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Distinctive chemo- and stereo-selective reactions of $[Fe(CO)_2Cp]^+$ and $[AuPPh_3]^+$ with the anionic thioketene complex, $[W(CO)_5\{C(OEt)(Ph)C(Ph){=}C{=}S\}]^-$. Crystal structures of *Z*-$[W(CO)_5\{C(SFe[CO]_2Cp)C(Ph){=}C(OEt)Ph\}]$ and *E*-$[W(CO)_5\{S{=}C(AuPPh_3)C(Ph){=}C(OEt)Ph\}]$ *

Helgard G. Raubenheimer, Gert J. Kruger, Charles F. Marais, Johannes T.Z. Hattingh, Lorna Linford

Department of Chemistry, Rand Afrikaans University, Johannesburg 2000 (Republic of South Africa)

and Petrus H. van Rooyen

National Chemical Research Laboratory, Council for Scientific and Industrial Research, Pretoria 0001 (Republic of South Africa)

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Abstract

Reaction of the unusual thioketone adduct $[W(CO)_5\{C(OEt)(Ph)C(Ph){=}C{=}S\}]Li$ with $[Fe(CO)_2CpI]$ gives two binuclear tungsten iron complex isomers of composition $[W(CO)_5\{C(SFe[CO]_2Cp)C(Ph){=}C(OEt)Ph\}]$ that differ only in the position of the iron substituent at the extremely short C(carbene)–S bond. Crystallization affords only the isomer in which the metal atoms are oriented *trans*, as is shown by the X-ray crystal structure. Both isomers have a *Z* configuration about the C=C double bond.

Treatment of the same adduct with $[AuC/PPh_3]$ affords a binuclear compound in which the tungsten and gold atoms are linked by a thione group. This conversion is also stereo-selective with regard to the alkene bond and only the *E* isomer is formed. The structure of the product $[W(CO)_5\{S{=}C(AuPPh_3)C(Ph){=}C(OEt)(Ph)\}]$ was determined by X-ray diffraction. Comparison of structural features with the related thioaldehyde complex, *E*-$[W(CO)_5\{S{=}CHC(Ph){=}C(Ph)(OEt)\}]$ reveals the significant electron-withdrawing effect of the gold fragment.

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* Dedicated to Professor E.O. Fischer on the occasion of his 70th birthday.

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Introduction

During our studies of the products from the reaction of the alkyne thiolate Li[SC≡CPh] with the Fischer-type carbene complex $[W(CO)_5\{C(OEt)Ph\}]$, followed by reaction with an electrophile we found that we had formed a synthon for the preparation of coordinated α,β-unsaturated thioaldehydes, dithioesters, and thiocarbenes (Scheme 1) [1].

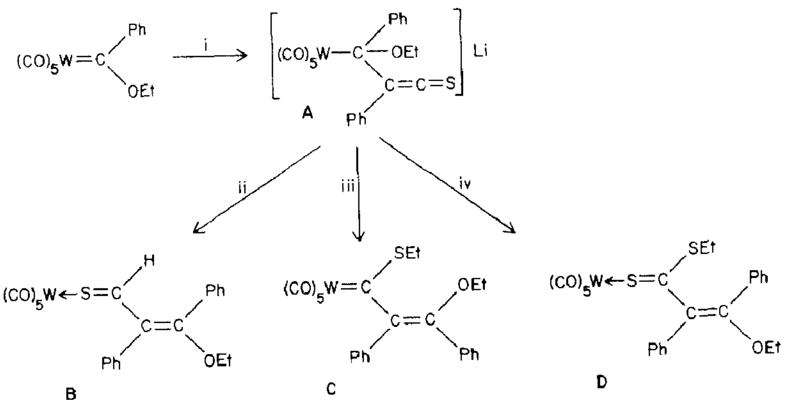
The net result of the two steps is a formal insertion of the alkyne thiolate into the M=C(carbene) bond of the original carbene complex, and is comparable to a class of reactions studied by Dötz and co-workers that involve the insertion of alkynes with group 15 substituents into metal–carbene bonds [2].

The chemo-selectivity and the stereo-chemistry at the C=C bond for compounds in our study seemed to be controlled by the electrophile added in the second step: H^+ gave *E*-thioaldehyde ligands, Et^+ (as $[Et_3O][BF_4]$) gave *Z*-thiocarbenes, and EtSSEt led to *E*-dithioester ligands [1c]. We could not account for the stereo- and chemo-selectivity of the reactions, and assumed that five- or six-membered metallo- or hetero-metallocycles were involved.

We now report on the selectivity exhibited by the two cationic metallic units, $[Fe(CO)_2Cp]^+$ and $[AuPPh_3]^+$ in $[Fe(CO)_2CpI]$ and $[AuClPPh_3]$, which afforded specific geometric isomers of tungsten coordinated iron-substituted thiocarbene and organo-gold thioacylate ligands, respectively. The crystal structures of the two compounds are compared with those of the thiocarbene and thioaldehyde complexes *Z*-$[W(CO)_5\{C(SEt)C(Ph)=C(OEt)Ph\}]$ and *E*-$[W(CO)_5\{S=CHC(Ph)=C(OEt)Ph\}]$ [1c]. The iron-containing carbene complex *Z*-$[W(CO)_5\{C(SFe[CO]_2Cp)C(Ph)=C(OEt)Ph\}]$ is unique in that the rotation barrier around the carbene–sulphur bond is large enough to permit observation of two isomers in solution.

Experimental

All manipulations were carried out under nitrogen, and solvents were dried and distilled under N_2 before use. Column chromatography was carried out at −10 °C. Phenylacetylene and $[Fe(CO)_2CpI]$ were used as purchased and $[W(CO)_5\{C(OEt)Ph\}]$ [3] and $[AuClPPh_3]$ [4] were prepared by published methods.



Scheme 1. Reagents. (1) Li[SC≡CPh]; (ii) HCl; (iii) $[Et_3O][BF_4]$; (iv) EtSSEt.

Table 1

Crystallographic data and details of the structure determinations of compounds **1** and **2**

Crystal data		
Compound	**1**	**2**
Formula	$C_{29}H_{20}O_8SFeW$	$C_{40}H_{30}O_6PSWAu$
Crystal habit	black plates	dark red prisms
Crystal size (mm)	0.13×0.33×0.33	0.14×0.39×0.36
Symmetry	Monoclinic, $P2_1/c$	Triclinic, $P\bar{1}$
Unit cell determination:		
least-squares fit to	25 reflections, θ(Mo) < 17°	25 reflections, θ(Mo) < 17°
Unit cell dimensions		
a	15.976(7) Å	12.503(2) Å
b	9.835(3) Å	12.852(4) Å
c	18.492(9) Å	13.869(3) Å
α	–	70.93(2)°
β	94.82(4)°	72.65(2)°
γ	–	65.77(3)°
Packing: V (Å^3), Z	2895.3, 4	1885.8, 2
D (g cm^{-3}), M, F(000)	1.76, 768.3, 1496	1.85, 1050.5, 1004
Experimental data		
Diffractometer	Enraf-Nonius CAD4	Enraf-Nonius CAD4
Radiation	Mo-K_α (0.7107 Å)	Mo-K_α (0.7107 Å)
Monochromator	Graphite	Graphite
Collection mode	$\omega-2\theta$ scans	$\omega-2\theta$scans
θ range:	3–27°	3–30°
scan width	$(0.50+0.34\tan\theta)°$	$(0.50+0.34\tan\theta)°$
scan speed	variable, 5.5° min^{-1} maximum	variable, 5.5° min^{-1} maximum
Reflections measured	5397	10940
Observable reflections	4176 with $F > 0$	9593 with $F > 0$
Stability	3 reflections every 60 min no variation	3 reflections every 120 min no variation
Corrections	Lp, absorption	Lp, absorption
μ (cm^{-1})	43.8	67.8
Absorption corrections	Empirical [a]	Empirical [a]
Solution and refinement		
Computer program	SHELX76 [b]	SHELX76 [b]
Scattering factors	Complex neutral atoms [c]	Complex neutral atoms [c]
Refinement	Least-squares, full matrix	Least-squares, blocked matrix
Number of variables	367	457
Reflections used	3149 observed with $F \geqslant 2\sigma$	7626 with $F \geqslant 4\sigma$
Weighting scheme	$w=(\sigma(F))^{-2}$	$w=(\sigma(F))^{-2}$
Final Δ peaks	2.2 eÅ^{-3} near the W atom	2.1 eÅ^{-3} near the W and Au
Final R, R_w	0.072, 0.055	0.038, 0.051

[a] A.C.T. North, D.C. Phillips and F.S. Mathews, Acta Cryst., A24 (1986) 351. [b] G.M. Sheldrick, H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld and G.C. Bassi (Eds.), Computing in Crystallography, Delft, University Press, 1978. [c] D.T. Cromer and J.T. Waber, in International Tables for X-ray Crystallography, Vol. IV, Kynoch Press, Birmingham (Present distributer D. Reidel, Dordrecht), 1974, p. 71.

Infrared spectra were recorded on a Perkin–Elmer 297, the ^{13}C NMR spectrum on a Varian VXR 200, ^{1}H NMR spectra on a Bruker WP 80 and Varian VXR 200, and mass spectra on a Finnigan Mat 8200 spectrometer. All NMR spectra were recorded for $CDCl_3$ solutions at room temperature, and chemical shifts are in ppm relative to internal TMS. Melting points were determined on a Kofler hot stage apparatus and are uncorrected. Elemental analyses were carried out by Pascher and Pascher, Bonn and the CSIR, Pretoria.

The crystal structures were determined by routine X-ray crystallographic procedures and experimental details are given in Table 1. Tables of thermal parameters and structure factors are available from the authors.

Preparation of lithium ethyne-thiolate, Li[SC≡CPh]

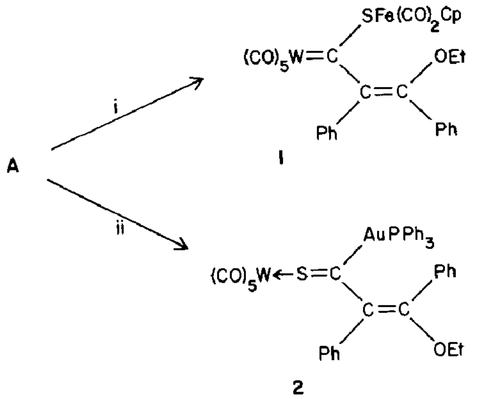
A THF solution (20 ml) of PhC≡CH (1.1 ml, 10.0 mmol) was cooled to −30 °C and one mole equivalent of LiBu added, after which the mixture was stirred for 30 min. To this yellow solution was added S_8 (0.32 g, 10.0 mmol S), and the red solution was slowly warmed to room temperature. When all the S_8 had dissolved the solution was stored at −20 °C.

Preparation of Z-[W(CO)$_5${C(SFe[CO]$_2$Cp)C(Ph)=C(OEt)Ph}] (1)

To a solution of Li[SC≡CPh] (4.0 mmol) in THF at −30 °C was added $[W(CO)_5\{C(OEt)Ph\}]$ (1.8 g, 3.9 mmol), and the mixture was allowed to warm to room temperature. An excess of $[Fe(CO)_2CpI]$ (3.1 g, 10 mmol) was added and after about 30 min the solvent was removed under reduced pressure. The residue was redissolved in CH_2Cl_2 and the solution filtered through a short column of SiO_2 then chromatographed on neutral alumina with hexane/CH_2Cl_2/Et_2O 4/0.2/3 as eluant. A red product was collected at −40 °C (1.07 g, 35.3%), and recrystallized from CH_2Cl_2/hexane to give analytically pure reddish-brown crystals, m.p. 120–122 °C. ^{1}H NMR (80 MHz) δ (ppm) 6.7–7.4 (m, Ph, 10H), 4.82 and 4.52 (2s, Cp, 5H), 4.12 and 3.72 (2q, OCH_2, 2H), 1.28 and 1.22 (2t, OCH_2CH_3, 3H); IR (CH_2Cl_2, ν(CO)) 2054w, 2038m, 1988m, 1920br,m cm^{-1}. Analysis. Found: C, 45.16; H, 2.67; S, 4.01; Fe, 7.17; $C_{29}H_{20}O_8SFeW$ calc: C, 45.33; H, 2.62; S, 4.17; Fe, 7.26%.

Preparation of E-[W(CO)$_5${S=C(AuPPh$_3$)C(Ph)=C(OEt)Ph}] (2)

A cooled (−30 °C) solution of $[W(CO)_5\{C(OEt)Ph\}]$ (1.0 g, 2.2 mmol) in THF was treated with Li[SC≡CPh] (2.2 mmol) and stirred for 30 min, then $[AuClPPh_3]$ (0.61 g, 2.2 mmol) was added, the red colour of the solution deepening immediately. The mixture was warmed to room temperature and stirred for 15 min. The solvent was removed under reduced pressure and the residue chromatographed on SiO_2 (hexane/CH_2Cl_2 10/1). Crystallization from Et_2O/pentane gave microcrystals (1.2 g, 52%), and crystals suitable for X-ray crystallography were obtained by solvent diffusion (Et_2O/pentane), m.p. ~ 160 °C (dec.). ^{1}H NMR (200 MHz) δ (ppm) 7.33–7.56 (m, Ph, 15H), 7.11–7.28 (m, Ph, 10H), 3.83 (q, OCH_2, 2H, J(H–H) 7.2 Hz), 1.20 (t, OCH_2CH_3, 3H, J(H–H) 7.2 Hz); ^{13}C NMR (200 MHz) 276.2 (C=S), 202.0 (*trans* CO), 197.2 (*cis* CO), 126.4–135.7 (C=C, Ph), 65.0 (OCH_2), 14.3 (OCH_2CH_3); IR (CH_2CH_3); IR (CH_2Cl_2, ν(CO)) 2065w, 1974sh, 1935st, 1873sh cm^{-1}. Analysis. Found: C, 45.63; H, 2.99; S, 2.91; Au, 19.5; $C_{40}H_{30}O_6PSAuW$ calc: C, 45.73; H, 2.88; S, 3.05; Au, 18.75%.



Scheme 2. Reagents. (i) $[Fe(CO)_2CpI]$; (ii) $[AuClPPh_3]$.

Results and discussion

Synthesis and isolation of the new complexes

Both compounds were prepared in simple two-step reactions by the addition of $[Fe(CO)_2CpI]$ or $[AuClPPh_3]$ to the adduct formed from $[W(CO)_5\{C(OEt)Ph\}]$ and $Li[SC{\equiv}CPh]$ (Scheme 2). In either case the reaction was both chemo- and stereoselective: $[Fe(CO)_2Cp]^+$ reacted at the heteroatom in **A** (Scheme 1) and formed only the *Z*-isomer of **1**; $[AuPPh_3]^+$ reacted at the carbon α to the heteroatom, and the *E*-isomer of **2** was obtained as the only product.

The products were purified by column chromatography and characterized spectroscopically as well as by X-ray diffraction studies. The complexes are soluble in polar solvents such as CH_2Cl_2 and Et_2O, but fairly insoluble in hexane. The thiocarbene complex is stable in the solid state, but decomposes in solution. The gold-containing thione compound is stable in solution in an inert atmosphere and as a solid.

Spectroscopic characterization

Infrared measurements

Owing to the insolubility of the compounds in hexane, the samples were dissolved in CH_2Cl_2 and so the spectra cannot be compared to those of the known thiocarbene and thioaldehyde complexes, **C** and **B**. For the iron-containing compound, the $\nu(CO)$ vibrations of the $Fe(CO)_2Cp$-unit overlap with those of $W(CO)_5$, and no vibrational assignments are attempted. Apart from this, the dichloromethane used as solvent caused marked broadening of the peaks.

NMR results

The ^1H NMR spectrum of **1** contains two distinct singlets for the Cp resonances, two quartets for OCH_2, and two overlapping triplets for the CH_3 resonances. Since there is considerable double bond character at the carbene–sulphur bond (bond length 1.623 Å vide infra), we suggest that the double resonances are caused by the *cis* and *trans* arrangments of the metal atoms at the carbene–sulphur bond. This

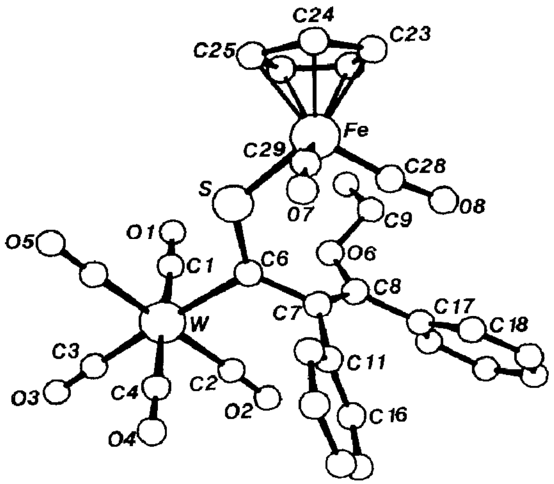


Fig. 1. The crystal structure of 1.

form of isomerism is common in aminocarbene complexes at room temperature [5], but has not been noted previously for thiocarbene ligands. Owing to the rapid decomposition of **1** in solution, its ^{13}C NMR spectrum was not obtained.

For compound **2** only single resonances are observed in the ^{1}H NMR spectrum. The S=C resonance in the ^{13}C NMR spectrum (276.2 ppm) is at much lower field than that for the thioaldehyde complex, **B** (217 ppm), and gives an indication of the substantial deshielding caused by the gold substituent.

Structural features

The molecular structures of **1** and **2** are shown in Figs. 1 and 2. The atomic coordinates, bond lengths and bond angles are given in Tables 2–5.

The iron-containing compound, **1**, is comparable to the α,β-unsaturated thiocarbene complex, *Z*-[W(CO)$_5${C(SEt)C(Ph)=C(OEt)Ph}] **C**, which is formed upon reaction of the adduct **A** with Meerwein's reagent [Et$_3$O][BF$_4$] [1a,c]. Both have the

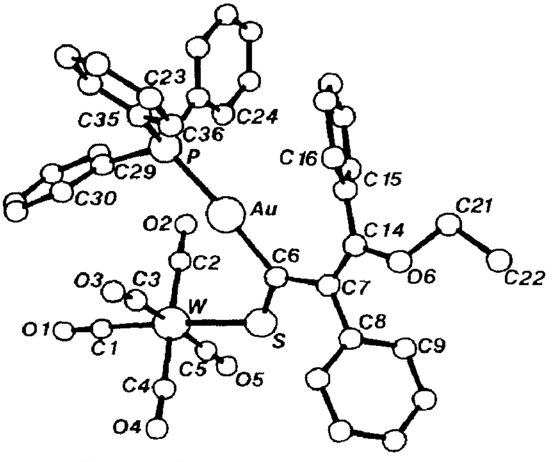


Fig. 2. The crystal structure of 2.

Table 2

Fractional coordinates ($\times 10^4$, $\times 10^5$, for W) and equivalent isotropic temperature factors (A^2, $\times 10^3$, $\times 10^4$ for W) of the non-H atoms for compound **1**

Atom	x/a	y/b	z/c	U_{eq} [a]
W	30178(5)	6159(8)	7392(4)	439(2)
Fe	3143(2)	5244(3)	2808(1)	62(1)
S	3229(3)	5259(4)	4040(2)	54(1)
O(1)	1684(10)	6735(17)	5551(9)	109(6)
O(2)	1546(10)	2286(17)	5852(8)	96(5)
O(3)	3146(13)	4637(17)	7433(7)	131(6)
O(4)	4291(12)	1950(18)	6002(8)	125(6)
O(5)	4519(11)	6356(19)	5622(9)	114(6)
O(6)	1203(8)	4189(13)	4191(6)	64(4)
O(7)	4616(13)	3656(32)	2764(9)	221(12)
O(8)	1994(12)	3075(16)	2426(7)	107(6)
C(1)	2171(13)	5825(25)	5617(10)	75(7)
C(2)	2065(12)	3104(31)	5810(10)	109(9)
C(3)	3086(17)	4578(18)	6812(12)	101(8)
C(4)	3843(14)	2857(22)	5870(9)	65(6)
C(5)	3694(14)	5478(40)	5642(12)	159(13)
C(6)	2848(11)	4091(15)	4540(8)	41(4)
C(7)	2368(12)	2846(7)	4252(8)	45(5)
C(8)	1574(12)	2947(20)	4083(9)	51(5)
C(9)	651(14)	4674(21)	3636(11)	90(7)
C(10)	227(20)	5800(29)	3845(15)	152(12)
C(11)	2877(11)	1521(17)	4337(8)	43(4)
C(12)	3710(12)	1513(18)	4125(8)	49(5)
C(13)	4222(13)	363(19)	4214(10)	69(6)
C(14)	3877(13)	−761(20)	4503(10)	66(6)
C(15)	3049(14)	−747(20)	4716(10)	68(6)
C(16)	2537(13)	386(17)	4655(9)	57(5)
C(17)	1022(12)	1745(19)	3845(10)	54(5)
C(18)	283(13)	1583(23)	4166(11)	74(6)
C(19)	−276(14)	483(24)	3968(13)	87(7)
C(20)	−53(16)	−370(24)	3444(13)	95(8)
C(21)	690(13)	−195(20)	3124(11)	71(6)
C(22)	1224(12)	845(19)	3318(9)	65(5)
C(23)	2323(33)	6514(38)	2221(27)	302(25)
C(24)	2866(49)	5925(43)	1776(22)	367(26)
C(25)	3612(29)	6504(34)	2041(21)	146(15)
C(26)	3531(30)	7212(31)	2708(20)	139(14)
C(27)	2652(31)	7134(35)	2764(19)	147(14)
C(28)	2469(16)	3910(23)	2622(10)	83(7)
C(29)	4031(16)	4370(40)	2768(12)	141(11)

[a] $U_{eq} = \frac{1}{3}\Sigma_i \Sigma_j U_{ij} a_i^\star a_j^\star (\mathbf{a}_i \cdot \mathbf{a}_j)$.

phenyl groups oriented *cis* at the double bond, but some notable differences also occur. (i) The W–C(carbene) bond in **1** is relatively long (2.23(2) Å, compared to 2.16(1) Å in **C**). (ii) The C(carbene)–S distance is very short 1.63(2) Å (1.68(1) Å in **C**), even shorter than the formal C=S double bonds in the coordinating thiones in **2** (1.65(1) Å) and **B** (1.66(2) and 1.63(2) Å), and contains considerable double bond character. The C(6)–S–Fe angle is 124(1)°, which indicates that the S atom is virtually sp^2-hybridized, and the W–C–S–Fe torsion angle of ca. 180° also shows

(*Continued on p. 347*)

Table 3

Fractional coordinates ($\times 10^4$, $\times 10^5$ for W and Au) and equivalent isotropic thermal parameters (Å^2, $\times 10^4$) for W and Au) for compound **2**

Atom	x/a	y/b	z/c	U_{eq} ^{a}
W	15173(3)	33349(3)	25492(3)	459(1)
C(1)	−30(8)	3503(9)	2238(8)	62(3)
O(1)	−880(6)	3604(7)	2044(6)	92(3)
C(2)	1850(8)	4356(8)	1193(9)	57(3)
O(2)	2072(8)	4916(7)	337(6)	94(3)
C(3)	677(9)	4624(8)	3303(9)	61(3)
O(3)	173(7)	5270(6)	3841(6)	80(2)
C(4)	1233(8)	2280(8)	3983(9)	59(3)
O(4)	986(7)	1699(6)	4731(6)	91(3)
C(5)	2405(10)	1939(9)	1940(9)	73(3)
O(5)	2944(8)	1123(7)	1592(7)	107(3)
S	3414(2)	3013(2)	3047(2)	52(1)
C(6)	3685(7)	4167(7)	3048(6)	43(2)
C(7)	4685(7)	3890(7)	3573(6)	38(2)
C(8)	5072(8)	2719(7)	4302(7)	42(2)
C(9)	6241(8)	1972(8)	4090(8)	58(3)
C(10)	6585(11)	843(10)	4764(10)	78(4)
C(11)	5845(12)	465(10)	5574(10)	84(4)
C(12)	4670(12)	1222(10)	5810(8)	78(4)
C(13)	4309(10)	2353(8)	5141(7)	58(3)
C(14)	5189(7)	4682(7)	3459(7)	41(2)
C(15)	5067(7)	5795(7)	2690(7)	45(2)
C(16)	4712(8)	6813(8)	3007(8)	58(3)
C(17)	4620(9)	7879(9)	2248(11)	85(4)
C(18)	4928(9)	7875(10)	1182(10)	82(4)
C(19)	5297(9)	6881(9)	895(9)	73(3)
C(20)	5354(8)	5850(9)	1635(7)	60(3)
O(6)	5924(5)	4363(5)	4135(5)	55(2)
C(21)	6878(8)	4835(9)	3872(8)	69(3)
C(22)	7711(8)	4054(10)	4621(8)	75(3)
Au	26762(3)	58238(3)	23697(3)	382(1)
P	1469(2)	7610(2)	1567(2)	41(1)
C(23)	875(8)	8776(7)	2243(7)	47(2)
C(24)	1408(9)	8671(9)	3053(7)	58(3)
C(25)	971(10)	9556(10)	3558(8)	71(3)
C(26)	−9(11)	10554(9)	3288(9)	77(4)
C(27)	−538(9)	10662(9)	2484(9)	67(3)
C(28)	−93(8)	9771(8)	1995(8)	58(3)
C(29)	146(7)	7518(7)	1347(7)	44(2)
C(30)	−786(8)	7444(8)	2187(8)	58(3)
C(31)	−1768(10)	7240(9)	2108(10)	76(4)
C(32)	−1812(10)	7110(11)	1223(13)	94(5)
C(33)	−961(12)	7250(12)	386(11)	103(5)
C(34)	106(9)	7442(9)	393(8)	69(3)
C(35)	2292(8)	8152(8)	314(7)	46(2)
C(36)	2909(8)	7372(8)	−289(8)	53(3)
C(37)	3610(10)	7707(10)	−1266(9)	75(3)
C(38)	3644(10)	8805(11)	−1596(9)	81(4)
C(39)	3008(10)	9584(9)	−954(10)	79(4)
C(40)	2317(8)	9249(8)	−5(8)	54(3)

[a] $U_{eq} = \frac{1}{3}\Sigma_i\Sigma_j U_{ij} a_i^* a_j^* (\mathbf{a}_i \cdot \mathbf{a}_j)$.

Table 4

Bond lenghts (Å) and angles (°) with e.s.d.'s for compound **1**

W–C(1)	1.94(2)	W–C(2)	2.02(2)
W–C(3)	2.00(2)	W–C(4)	1.99(2)
W–C(5)	1.95(2)	W–C(6)	2.23(2)
Fe–S	2.269(5)	Fe–C(23)	2.05(3)
Fe–C(24)	2.04(4)	Fe–C(25)	2.07(3)
Fe–C(26)	2.05(3)	Fe–C(27)	2.02(3)
Fe–C(28)	1.71(2)	Fe–C(29)	1.67(3)
S–C(6)	1.63(2)	O(1)–C(1)	1.18(3)
O(2)–C(2)	1.16(3)	O(3)–C(3)	1.15(2)
O(4)–C(4)	1.16(2)	O(5)–C(5)	1.24(4)
O(6)–C(8)	1.38(2)	O(6)–C(9)	1.38(2)
O(7)–C(29)	1.17(3)	O(8)–C(28)	1.16(3)
C(6)–C(7)	1.52(2)	C(7)–C(8)	1.28(2)
C(7)–C(11)	1.54(2)	C(8)–C(17)	1.52(3)
C(9)–C(10)	1.37(3)	C(11)–C(12)	1.42(3)
C(11)–C(16)	1.39(2)	C(12)–C(13)	1.40(2)
C(13)–C(14)	1.36(3)	C(14)–C(15)	1.41(3)
C(15)–C(16)	1.38(3)	C(17)–C(18)	1.37(3)
C(17)–C(22)	1.38(3)	C(18)–C(19)	1.43(3)
C(19)–C(20)	1.35(3)	C(20)–C(21)	1.38(3)
C(21)–C(22)	1.36(2)	C(23)–C(24)	1.37(10)
C(23)–C(27)	1.25(5)	C(24)–C(25)	1.37(8)
C(25)–C(26)	1.43(4)	C(26)–C(27)	1.42(4)
C(6)–W–C(1)	87.3(6)	C(6)–W–C(2)	87.2(6)
C(6)–W–C(3)	176.0(7)	C(6)–W–C(4)	92.9(6)
C(6)–W–C(5)	91.6(6)	C(1)–W–C(2)	87.1(9)
C(1)–W–C(3)	91.6(8)	C(2)–W–C(3)	88.9(8)
C(1)–W–C(4)	177.3(9)	C(2)–W–C(4)	90.2(9)
C(3)–W–C(4)	88.1(7)	C(1)–W–C(5)	95.8(10)
C(2)–W–C(5)	176.8(10)	C(3)–W–C(5)	92.4(8)
C(4)–W–C(5)	86.9(10)	W–C(6)–S	117(1)
W–C(6)–C(7)	118(1)	W–C(1)–O(1)	177(2)
W–C(2)–O(2)	177(2)	W–C(3)–O(3)	176(2)
W–C(4)–O(4)	175(2)	W–C(5)–O(5)	175(2)
S–Fe–C(28)	101(1)	S–Fe–C(29)	93.9(9)
C(28)–Fe–C(29)	97(2)	Fe–S–C(6)	124(1)
C(8)–O(6)–C(9)	117(2)	S–C(6)–C(7)	124(1)
C(6)–C(7)–C(8)	119(2)	C(6)–C(7)–C(11)	114(2)
C(8)–C(7)–C(11)	126(2)	O(6)–C(8)–C(7)	117(2)
O(6)–C(8)–C(17)	119(2)	C(7)–C(8)–C(17)	123(2)
O(6)–C(9)–C(10)	112(2)	C(7)–C(11)–C(12)	119(2)
C(7)–C(11)–C(16)	120(2)	C(12)–C(11)–C(16)	121(2)
C(11)–C(12)–C(13)	122(2)	C(12)–C(13)–C(14)	117(2)
C(13)–C(14)–C(15)	121(2)	C(14)–C(15)–C(16)	123(2)
C(11)–C(16)–C(15)	116(2)	C(8)–C(17)–C(18)	118(2)
C(8)–C(17)–C(22)	123(2)	C(18)–C(17)–C(22)	120(2)
C(17)–C(18)–C(19)	121(2)	C(18)–C(19)–C(20)	117(3)
C(19)–C(20)–C(21)	121(3)	C(20–C(21)–C(22)	122(2)
C(17)–C(22)–C(21)	119(2)	C(24)–C(23)–C(27)	116(6)
C(23)–C(24)–C(25)	101(4)	C(24)–C(25)–C(26)	112(5)
C(25)–C(26)–C(27)	102(4)	C(23)–C(27)–C(26)	109(5)
Fe–C(28)–O(8)	173(2)	Fe–C(29)–O(7)	174(4)

Table 5

Bond lengths (Å) and angles (°) with e.s.d.'s for compound **2**

W-C(1)	2.2(1)	W-C(2)	1.95(1)
W-C(3)	2.000(1)	W-C(4)	1.95(1)
W-C(5)	1.90(1)	W-S	2.501(3)
C(1)-O(1)	1.12(2)	C(2)-O(2)	1.19(1)
C(3)-O(3)	1.16(1)	C(4)-C(4)	1.19(1)
C(5)-O(5)	1.16(1)	S-C(6)	1.65(1)
C(6)-C(7)	1.49(1)	C(6)-Au	2.051(7)
C(7)-C(8)	1.49(1)	C(7)-C(14)	1.35(2)
C(8)-C(9)	1.39(1)	C(8)-C(13)	1.35(1)
C(9)-C(10)	1.42(1)	C(10)-C(11)	1.32(2)
C(11)-C(12)	1.40(2)	C(12)-C(13)	1.42(1)
C(14)-C(15)	1.46(2)	C(14)-O(6)	1.36(1)
C(15)-C(16)	1.37(2)	C(15)-C(20)	1.38(1)
C(16)-C(17)	1.41(1)	C(17)-C(18)	1.41(2)
C(18)-C(19)	1.32(2)	C(19)-C(20)	1.37(1)
O(6)-C(21)	1.45(1)	C(21)-C(22)	1.51(1)
Au-P	2.297(2)	P-C(23)	1.81(1)
P-C(29)	1.82(1)	P-C(35)	1.82(1)
C(23)-C(24)	1.41(2)	C(23)-C(28)	1.38(2)
C(24)-C(25)	1.37(2)	C(25)-C(26)	1.400(2)
C(26)-C(27)	1.40(2)	C(27)-C(28)	1.36(2)
C(29)-C(30)	1.39(2)	C(29)-C(34)	1.38(2)
C(30)-C(31)	1.40(2)	C(31)-C(32)	1.31(2)
C(32)-C(33)	1.34(2)	C(33)-C(34)	1.46(2)
C(35)-C(36)	1.35(2)	C(35)-C(40)	1.34(2)
C(36)-C(37)	1.42(2)	C(37)-C(38)	1.35(2)
C(38)-C(39)	1.39(2)	C(39)-C(40)	1.39(2)
C(1)-W-C(2)	90.0(4)	C(1)-W-C(3)	91.4(5)
C(2)-W-C(3)	95.3(4)	C(1)-W-C(4)	91.0(4)
C(2)-W-C(4)	178.3(3)	C(3)-W-C(4)	86.0(4)
C(1)-W-C(5)	91.6(5)	C(2)-W-C(5)	90.0(4)
C(3)-W-C(5)	173.9(4)	C(4)-W-C(5)	88.6(4)
C(1)-W-S	175.9(3)	C(2)-W-S	94.0(4)
C(3)-W-S	89.0(4)	C(4)-W-S	84.9(3)
C(5)-W-S	87.7(4)	W-C(1)-O(1)	178.5(9)
W-C(2)-O(2)	175.5(11)	W-C(3)-O(3)	172.1(8)
W-C(4)-O(4)	175.3(7)	W-C(5)-O(5)	178.5(12)
W-S-C(6)	118.7(3)	S-C(6)-C(7)	114.8(5)
S-C(6)-Au	120.2(6)	C(7)-C(6)-Au	125.0(7)
C(6)-C(7)-C(8)	117.9(9)	C(6)-C(7)-C(14)	122.4(7)
C(8)-C(7)-C(14)	119.6(9)	C(7)-C(8)-C(9)	118.5(7)
C(7)-C(8)-C(13)	122.1(7)	C(9)-C(8)-C(13)	119.4(7)
C(8)-C(9)-C(10)	118.0(9)	C(9)-C(10)-C(11)	123.3(10)
C(10)-C(11)-C(12)	119.1(10)	C(11)-C(12)-C(13)	118.3(10)
C(8)-C(13)-C(12)	121.8(9)	C(7)-C(14)-C(15)	128.0(9)
C(7)-C(14)-O(6)	114.4(7)	C(15)-C(14)-O(6)	117.5(9)
C(14)-C(15)-C(16)	119.9(9)	C(14)-C(15)-C(20)	121.6(9)
C(16)-C(15)-C(20)	118.4(8)	C(15)-C(16)-C(17)	119.0(11)
C(16)-C(17)-C(18)	119.7(12)	C(17)-C(18)-C(19)	120.2(10)
C(18)-C(19)-C(20)	119.9(11)	C(15)-C(20)-C(19)	122.7(11)
C(14)-O(6)-C(21)	120.5(7)	O(6)-C(21)-C(22)	106.0(8)
C(6)-Au-P	175.4(3)	Au-P-C(23)	116.8(3)
Au-P-C(29)	112.2(3)	C(23)-P-C(29)	104.0(4)
Au-P-C(35)	109.7(3)	C(23)-P-C(35)	105.8(4)

Table 5 (continued)

C(29)-P-C(35)	107.9(5)	P-C(23)-C(24)	119.4(6)
P-C(23)-C(28)	121.9(9)	C(24)-C(23)-C(28)	118.7(10)
C(23)-C(24)-C(25)	119.6(8)	C(24)-C(25)-C(26)	120.4(13)
C(25)-C(26)-C(27)	120.2(12)	C(26)-C(27)-C(28)	118.5(9)
C(23)-C(28)-C(27)	122.6(11)	P-C(29)-C(30)	118.3(9)
P-C(29)-C(34)	120.8(7)	C(30)-C(29)-C(34)	120.8(11)
C(29)-C(30)-C(31)	121.6(11)	C(30)-C(31)-C(32)	119.4(11)
C(31)-C(32)-C(33)	120.0(16)	C(32)-C(33)-C(34)	125.0(16)
C(29)-C(34)-C(33)	113.4(9)	P-C(35)-C(36)	115.8(7)
P-C(35)-C(40)	123.2(7)	C(36)-C(35)-C(40)	121.0(8)
C(35)-C(36)-C(37)	119.7(10)	C(36)-C(37)-C(38)	120.0(11)
C(37)-C(38)-C(39)	119.0(10)	C(38)-C(39)-C(40)	120.5(11)
C(35)-C(40)-C(39)	119.9(10)		

that the carbene substituent has the correct orientation for π-bonding with the carbene carbon. It seems that the Fe-substituent enhances the ability of the S atom to donate electrons for π-bonding, thereby, for the first time, creating a thiocarbene complex in which isomerism at the C(carbene)-S bond is detectable at room temperature. Only one isomer, with an *E*-configuration at the C-S bond (the two metals *trans* to each other), was isolated, but in solution the ^{1}H NMR spectrum showed the presence of two isomers, as was reflected by the double signals observed for Cp and OEt. (iii) The C(carbene)-C bond of 1.52(2) Å is too long to have much double bond character and precludes the possibility of rotational isomerism at this bond. The torsion angle W-C-C-C is 92°, and this further rules out delocalization of the formal double bond in the solid state. (iv) The C=C bond length of 1.28(2) Å (compared to 1.35(1) Å in C) indicates that the π-electrons are not used to relieve the electron deficiency normally observed for carbene carbon atoms [6].

The Fe-S bond length (2.269(5) Å) is somewhat shorter than that (2.282(3) Å) in [$\{Fe(CO)_2Cp\}_2S_3$] [7], but does not differ much from those in [$\{Fe(CO)_2Cp\}_2S_4$] (2.276(2) Å [7]), [$Cp_2Fe_2(S_2)_2(CO)$] (2.27(2) Å [8]), and [$\{CH_2SFe_2(CO)_6\}_2S$] (2.274(9) Å [9]).

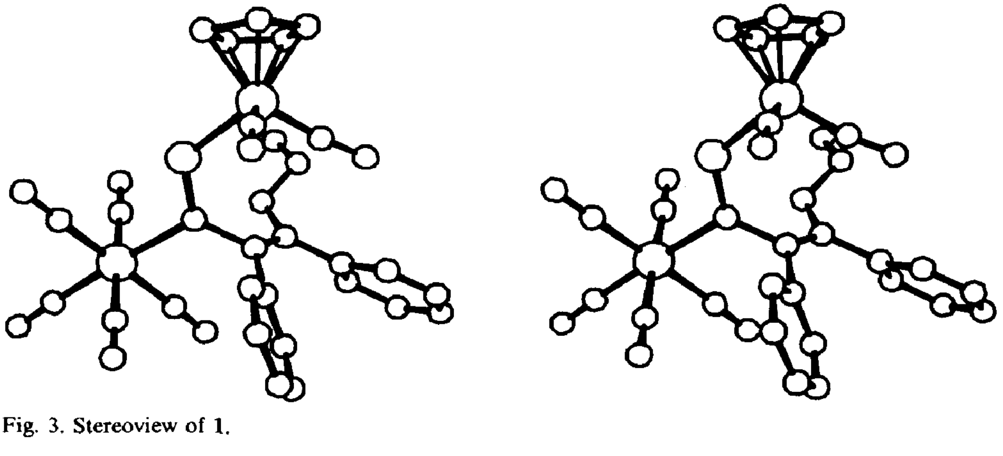


Fig. 3. Stereoview of 1.

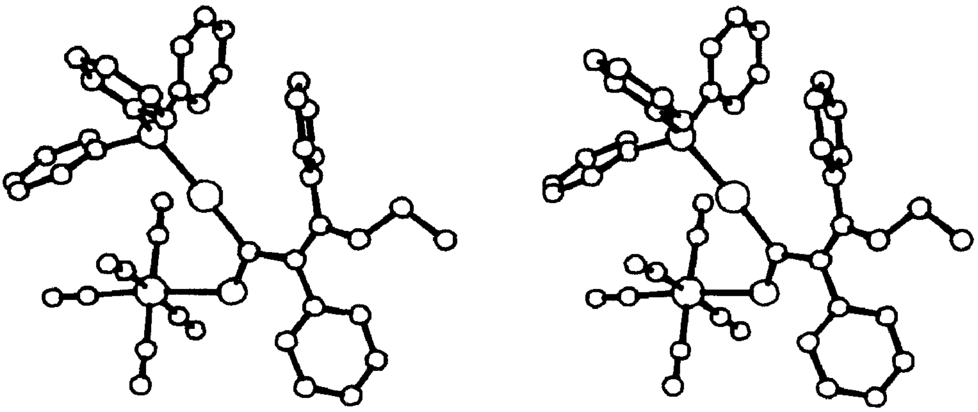


Fig. 4. Stereoview of 2.

The gold compound, 2, belongs to the class of mononuclear gold compounds with CN = 2 [10]. The gold(I) ion is bound to a substituted σ-allyl and the arrangement of the carbon and phosphorus donor atoms at the gold centre is essentially linear.

Compared with that in [$C_6F_5AuPPh_3$] (2.07(2) Å), the Au–C bond length of 2.051(7) Å in 2 indicates a comparably strong covalent interaction. The Au–P interaction is somewhat weaker, and we observed a bond length of 2.297(2) Å compared to that of 2.27(1) Å in [$C_6F_5AuPPh_3$] [11].

The structural effects of the gold fragment are revealed by comparing the structure of 2 with that of the thioaldehyde complex **B**, *E*-[W(CO)$_5$-{S=CHC(Ph)=C(OEt)Ph}], which formed stereo-selectively upon treatment of the anionic thioketene complex **A** with H^+ (Scheme 1). Compound 2 contains the same W–S=C–C(Ph)=C(OEt)Ph backbone as **D**, and the phenyl groups are also oriented *trans* at the double bond (*E*-configuration). The presence of a gold atom rather than a proton produces a number of significant structural changes in the W–S=C–C(Ph)=C(OEt)Ph unit: the gold substituent effectively removes electrons from the conjugated system and the C–C single bonds are lengthened by 0.09 Å. This provides a further manifestation of the high electronegativity of gold, already implied by the large deshielding effect on the C=S carbon in the ^{13}C NMR spectrum. These changes do not affect the W–S and S=C distances significantly, although the latter is longer by 0.02 Å. The S=C–C=C torsional angle in the gold-containing compound is only 166°, compared to 177° in the thioaldehyde complex, and this is probably due to steric hindrance by the bulky $AuPPh_3$ group.

Summary and Conclusion

We have demonstrated that certain electrophiles react stereo-selectively with the adduct [W(CO)$_5${C(OEt)(Ph)C(Ph)=C=S}]Li, either at the α-thio carbon atom, to give α,β-unsaturated thione complexes, or at the sulphur atom to give α,β-unsaturated carbene complexes. Despite the isolobal relationship between Et^+, H^+, $[Fe(CO)_2Cp]^+$ and $[AuPPh_3]^+$, the soft metal fragment $[AuPPh_3]^+$ and the proton, which is normally regarded as hard, both attach themselves to the carbon, and give products with an *E*-configuration, whereas Et^+ and the iron complex fragment

$[Fe(CO)_2Cp]^+$ react at the sulphur to give thiocarbene complexes of *Z*-configuration. No mercaptocarbene complexes of group 6 metals are known and it is possible that the proton, like Et^+, initially adds to the sulphur to form a carbene ligand, but then migrates to form the coordinated thioaldehyde.

The final outcome of the formation of an adduct from a carbene complex and ethynethiolate followed by electrophilic addition of $[Fe(CO)_2Cp]^+$ or $[AuPPh_3]^+$ is a formal insertion of the uniquely modified PhC_2S fragments, $[PhC{\equiv}CSFe(CO)_2Cp]$ or $[PhCC(=S)Au(PPh_3)]$ into a metal–carbene bond.

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