2-Phenylthiazole was synthesised in 75% yield following a modified method† to the one described in the literature.[47]

Melting points were determined with a Stuart Scientific SMP3 instrument or with a Fischer Scientific (Pittsburgh PA, St. Louis MO) and Eimer & Amend (New York NY) hot stage apparatus and are uncorrected. FAB mass spectra (nitrobenzyl alcohol matrices) were performed on a VG 70 SEQ mass spectrometer by the University of the Witwatersrand. IR spectra were recorded at 4 cm^{-1} resolution on a Nicolet Avatar 300 FT-IR instrument equipped with a Smart Performer ZnSe disk ATR accessory; spectra were corrected for ATR effects using Omnic software supplied with the spectrometer. ^1H, ^{13}C and ^{31}P NMR spectra were recorded at the indicated frequency on a Varian VNMRS 300 or Varian Unity Inova 400 spectrometer. ^1H and ^{13}C spectra were referenced to residual solvent peaks and the ^{31}P spectrum is externally referenced to 85% H_3PO_4. Elemental analyses were performed by the University of Cape Town or Stellenbosch University.

Tetramethylammonium pentacarbonyl{[2-(1-piperidinyl)thiazol-5-yl]carbonyl}tungstate(1–), 1a. A solution of 2-(1-piperidinyl)-thiazole (1.068 g, 6.35 mmol) in thf (30 cm^3) was cooled to −78 °C. Butyllithium (6.1 cm^3, 1.05 M in hexanes, 6.41 mmol) was added dropwise by syringe and after stirring for 1 h, solid $[W(CO)_6]$ (2.172 g, 6.17 mmol) was added, whereupon the light yellow solution slowly turned brownish-red. After 2.5 h, the temperature had risen to –25 °C and the cooling bath was removed. The suspension was stirred for another 1.5 h at room temperature, whereupon the solvents were removed *in vacuo*. A golden-red foam of the lithium salt was obtained, which was washed with pentane (60 cm^3) to remove excess $[W(CO)_6]$. In an extraction funnel under inert atmosphere, $[NMe_4]Cl$ (819 mg, 7.47 mmol) was dissolved in deoxygenised water (20 cm^3) and CH_2Cl_2 (100 cm^3) was added. The lithium salt was dissolved in deoxygenised water (50 cm^3), affording a blood-red solution which was filtered through a pad of Celite into the extraction funnel. A first black-red organic phase was separated, a yellow precipitate of **1a** remained in the extraction funnel. Another extraction with CH_2Cl_2–acetonitrile (4 : 1) yielded a red organic phase. Both fractions were evaporated to dryness. The CH_2Cl_2 extract formed an ochre precipitate while the MeCN–CH_2Cl_2 fraction yielded an orange crystalline solid. Crystals suitable for X-ray diffraction were grown from the MeCN–CH_2Cl_2 fraction in acetonitrile layered with diethyl ether. Yield of **1a**: 55%, 2.00 g, mp 145 °C (dec.). Found: C, 36.4; H, 3.9; N, 7.1. $C_{18}H_{23}N_3O_6SW$ requires C, 36.4; H, 3.9; N, 7.1%. δ_H (400 MHz, CD_3OD) 7.80 (1 H, s, CH thiazole), 3.48 (4 H, m, NCH_2), 3.18 (12 H, t, $^2J_{NH}$ 0.59, NMe_4) and 1.66 (6 H, m, $NCH_2(CH_2)_3$). δ_C (101 MHz, CD_3OD) 271.8 (s, d, $^1J_{WC}$ 85.8, carbene), 206.8 (s, d, $^1J_{WC}$ 133.1, *trans*-CO), 203.1 (s, d, $^1J_{WC}$ 127.3, *cis*-CO), 174.7 (s, C2 thiazole), 150.8 (s, d, $^1J_{WC}$ 21.2, C4/C5 thiazole), 148.8 (s, C5/C4 thiazole), 55.9 (t, $^2J_{NC}$ 4, NMe_4), 50.3 (s, $NCH_2CH_2CH_2$), 26.2 (s, $NCH_2CH_2CH_2$) and 25.0 (s, $NCH_2CH_2CH_2$). ν_{max}/cm^{-1} (ATR) 2044s ($A_1^{(1)}$ CO), 1949m (B_1 CO), 1881, 1859vs (E and $A_1^{(2)}$ CO) and 1840vs (acyl group). m/z 667 [(M + NMe_4)$^+$, 12%], 520 [(M–NMe_4 + H)$^+$, 12], 519 [(M–NMe_4)$^+$, 5], 492 [(M–NMe_4–CO + H)$^+$, 7],

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Table 3 Crystallographic and data collection parameters

Compound	**1a**	**1b**	**2**·C_5H_{12}	**3b**	**4**	**5**	**6a**	**6b**
Empirical formula	$C_{18}H_{23}N_3O_6SW$	$C_{19}H_{18}N_2O_6SW$	$C_{33}H_{21}AuNO_6PSW \cdot C_5H_{12}$	$C_{16}H_9NO_6SW$	$C_{18}H_{24}N_3O_6SW \cdot C_{14}H_{11}N_2O_6SW \cdot 2CHCl_3$	$C_{11}H_9AuClNOS$	$C_{21}H_{21}ClN_4O_2SW$	$C_{22}H_{16}ClN_3O_2SW \cdot CH_2Cl_2$
M_r	593.30	586.26	1043.5	527.15	1352.2	435.67	612.78	690.66
Crystal habit	Orange prism	Orange needle	Orange prism	Dark orange needle	Orange needle	Orange prism	Orange prism	Red needle
Crystal size/mm	0.19 × 0.15 × 0.13	0.48 × 0.12 × 0.03	0.13 × 0.09 × 0.07	0.56 × 0.05 × 0.03	0.10 × 0.03 × 0.01	0.21 × 0.13 × 0.10	0.18 × 0.10 × 0.03	0.57 × 0.08 × 0.07
Crystal system	Monoclinic	Orthorhombic	Triclinic	Orthorhombic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*C*2/*c* (No. 15)	*Pbca* (No. 61)	$P\bar{1}$ (No. 2)	*Pccn* (No. 56)	*C*2/*c* (No. 15)	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)	$P\bar{1}$ (No. 2)
a/Å	22.688(4)	12.602(1)	11.5111(7)	17.336(3)	26.273(7)	14.223(2)	8.657(2)	9.1923(7)
b/Å	9.098(2)	19.302(2)	12.0437(8)	26.055(3)	11.491(3)	11.5834(9)	8.917(2)	9.2850(8)
c/Å	21.294(3)	34.983(3)	13.8342(9)	7.4114(9)	16.925(5)	14.811(2)	16.718(4)	15.704(2)
α (°)	90	90	100.005(1)	90	90	90	98.687(4)	101.302(1)
β (°)	92.674(2)	90	102.850(1)	90	111.940(4)	106.345(1)	96.490(4)	92.103(1)
γ (°)	90	90	94.026(1)	90	90	90	118.054(3)	105.720(1)
V/Å^3	4391(2)	8510(2)	1829.6(2)	3347.5(7)	4740(2)	2341.5(3)	1100.5(4)	1259.4(2)
Z, D_c/Mg m^{-3}	8, 1.795	16, 1.830	2, 1.894	8, 2.092	4, 1.895	8, 2.472	2, 1.849	2, 1.821
μ(Mo Kα)/mm^{-1}	5.395	5.565	7.293	7.059	5.336	12.947	5.490	5.013
No. of reflections	12017	47050	7474	17901	13592	13330	11537	13500
Unique reflections	4456	8711	19796	3425	5220	4783	4490	5154
R_{int}	0.0351	0.0383	0.0346	0.0406	0.0507	0.0287	0.0289	0.0237
Data, restraints, parameters	4102, 0, 266	7556, 0, 531	6485, 2, 444	3009, 0, 226	4051, 6, 290	4444, 0, 291	4202, 0, 271	4908, 0, 298
F(000)	2320	4544	1000	2000	2616	1616	596	668
R_1, wR_2[a] [$I > 2\sigma(I)$]	0.0387, 0.0974	0.0241, 0.0547	0.0397, 0.0870	0.0312, 0.0697	0.0525, 0.1153	0.0234, 0.0548	0.0268, 0.0661	0.0241, 0.0572
R_1, wR_2 (all data)	0.0415, 0.1000	0.0309, 0.0572	0.0473, 0.0898	0.0366, 0.0719	0.0731, 0.1245	0.0260, 0.0560	0.0293, 0.0671	0.0257, 0.0579
Goodness-of-fit	1.080	1.049	1.075	1.102	1.025	1.040	1.082	1.081

[a] $w = 1/[\sigma^2(F_o)^2 + aP^2 + bP]$ where $P = (F_o^2 + 2F_c^2)/3$.

491 [(M–NMe_4–CO)$^+$, 7], 464 [(M–NMe_4–2CO + H)$^+$, 17], 463 [(M–NMe_4–2CO)$^+$, 2], 436 [(M–NMe_4–3CO + H)$^+$, 7], 435 [(M–NMe_4–3CO)$^+$, 7], 408 [(M–NMe_4–4CO + H)$^+$, 8] and 407 [(M–NMe_4–4CO)$^+$, 10].

Tetramethylammonium pentacarbonyl[(2-phenylthiazol-5-yl)-carbonyl]tungstate(1–), 1b. Compound **1b** was obtained following the same procedure as described for **1a**, employing 2-phenylthiazole (1.681 g, 10.4 mmol), butyllithium in hexanes (7.0 cm^3, 1.4 M, 9.8 mmol) and $[W(CO)_6]$ (3.71 g, 10.5 mmol). The product was extracted with CH_2Cl_2–MeCN (4 : 1) yielding a blood-red solution. Upon removal of the solvents, the blood-red (purple when wet with solvent) crystals were washed with toluene to remove residual $[W(CO)_6]$ and free 2-phenylthiazole. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexanes. Yield: 75%, 5.78 g, mp 80 °C (dec.). Found: C, 38.6; H, 3.5; N, 4.8. $C_{19}H_{18}N_2O_6SW$ requires C, 38.9; H, 3.1; N, 4.8%. δ_H (400 MHz, CD_2Cl_2) 8.38 (1 H, s, CH thiazole), 7.98 (2 H, m, *o*-Ph), 7.42 (3 H, m, *m*- and *p*-Ph) and 3.35 (12 H, m, NMe_4). δ_C see Table 1. ν_{max}/cm^{-1} 2046s ($A_1^{(1)}$ CO), 1941sh (B_1 CO), 1870vs (*E* CO) and 1835vs (acyl group). ν_{max}/cm^{-1} (CH_2Cl_2) 2050s ($A_1^{(1)}$), 1955m (B_1) and 1907vs (*E*, $A_1^{(2)}$ and acyl group). *m*/*z* 660 [(M + NMe_4)$^+$, 8%], 512 [(M–NMe_4)$^+$, 2], 485 [(M–NMe_4–CO + H)$^+$, 1], 484 [(M–NMe_4–CO)$^+$, 1], 457 [(M–NMe_4–2CO + H)$^+$, 1] and 456 [(M–NMe_4–2CO)$^+$, 2].

Pentacarbonyl-2κ^5*C*-[μ-(2-phenylthiazol-5-yl)carbonyl-1κ*C*:2κ*O*]-(triphenylphosphine-1κ*P*)goldtungsten, 2. A solution of [(Ph_3P)AuCl] in thf, prepared from PPh_3 (202 mg, 0.77 mmol) and [(Me_2S)AuCl] (227 mg, 0.77 mmol), was cooled to −50 °C and **1b** (568 mg, 0.97 mmol) was added as a solid. After 2 h, the mixture had reached 10 °C and Na[BF_4] (88 mg, 0.80 mmol) was added to aid the abstraction of chloride from [(Ph_3P)AuCl]. The slightly turbid orange solution was stirred for another hour at room temperature. TLC analysis (silica plate with CH_2Cl_2 as eluent) of the reaction mixture revealed two products. The solvent was removed *in vacuo* affording an orange-brown oil, which was subjected to column chromatography under inert conditions on Florisil (15 × 5 cm) at −30 °C, eluting with CH_2Cl_2 (200 cm^3), CH_2Cl_2/thf 19 : 1 (100 cm^3) and CH_2Cl_2/thf 12 : 1. Two product fractions were obtained; the first one contained a mixture of two products, the second contained **2**. Crystals suitable for X-ray diffraction were obtained from a thf solution layered with pentane. Yield: 57%, 0.414 g, mp 90 °C (dec.). Found: C, 40.8; H, 2.3; N, 1.2. $C_{33}H_{21}AuNO_6PSW$ requires C, 40.8; H, 2.2; N, 1.4%. δ_H (400 MHz, $CDCl_3$) 8.62 (1 H, s, d, $^1J_{CH}$ 184.4, CH thiazole), 8.01 (2 H, m, *o*-Ph) and 7.52 (18 H, m, *m*-Ph, *p*-Ph, PPh_3). δ_C (101 MHz, $CDCl_3$) 252.3 (d, $^2J_{PC}$ 133.7, carbene), 202.6 (s, *trans*-CO), 198.7 (s, d, $^1J_{WC}$ 131.2, *cis*-CO), 171.6 (s, C2 thiazole), 150.1 (s, C4 thiazole), 143.6 (s, C5 thiazole), 134.2 (d, $^2J_{PC}$ 13.4, *o*-PPh), 133.8 (s, *i*-Ph), 131.5 (d, $^4J_{PC}$ 1.3, *p*-PPh), 130.7 (s, *p*-Ph), 129.8 (d, $^1J_{PC}$ 50.3, *i*-PPh), 129.2 (d, $^3J_{PC}$ 10.8, *m*-PPh), 128.9 (s, *o*-Ph) and 126.9 (s, *m*-Ph). δ_P (162 MHz, $CDCl_3$) 38.8 (s). ν_{max}/cm^{-1} (CH_2Cl_2) 2069w ($A_1^{(1)}$ CO) and 1922m (*E* and $A_1^{(2)}$ CO). *m*/*z* 1078 [(M–$W(CO)_5$ + $AuPPh_3$–CO)$^+$, 4%], 887 [(M − 3CO)$^+$, 1], 721 {[$Au(PPh_3)_2$]$^+$, 22}, 648 [(M–$W(CO)_5$ + H)$^+$, 25] and 459 {[$Au(PPh_3)$]$^+$, 100}.

Pentacarbonyl{methoxy[2-(1-piperidinyl)thiazol-5-yl]methylidene}-tungsten, 3a. In a Schlenk flask, **1a** (927 mg, 1.56 mmol) was suspended in CH_2Cl_2 (20 cm^3) and the suspension cooled to 0 °C. A solution of [Me_3O][BF_4] (250 mg, 1.69 mmol, 1.1 mol eq.) in acetonitrile (40 cm^3) was slowly added *via* a dropping funnel. After stirring for 3 h, all volatiles were removed *in vacuo* and the crude product was subjected to flash chromatography (column dimensions 9 × 5 cm) at −20 °C, eluting with 150 cm^3 CH_2Cl_2–pentane (1 : 1) and 150 cm^3 CH_2Cl_2–diethyl ether (1 : 1). Two fractions were collected. The second orange fraction contained 62 mg (7.4%) of **3a**. mp 106 °C (decomp.). Found: C, 33.8; H, 2.9; N, 5.4. $C_{15}H_{14}N_2O_6SW$ requires C, 33.7; H, 2.6; N, 5.2%. δ_H (400 MHz, $CDCl_3$) 8.50 (1 H, s, d, $^1J_{CH}$ 184.0, CH thiazole), 4.49 (3 H, s, d, $^1J_{CH}$ 146.7, OMe), 3.67 [4 H, m, NCH_2 and 1.73 (6 H, m, $NCH_2(CH_2)_3$)]. δ_C (101 MHz, $CDCl_3$) 274.3 (s, d, $^1J_{WC}$ 97.4, carbene), 202.1 (s, d, $^1J_{WC}$ 124.2, *trans*-CO), 198.1 (s, d, $^1J_{WC}$ 126.7, *cis*-CO), 176.6 (s, C2 thiazole), 163.5 (br s, C4 thiazole), 140.2 (s, C5 thiazole), 67.2 (s, OMe), 49.9 (s, NCH_2), 25.3 (s, $NCH_2CH_2CH_2$) and 23.8 (s, $NCH_2CH_2CH_2$). ν_{max}/cm^{-1} 2058 ($A_1^{(1)}$ CO), 1969m, (B_1 CO) and 1981vs (*E* and $A_1^{(2)}$ CO). *m*/*z* 535 [3%, (M + H)$^+$], 534 (3, M$^+$), 506 [3, (M–CO)$^+$], 478 [8, (M–2CO)$^+$], 450 [1, (M–C_5H_{11} + H)$^+$], 449 [1, (M–C_5H_{11})$^+$] and 422 [3, (M–C_5H_{11}–CO)$^+$].

Pentacarbonyl[methoxy(2-phenylthiazol-5-yl)methylidene]-tungsten, 3b. In a preparation similar to **3a**, compound **1b** (1.140 g, 1.94 mmol) and [Me_3O][BF_4] (293 mg, 1.98 mmol, 1.02 eq.) were used. Inert flash chromatography (11 × 5 cm, −20 °C) was performed, eluting with 150 cm^3 CH_2Cl_2–hexane (1 : 1) and subsequently 200 cm^3 CH_2Cl_2–diethyl ether–hexane (2 : 1 : 1). The second, dark purple fraction afforded 356 mg (35%) of a purplish-black microcrystalline solid. Crystals suitable for X-ray diffraction were grown from CH_2Cl_2 layered with hexane. mp 147 °C. Found: C, 36.7; H, 1.9; N, 2.7. $C_{16}H_9NO_6SW$ requires C, 36.5; H, 1.7; N, 2.7%. δ_H (400 MHz, $CDCl_3$) 8.83 (1 H, s, d, $^1J_{CH}$ 187.0, CH thiazole), 8.07 (2 H, m, *o*-Ph), 7.51 (3 H, m, *m*/*p*-Ph) and 4.70 (3 H, s, d, $^1J_{CH}$ 147.8, OMe). δ_C (101 MHz, $CDCl_3$) 291.6 (s, d, $^1J_{WC}$ 103.8, carbene), 202.1 (s, d, $^1J_{WC}$ 117.2, *trans*-CO), 197.1 (s, d, $^1J_{WC}$ 127.4, *cis*-CO), 174.8 (s, C2 thiazole), 156.7 (s, C4 thiazole), 152.7 (s, C5 thiazole), 132.8 (s, *i*-Ph), 131.9 (s, *p*-Ph), 129.2 (s, *m*-Ph), 127.1 (s, *o*-Ph) and 68.7 (s, OMe). ν_{max}/cm^{-1} 2070s ($A_1^{(1)}$ CO), 1969s (B_1 CO) and 1880vs (*E* and $A_1^{(2)}$ CO). *m*/*z* 528 [10%, (M + H)$^+$], 527 (8, M$^+$), 499 [16, (M–CO)$^+$], 472 [7, (M–2CO + H)$^+$], 471 [11, (M–2CO)$^+$] and 443 [12, (M–3CO)$^+$].

Chloro[methoxy(2-phenylthiazol-5-yl)methylidene]gold, 5. Compound **3b** (145 mg, 0.28 mmol) was dissolved in thf (10 cm^3) and the Schlenk tube was cooled to −5 °C. Solid [ClAu(tht)] (89 mg, 0.28 mmol) was added and stirring commenced for 1 h, whereupon the temperature reached 5 °C. All volatiles were removed *in vacuo* and the resulting solid was re-dissolved in CH_2Cl_2 (30 cm^3) followed by a filterstick filtration. The solution was layered with hexane (60 cm^3) and stored at −20 °C. Well-defined red faceted

crystals of **5** (75 mg, 62%) suitable for X-ray diffraction were isolated. mp 75 °C (dec.). Found: C, 30.0; H, 2.2; N, 3.4. $C_{11}H_9AuClNOS$ requires C, 30.3; H, 2.1; N, 3.2%. δ_H (400 MHz, CD_2Cl_2) 9.21 (1 H, br s, CH thiazole), 8.14 (2 H, m, *o*-Ph), 7.64 (1 H, m, *p*-Ph), 7.54 (2 H, m, *m*-Ph) and 4.84 (3 H, s, d, $^1J_{CH}$ 150.4, OMe). δ_C (101 MHz, CD_2Cl_2) 248.6 (s, carbene), 183.1 (s, C2 thiazole), 168.9 (br s, C4 thiazole), 144.4 (br s, C5 thiazole), 134.1 (s, *p*-Ph), 132.7 (s, *i*-Ph), 130.1 (s, *m*-Ph), 128.6 (s, *o*-Ph) and 71.7 (s, OMe). *m*/*z* 386 [4%, $(M–Cl–CH_3 + H)^+$], 377 (3) and 358 [3, $(M–Cl–CH_3–CO + H)^+$].

***cis*-Dicarbonylchloro{[2-(1-piperidinyl)thiazol-5-yl]methylidyne}-*cis*-bis(pyridine)tungsten, 6a.** Two Schlenk tubes were prepared containing the freshly prepared Li^+-analogue of **1a** (499 mg, 0.95 mmol) and $(Cl_3CO)_2CO$ (104 mg, 0.35 mmol, 1.1 mol eq.) and CH_2Cl_2 (30 cm^3 and 10 cm^3, respectively). After cooling to −78 °C, the triphosgene solution was transferred to the lithium acyl suspension *via* a Teflon cannula; the colour immediately changed to dark red. Stirring was continued for 1.5 h at −78 °C and 30 min at 0 °C. Freshly distilled pyridine (3 cm^3) was added with a glass pipette and stirring commenced at room temperature for 2.3 h. Excessive triphosgene was quenched with several drops of MeOH and all volatiles were removed *in vacuo*. The crude product was subjected to inert flash chromatography (7 × 5 cm, −30 °C), eluting with CH_2Cl_2 (100 cm^3), CH_2Cl_2–MeOH (19 : 1; 50 cm^3) and CH_2Cl_2–MeOH (16 : 1; 80 cm^3). The orange-brown fraction yielded 285 mg of **6a**. Crystals suitable for X-ray diffraction were grown by layering a CH_2Cl_2 solution with hexane. mp 73 °C (dec. with evolution of gas). Found: C, 41.3; H, 3.4; N, 9.2. $C_{21}H_{21}ClN_4O_2SW$ requires C, 41.2; H, 3.45; N, 9.1%. δ_H (300 MHz, $CDCl_3$) 9.08 (4 H, m, *o*-py), 8.69 (1 H, br s, CH thiazole), 7.81 (2 H, tt, $^3J_{HH}$ 7.65, $^4J_{HH}$ 1.67, *p*-py), 7.33 (4 H, m, *m*-py), 3.52 (4 H, m, NCH_2) and 1.73 (6 H, m, $NCH_2(CH_2)_3$). δ_C (75.4 MHz, $CDCl_3$) 245.1 (s, carbyne), 220.9 (s, d, $^1J_{WC}$ 170.7, CO), 169.7 (s, C2 thiazole), 152.8 (s, *o*-py), 149.6 (br s, C4/C5 thiazole), 142.2 (s, C5/C4 thiazole), 138.1 (s, *p*-py), 125.0 (s, *m*-py), 49.5 (s, NCH_2), 25.1 (s, $NCH_2CH_2CH_2$) and 24.0 (s, $NCH_2CH_2CH_2$). ν_{max}/cm^{-1} 1965vs (*A′* CO) and 1877vs (*A″* CO). *m*/*z* 613 [1%, $(M + H)^+$], 612 (1, M^+), 584 [3, $(M–CO)^+$], 577 [2, $(M–Cl)^+$], 505 [3, $(M–C_5H_5N–CO)^+$] and 477 [3, $M–C_5H_5N–2CO)^+$].

***cis*-Dicarbonylchloro[(2-phenylthiazol-5-yl)methylidyne]-*cis*-bis(pyridine)tungsten, 6b.** The compound was prepared following the procedure described for **6a**, employing **1b** (1.015 g, 1.73 mmol) and $(Cl_3CO)_2CO$ (208 mg, 0.70 mmol, 1.2 eq.). After warming to room temperature, a freshly distilled 2 : 1 mixture of pyridine and ^{t}BuOH (5 cm^3) was added *via* a glass pipette. The crude product was purified by inert flash chromatography (5 × 5 cm, −30 °C), eluting with CH_2Cl_2 (80 cm^3), CH_2Cl_2–MeCN (19 : 1; 100 cm^3) and CH_2Cl_2–MeCN (9 : 1; 100 cm^3), yielding 562 mg (54%) of a red oil. Trituration with diethyl ether and drying in high vacuum afforded an orange foam. Crystals of the dichloromethane solvate suitable for X-ray diffraction were obtained from a CH_2Cl_2 solution layered with hexane. mp (**6b**·CH_2Cl_2) 84 °C (dec. with evolution of gas). Found: C, 43.5; H, 2.7; N, 7.8. $C_{22}H_{16}ClN_3O_2SW$ requires C, 43.2; H, 2.8; N, 8.0%. δ_H (400 MHz, $CDCl_3$) 9.09 (4 H, m, *o*-py), 7.91 (2 H, m, *o*-Ph), 7.83 (2 H, tt, $^3J_{HH}$ 7.65, $^4J_{HH}$ 1.71, *p*-py), 7.79 (1 H, s, CH thiazole), 7.44 (3 H, m, *m*/*p*-Ph) and 7.36 (4 H, m, *m*-py). δ_C (101 MHz, $CDCl_3$) 240.8 (s, d, $^1J_{WC}$ 205.7, carbyne), 220.1 (s, d, $^1J_{WC}$ 168.8, CO), 165.7 (s, C2 thiazole), 152.7 (s, *o*-py), 148.0 (s, C4/C5 thiazole), 143.9 (s, C5/C4 thiazole), 138.4 (s, *p*-py), 133.4 (s, *i*-Ph), 130.2 (s, *p*-Ph), 129.0 (s, *m*-Ph), 126.4 (s, *o*-Ph) and 125.2 (s, *m*-py). ν_{max}/cm^{-1} 1972vs (*A′* CO) and 1870vs (*A″* CO). *m*/*z* 606 [2%, $(M + H)^+$], 605 (3, M^+), 577 [16, $(M–CO)^+$], 570 [7, $(M–Cl)^+$], 549 [15, $(M–2CO)^+$], 527 [3, $(M–C_5H_5N + H)^+$], 526 [1, $(M–C_5H_5N)^+$], 498 [5, $(M–C_5H_5N–CO)^+$], 471 [2, $(M–C_5H_5N–2CO + H)^+$], 470 [4, $(M–C_5H_5N–2CO)^+$] and 367 {18, $[W(\equiv CH)Cl(C_5H_5N)(CO)_2]^+$}.

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