

Supplementary Information

Fischer-type tungsten carbenate, carbene and carbyne complexes bearing unusual heterocyclic substituents: interaction with gold(I) fragments

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Molecular structures of 7·0.5C₄H₈O and 8

Data associated with the crystal structures are summarised in Table S1. The crystal structure of **7** contains half a thf molecule per formula unit that is disordered around a centre of inversion, it could not be modelled. Its electron density was removed using the Squeeze routine in the Platon set of programmes.^{S1} N4 was refined by constraining it to approximate isotropic behaviour. CCDC reference numbers 744828 and 744829 for 7·0.5C₄H₈O and dicarbonylchloro[(4-methylphenyl)methylidyne]bis(pyridine)tungsten, **8**, respectively.

The molecular structure of **7** unambiguously shows the AuCl fragment to be coordinated to the formal W–C triple bond. An alternative site at the thiazole imine nitrogen atom, which, owing to the neighbouring piperidynyl group, should exhibit sufficient electron density to also act as a ligand towards AuCl, is not preferred. This may also be due to an attractive Au⁺–S contact which can be formed if the gold atom is coordinated to the carbyne bond.

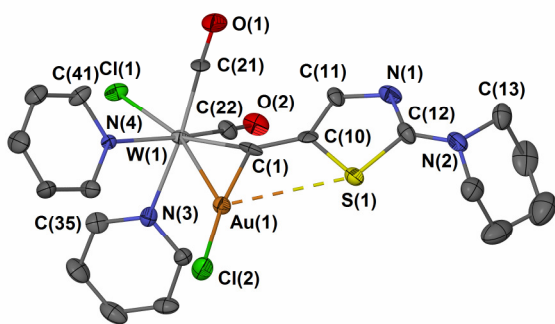


Fig S1 Molecular structure of 7·0.5C₄H₈O, the disordered thf molecule is not shown. Selected bond lengths/Å and angles/°: Au(1)–W(1) 2.7826(7), W(1)–C(1) 1.890(13), Au(1)–C(1) 2.029(10), W(1)–Cl(1) 2.451(3), Au(1)–Cl(2) 2.281(3), Au(1)–S(1) 3.361(3), W(1)–C(21) 1.973(10), W(1)–C(22) 1.976(12), W(1)–N(3) 2.269(9), W(1)–N(4) 2.246(9), Cl(1)–W(1)–C(1) 152.3(3) W(1)–C(1)–C(10) 152.4(8).

Chloro-*cis*-dicarbonyl-*cis*-bis(pyridine)[(4-methylphenyl)methylidyne]tungsten, **8**, was synthesised according to the synthetic protocol in the publication. The molecular structure, shown in Fig. S2, also confirms the *cis*-dicarbonyl and *cis*-bis(pyridine) configuration.

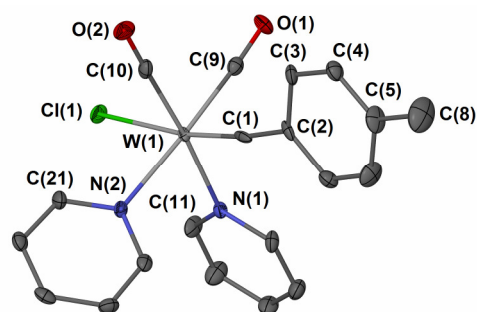


Fig. S2 Molecular structure of **8**. Selected bond lengths/Å and angles/°: W(1)–C(1) 1.806(9), W(1)–Cl(1) 2.524(2), W(1)–C(9) 1.994(8), W(1)–C(10) 1.984(8), W(1)–N(1) 2.261(7), W(1)–N(2) 2.269(7), C(1)–C(2) 1.456(12), Cl(1)–W(1)–C(1) 171.2(2), W(1)–C(1)–C(2) 172.4(6).

Table S1 Crystallographic and data collection parameters.

Compound	7·0.5C ₄ H ₈ O	8
Empirical formula	C ₂₁ H ₂₁ AuCl ₂ N ₄ O ₂ SW·0.5C ₄ H ₈ O	C ₂₀ H ₁₇ ClN ₂ O ₂ W
<i>M_r</i>	881.25	536.66
Crystal habit	Orange plate	Orange needle
Crystal size/mm	0.10 × 0.09 × 0.04	0.32 × 0.09 × 0.04
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> 1 (No. 2)	<i>C</i> 2/ <i>c</i> (No. 15)
<i>a</i> /Å	10.603(2)	26.655(4)
<i>b</i> /Å	11.881(2)	7.127(2)
<i>c</i> /Å	11.932(2)	23.559(4)
<i>α</i> /°	70.039(2)	90
<i>β</i> /°	83.042(2)	121.419(2)
<i>γ</i> /°	69.143(3)	90
<i>V</i> /Å ³	1320.2(3)	3819(1)
<i>Z</i> , <i>D_s</i> /Mg m ⁻³	2, 2.126	8, 1.867
<i>μ</i> (Mo-Kα)/mm ⁻¹	10.208	6.205
No. of reflections	14111	10600
Unique reflections	5400	3889
<i>R</i> _{int}	0.0489	0.0431
Data, restraints, parameters	4425, 6, 289	3340, 0, 236
<i>F</i> (000)	828	2064
<i>R</i> ₁ , <i>wR</i> ₂ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0623, 0.1199	0.0500, 0.1295
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0806, 0.1259	0.0586, 0.1349
Goodness-of-fit	1.218	1.064

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

Synthesis of 2-phenylthiazole

The compound was prepared following a modified literature procedure.^{S2} In a round-bottom flask equipped with a reflux condenser thiobenzamide (4.33 g, 31.6 mmol) was dissolved in acetone (30 cm³). 1-Bromo-2,2-diethoxyethane (5.0 cm³, 32 mmol) was added with a syringe followed by water (2 cm³) and *ca.* 2–3 mg of toluenesulfonic acid monohydrate. After refluxing for 5 h, all volatiles were removed *in vacuo*, the residue was treated with CH₂Cl₂ (40 cm³) and 0.5 M NaOH solution (70 cm³). The aqueous phase was washed twice with CH₂Cl₂ (40 cm³) and the combined organic phase distilled in an oil pump vacuum to yield 3.82 g (75%) of a yellowish oil boiling between 96.5 and 98.5 °C. δ_{H} (400 MHz, CDCl₃) 7.98 (2 H, m, *o*-Ph), 7.42 (3 H, m, *m*- and *p*-Ph), 7.87 (1 H, d, ³J_{CH} 3.2, NCH) and 7.30 (1 H, d, ³J_{CH} 3.2, SCH). δ_{C} (101 MHz, CDCl₃) 168.2 (s, C2 thiazole), 143.6 (s, C4 thiazole), 133.5 (s, *i*-Ph), 129.9 (s, *p*-Ph), 128.8 (s, *m*-Ph), 126.5 (s, *o*-Ph) and 118.7 (s, C5 thiazole).

Synthesis of the control product,

dicarbonylchloro[(4-methylphenyl)methylidyne]-bis(pyridine)tungsten, **8**^{S3}

Bis(trichloromethyl)carbonate (104 mg, 0.35 mmol) and tetramethylammonium [(4-methylphenyl)carbonyl]pentacarbonyltungstate (525 mg, 1.02 mmol) were dissolved in

25 dichloromethane (25 cm³ each) and cooled to –78 °C. The triphosgene solution was transferred to the acylmetallate *via* a Teflon cannula and the homogeneous solution was stirred for 1.5 h, whereupon it was warmed to 0°C. Freshly distilled pyridine (1 cm³, excess) was added with a glass pipet and the mixture stirred at room temperature for another 25 min. After filtration under inert conditions and removal of all volatiles *in vacuo* 476 mg (87%) of yellow needles were obtained. Mp. 115°C (decomposition without melting). δ_{H} (300 MHz, CDCl₃) 9.09 (4 H, m, *o*-CH pyridine), 7.82 (4 H, m, *p*-CH pyridine), 7.33 (4 H, m, *m*-CH pyridine), 7.27 (2 H, m, *o*-C₆H₄), 7.12 (2 H, m, *m*-C₆H₄) and 2.31 (3 H, s, CH₃). δ_{C} (75.4 MHz, CDCl₃) 263.7 (s/d, ¹J_{WC} 196, C_{carbyne}), 221.5 (s/d, ¹J_{WC} 171, CO), 153.1 (s, *o*-pyridine), 147.0 (s/d, ²J_{WC} 21, WCC), 138.6 (s, *p*-pyridine), 138.4 (s, CCH₃), 129.5 (s, *o/m*-C₆H₄), 129.0 (s, *m/o*-C₆H₄), 125.4 (s, *m*-pyridine) and 21.6 (s, CH₃). $\nu_{\text{max}}/\text{cm}^{-1}$ 1978vs (A') and 1876vs (A'').

References

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