Synthesis and Structure of novel Triphenylarsine-substituted Tungsten(0) Fischer carbene complexes

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Supporting information

Optimized Cartesian coordinates (Å)	S2
Crystallographic supplementary material	S7
Schemes	S24

Optimized Cartesian coordinates (Å)

Density functional theory (DFT) calculations of this study were performed with the hybrid functional B3LYP [1,2] as implemented in the Gaussian 09 program package [3]. Geometries of the neutral complexes were optimized in gas phase with the triple-ζ basis set 6-311G(d,p) on all atoms except W, where def2-TZVPP [4] was used. Energies reported are gas phase electronic energies.

1 [W(AsPh3)(CO)4C(OEt)(2-thienyl)]

W	0.809400000	-1.345997000	-0.425775000
As	-1.342639000	0.226229000	0.166625000
O	-1.141200000	-3.876078000	-0.344600000
O	1.162873000	-1.688433000	2.745537000
O	3.222423000	-3.354020000	-0.768052000
O	0.334117000	-1.513387000	-3.588725000
O	2.323295000	1.362137000	-1.379607000
S	4.374061000	1.978926000	0.316157000
C	-0.454429000	-2.948846000	-0.366162000
C	1.040895000	-1.519065000	1.614489000
C	2.340974000	-2.616158000	-0.664255000
C	0.513080000	-1.387886000	-2.455084000
C	2.269444000	0.329960000	-0.530096000
C	3.423239000	0.485985000	0.350964000
C	3.984110000	-0.396502000	1.257568000
H	3.597801000	-1.388503000	1.426752000
C	5.128059000	0.105844000	1.916683000
H	5.690439000	-0.451119000	2.653768000
C	5.447597000	1.378061000	1.518755000
H	6.261458000	1.995253000	1.869824000
C	1.368922000	1.586407000	-2.438207000
H	0.362302000	1.435684000	-2.048765000
H	1.560241000	0.854342000	-3.223695000
C	1.569795000	3.002611000	-2.939978000
H	0.885918000	3.194567000	-3.770766000
H	2.592005000	3.147517000	-3.295815000
H	1.365367000	3.727908000	-2.150485000
C	-1.067184000	2.181048000	0.279293000
C	0.056781000	2.653728000	0.966231000
H	0.751894000	1.956667000	1.420963000
C	0.294495000	4.022409000	1.071103000
H	1.166553000	4.375320000	1.609875000
C	-0.580446000	4.931614000	0.478009000
H	-0.392334000	5.996626000	0.554753000
C	-1.694457000	4.466399000	-0.216207000
H	-2.377483000	5.168111000	-0.682150000
C	-1.941223000	3.096601000	-0.313450000
H	-2.815085000	2.748422000	-0.850412000
C	-2.950917000	0.125450000	-0.973876000
C	-4.235289000	0.275960000	-0.440473000
H	-4.369743000	0.431796000	0.622970000
C	-5.352184000	0.215980000	-1.272004000
H	-6.343355000	0.328907000	-0.846872000
C	-5.197865000	0.005866000	-2.640667000

H	-6.068344000	-0.045430000	-3.284927000
C	-3.921634000	-0.147610000	-3.176459000
H	-3.792522000	-0.321824000	-4.238685000
C	-2.802994000	-0.091682000	-2.346651000
H	-1.820373000	-0.232863000	-2.777133000
C	-2.146514000	-0.133731000	1.935105000
C	-2.473788000	-1.454746000	2.261727000
H	-2.288476000	-2.258524000	1.559516000
C	-3.046278000	-1.751738000	3.495695000
H	-3.296086000	-2.778876000	3.736300000
C	-3.289481000	-0.736219000	4.418854000
H	-3.729213000	-0.970160000	5.381816000
C	-2.961343000	0.578316000	4.100595000
H	-3.145068000	1.374055000	4.814056000
C	-2.393838000	0.881363000	2.862567000
H	-2.146616000	1.909253000	2.628529000

2 [W(AsPh3)(CO)4C(OEt)(2-furyl)]

W	-1.191783000	-1.003341000	-0.624592000
As	1.195026000	0.041460000	0.164432000
O	0.386070000	-3.294312000	-2.213148000
O	-1.058580000	-2.910315000	1.943645000
O	-3.829704000	-2.527867000	-1.465111000
O	-1.196724000	0.486462000	-3.472903000
O	-1.302122000	2.420015000	-1.000200000
O	-3.338753000	0.598724000	1.188710000
C	-0.154584000	-2.466187000	-1.623857000
C	-1.123276000	-2.176637000	1.054209000
C	-2.874131000	-1.952395000	-1.161972000
C	-1.195634000	0.008268000	-2.428131000
C	-2.368407000	0.633510000	0.261050000
C	-2.294483000	2.030675000	-0.134520000
C	-3.044757000	3.139361000	0.198950000
H	-3.894182000	3.136244000	0.861079000
C	-2.487662000	4.243407000	-0.494920000
H	-2.819443000	5.269303000	-0.476704000
C	-1.431847000	3.745240000	-1.204406000
H	-0.706410000	4.189987000	-1.865082000
C	-3.757916000	-0.622852000	1.832512000
H	-2.940118000	-0.984154000	2.457810000
H	-3.974123000	-1.371218000	1.070206000
C	-4.985508000	-0.295744000	2.660115000
H	-5.330704000	-1.195796000	3.175031000
H	-5.796322000	0.069545000	2.026261000
H	-4.760658000	0.464788000	3.411290000
C	2.728122000	-1.194699000	0.009723000
C	3.934077000	-0.823621000	-0.590261000
H	4.060211000	0.173097000	-0.994321000
C	4.985696000	-1.736589000	-0.676536000
H	5.915492000	-1.439070000	-1.148761000
C	4.843300000	-3.021425000	-0.160698000
H	5.660732000	-3.730224000	-0.230368000
C	3.642874000	-3.395340000	0.440894000
H	3.521356000	-4.395798000	0.840408000
C	2.588866000	-2.489531000	0.522025000
H	1.659961000	-2.799899000	0.985777000
C	1.380056000	0.583074000	2.056491000

C	2.598316000	0.467152000	2.733889000
H	3.466237000	0.060841000	2.228879000
C	2.701742000	0.863496000	4.066111000
H	3.649897000	0.764455000	4.582986000
C	1.592495000	1.379815000	4.732636000
H	1.674373000	1.684676000	5.769917000
C	0.376619000	1.496063000	4.063324000
H	-0.492342000	1.892434000	4.576722000
C	0.269236000	1.095745000	2.732347000
H	-0.684687000	1.177667000	2.226220000
C	1.897967000	1.631379000	-0.770441000
C	1.919266000	1.624370000	-2.169222000
H	1.568076000	0.758110000	-2.717185000
C	2.388136000	2.731778000	-2.871881000
H	2.403200000	2.712272000	-3.955848000
C	2.830236000	3.861378000	-2.183603000
H	3.193482000	4.724265000	-2.730645000
C	2.803988000	3.875543000	-0.791326000
H	3.145665000	4.750438000	-0.249144000
C	2.341688000	2.764381000	-0.085226000
H	2.328067000	2.787766000	0.997367000

3 [W(AsPh3)(CO)4C(OEt)(2-(N-methylpyrrolyl))]

W	0.813015000	-1.406371000	-0.395052000
As	-1.311217000	0.210287000	0.151142000
N	4.212085000	1.613515000	0.593813000
O	2.323889000	1.335721000	-1.317063000
O	3.229432000	-3.414962000	-0.693548000
O	1.055481000	-1.764768000	2.785448000
O	-1.141811000	-3.923093000	-0.351772000
O	0.429383000	-1.635117000	-3.564169000
C	4.101816000	2.915490000	-0.059792000
H	3.093580000	3.313277000	0.039005000
H	4.346081000	2.844368000	-1.118670000
H	4.803612000	3.592294000	0.428799000
C	5.171667000	1.358136000	1.518577000
H	5.893550000	2.117349000	1.778501000
C	5.024748000	0.068412000	2.003491000
H	5.653841000	-0.410099000	2.736701000
C	3.914305000	-0.477990000	1.356026000
H	3.540420000	-1.477540000	1.480954000
C	3.388309000	0.474403000	0.467601000
C	2.281931000	0.311002000	-0.452197000
C	1.398055000	1.485685000	-2.411560000
H	0.384820000	1.311731000	-2.050584000
H	1.637483000	0.732561000	-3.163046000
C	1.554457000	2.887228000	-2.969096000
H	0.884194000	3.012749000	-3.823370000
H	2.576465000	3.062810000	-3.312760000
H	1.297040000	3.639871000	-2.221170000
C	2.347496000	-2.675086000	-0.602117000
C	0.979284000	-1.585640000	1.651340000
C	-0.450430000	-2.996373000	-0.359962000
C	0.576171000	-1.482355000	-2.427720000
C	-0.933782000	2.136257000	0.418076000
C	0.085943000	2.490724000	1.309865000
H	0.639741000	1.722037000	1.837775000

C	0.395635000	3.830867000	1.530750000
H	1.174951000	4.092098000	2.238347000
C	-0.294661000	4.831768000	0.846768000
H	-0.051680000	5.874717000	1.016692000
C	-1.298550000	4.484693000	-0.053182000
H	-1.839698000	5.256587000	-0.589385000
C	-1.621808000	3.142986000	-0.263773000
H	-2.413892000	2.888483000	-0.957484000
C	-2.843283000	0.292087000	-1.095162000
C	-2.637728000	0.032166000	-2.452525000
H	-1.655230000	-0.239856000	-2.814862000
C	-3.700770000	0.098105000	-3.352635000
H	-3.527951000	-0.112345000	-4.402049000
C	-4.978834000	0.417687000	-2.902257000
H	-5.806980000	0.461609000	-3.600670000
C	-5.191997000	0.669560000	-1.548083000
H	-6.186748000	0.909487000	-1.189089000
C	-4.130932000	0.606805000	-0.647209000
H	-4.312262000	0.793211000	0.404443000
C	-2.265567000	-0.194838000	1.835506000
C	-2.610945000	0.797644000	2.756840000
H	-2.345952000	1.831288000	2.573272000
C	-3.298247000	0.464548000	3.924209000
H	-3.557594000	1.242949000	4.633417000
C	-3.648535000	-0.858409000	4.178265000
H	-4.181098000	-1.116103000	5.086813000
C	-3.307813000	-1.850994000	3.261457000
H	-3.573801000	-2.884491000	3.452317000
C	-2.616729000	-1.523591000	2.097569000
H	-2.356624000	-2.309798000	1.400010000

4 [W(AsPh3)(CO)4C(OEt)(2,2'-bithienyl)]

As	2.087361000	0.525028000	0.227425000
W	0.516759000	-1.656365000	-0.248391000
S	-3.826860000	0.573265000	-0.989639000
S	-7.349586000	0.230323000	1.603928000
O	2.926669000	-3.510553000	0.730182000
O	-1.262677000	-4.260670000	-0.386008000
O	-0.385251000	-1.372155000	2.818702000
O	1.608240000	-2.352438000	-3.178459000
O	-1.344281000	0.293030000	-2.068217000
C	2.068698000	-2.819096000	0.385839000
C	-0.609339000	-3.309402000	-0.357733000
C	-0.073706000	-1.434749000	1.713162000
C	1.198368000	-2.046227000	-2.143613000
C	-1.241178000	-0.499072000	-0.991026000
C	-0.261233000	0.562175000	-2.980588000
H	-0.143471000	-0.308752000	-3.627456000
H	0.658003000	0.707501000	-2.414194000
C	-0.630786000	1.798911000	-3.775577000
H	0.157549000	2.015212000	-4.501215000
H	-0.741569000	2.662804000	-3.117708000
H	-1.565810000	1.647383000	-4.319102000
C	-2.560587000	-0.507685000	-0.382856000
C	-3.072908000	-1.285588000	0.643360000
H	-2.495031000	-2.043687000	1.146357000
C	-4.421934000	-1.035256000	0.939670000

H	-4.976257000	-1.576538000	1.694927000
C	-4.988195000	-0.051291000	0.147726000
C	-6.342628000	0.453607000	0.185128000
C	-7.038080000	1.137452000	-0.787746000
H	-6.613525000	1.369165000	-1.755656000
C	-8.363403000	1.472763000	-0.407619000
H	-9.058249000	2.001300000	-1.046319000
C	-8.677516000	1.045046000	0.851530000
H	-9.606759000	1.159278000	1.387976000

Crystallographic supplementary material

Complex **1:**

Identification code	shelx	
Empirical formula	C29 H23 As O41 S W	
Formula weight	1318.30	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 10.0841(6) Å	α= 90°.
	b = 28.0366(16) Å	β= 113.345(2)°.
	c = 10.5955(7) Å	γ = 90°.
Volume	2750.4(3) $Å^3$	
Z	4	
Density (calculated)	3.184 Mg/m^3	
Absorption coefficient	5.677 mm^{-1}	
F(000)	2592	
Crystal size	0.167 x 0.075 x 0.025 mm^3	
Theta range for data collection	2.317 to 27.185°.	
Index ranges	-12<=h<=12, -35<=k<=35, -13<=l<=13	
Reflections collected	94986	
Independent reflections	6108 [R(int) = 0.2841]	
Completeness to theta = 25.242°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7455 and 0.5439	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6108 / 0 / 335	
Goodness-of-fit on F^2	1.122	
Final R indices [I>2sigma(I)]	R1 = 0.0514, wR2 = 0.1212	
R indices (all data)	R1 = 0.0806, wR2 = 0.1450	
Extinction coefficient	0.00061(18)	
Largest diff. peak and hole	3.360 and -2.440 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **1**

W(1)-C(3)	1.979(9)
W(1)-C(1)	2.008(7)
W(1)-C(2)	2.034(9)
W(1)-C(4)	2.038(9)
W(1)-C(6)	2.175(7)
W(1)-As(1)	2.6242(8)
As(1)-C(13)	1.950(7)
As(1)-C(19)	1.959(7)
As(1)-C(25)	1.965(7)
O(1)-C(1)	1.136(9)
O(2)-C(2)	1.143(10)
O(3)-C(3)	1.151(10)
O(4)-C(4)	1.138(10)
O(6)-C(6)	1.345(10)
O(6)-C(11)	1.442(12)
S(1)-C(7)	1.724(8)
S(1)-C(10)	1.725(14)
C(6)-C(7)	1.457(12)
C(7)-C(8)	1.387(13)
C(8)-C(9)	1.380(12)
C(9)-C(10)	1.345(17)
C(11)-C(12)	1.496(12)
C(13)-C(18)	1.370(11)
C(13)-C(14)	1.400(10)
C(14)-C(15)	1.373(11)
C(15)-C(16)	1.371(14)
C(16)-C(17)	1.392(13)
C(17)-C(18)	1.388(11)
C(19)-C(20)	1.374(11)
C(19)-C(24)	1.380(11)
C(20)-C(21)	1.391(11)
C(21)-C(22)	1.380(12)
C(22)-C(23)	1.379(13)
C(23)-C(24)	1.391(12)
C(25)-C(30)	1.370(11)
C(25)-C(26)	1.390(10)
C(26)-C(27)	1.376(11)

C(27)-C(28)	1.366(12)
C(28)-C(29)	1.394(12)
C(29)-C(30)	1.384(11)

C(3)-W(1)-C(1)	88.0(3)
C(3)-W(1)-C(2)	90.4(3)
C(1)-W(1)-C(2)	88.7(3)
C(3)-W(1)-C(4)	87.4(3)
C(1)-W(1)-C(4)	87.1(3)
C(2)-W(1)-C(4)	175.4(3)
C(3)-W(1)-C(6)	90.5(3)
C(1)-W(1)-C(6)	177.9(3)
C(2)-W(1)-C(6)	92.8(3)
C(4)-W(1)-C(6)	91.3(3)
C(3)-W(1)-As(1)	170.3(3)
C(1)-W(1)-As(1)	84.3(2)
C(2)-W(1)-As(1)	83.4(2)
C(4)-W(1)-As(1)	98.2(2)
C(6)-W(1)-As(1)	97.3(2)
C(13)-As(1)-C(19)	104.6(3)
C(13)-As(1)-C(25)	99.7(3)
C(19)-As(1)-C(25)	99.9(3)
C(13)-As(1)-W(1)	121.4(2)
C(19)-As(1)-W(1)	116.2(2)
C(25)-As(1)-W(1)	111.7(2)
C(6)-O(6)-C(11)	122.8(7)
C(7)-S(1)-C(10)	91.2(6)
O(1)-C(1)-W(1)	178.6(8)
O(2)-C(2)-W(1)	175.2(7)
O(3)-C(3)-W(1)	178.8(8)
O(4)-C(4)-W(1)	175.5(7)
O(6)-C(6)-C(7)	106.4(6)
O(6)-C(6)-W(1)	129.9(6)
C(7)-C(6)-W(1)	123.6(6)
C(8)-C(7)-C(6)	129.9(7)
C(8)-C(7)-S(1)	108.8(6)
C(6)-C(7)-S(1)	121.3(7)
C(9)-C(8)-C(7)	115.7(8)
C(10)-C(9)-C(8)	111.0(11)

C(9)-C(10)-S(1)	113.1(8)
O(6)-C(11)-C(12)	105.6(9)
C(18)-C(13)-C(14)	119.5(7)
C(18)-C(13)-As(1)	123.6(6)
C(14)-C(13)-As(1)	116.9(5)
C(15)-C(14)-C(13)	120.2(8)
C(16)-C(15)-C(14)	120.7(8)
C(15)-C(16)-C(17)	119.2(7)
C(18)-C(17)-C(16)	120.5(9)
C(13)-C(18)-C(17)	119.9(8)
C(20)-C(19)-C(24)	120.3(7)
C(20)-C(19)-As(1)	120.8(6)
C(24)-C(19)-As(1)	118.9(6)
C(19)-C(20)-C(21)	120.5(8)
C(22)-C(21)-C(20)	118.8(8)
C(21)-C(22)-C(23)	121.2(8)
C(22)-C(23)-C(24)	119.4(8)
C(19)-C(24)-C(23)	119.8(8)
C(30)-C(25)-C(26)	119.7(7)
C(30)-C(25)-As(1)	122.7(6)
C(26)-C(25)-As(1)	117.5(6)
C(27)-C(26)-C(25)	119.3(8)
C(28)-C(27)-C(26)	121.3(7)
C(27)-C(28)-C(29)	119.6(8)
C(30)-C(29)-C(28)	119.2(8)
C(25)-C(30)-C(29)	120.9(7)

Complex **2:**

Identification code	shelx	
Empirical formula	C_{29} H_{23} As O_6 W	
Formula weight	726.24	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 10.6393(10) Å	α= 90°.
	b = 12.6136(11) Å	β= 102.423(3)°.
	c = 20.7162(18) Å	γ = 90°.
Volume	2715.0(4) $Å^3$	
Z	4	
Density (calculated)	1.777 Mg/m^3	
Absorption coefficient	5.505 mm^{-1}	
F(000)	1408	
Crystal size	0.282 x 0.194 x 0.114 mm^3	
Theta range for data collection	2.490 to 26.372°.	
Index ranges	-13<=h<=13, -15<=k<=15, -25<=l<=25	
Reflections collected	88074	
Independent reflections	5486 [R(int) = 0.0543]	
Completeness to theta = 25.242°	98.6 %	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5486 / 0 / 334	
Goodness-of-fit on F^2	1.117	
Final R indices [I>2sigma(I)]	R1 = 0.0283, wR2 = 0.0587	
R indices (all data)	R1 = 0.0422, wR2 = 0.0609	
Largest diff. peak and hole	1.811 and -0.433 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **2**

W(1)-C(2)	1.977(4)
W(1)-C(1)	2.018(4)
W(1)-C(3)	2.030(4)
W(1)-C(5)	2.040(4)
W(1)-C(6)	2.179(3)
W(1)-As(1)	2.6281(4)
As(1)-C(30)	1.933(3)
As(1)-C(40)	1.946(3)
As(1)-C(20)	1.948(3)
O(1)-C(1)	1.148(4)
O(2)-C(2)	1.156(4)
O(3)-C(3)	1.150(4)
O(5)-C(5)	1.142(5)
O(6)-C(6)	1.329(4)
O(6)-C(11)	1.448(4)
O(7)-C(10)	1.356(4)
O(7)-C(7)	1.370(4)
C(6)-C(7)	1.445(5)
C(7)-C(8)	1.372(5)
C(8)-C(9)	1.405(5)
C(9)-C(10)	1.342(6)
C(11)-C(12)	1.455(6)
C(20)-C(21)	1.375(4)
C(20)-C(25)	1.399(4)
C(21)-C(22)	1.396(5)
C(22)-C(23)	1.375(6)
C(23)-C(24)	1.375(6)
C(24)-C(25)	1.385(5)
C(30)-C(35)	1.385(5)
C(30)-C(31)	1.389(5)
C(31)-C(32)	1.393(5)
C(32)-C(33)	1.377(6)
C(33)-C(34)	1.364(6)
C(34)-C(35)	1.388(5)
C(40)-C(45)	1.384(4)
C(40)-C(41)	1.399(4)
C(41)-C(42)	1.383(5)

C(42)-C(43)	1.376(5)
C(43)-C(44)	1.377(6)
C(44)-C(45)	1.391(5)

C(2)-W(1)-C(1)	87.87(15)
C(2)-W(1)-C(3)	88.33(15)
C(1)-W(1)-C(3)	86.83(15)
C(2)-W(1)-C(5)	90.64(15)
C(1)-W(1)-C(5)	89.21(16)
C(3)-W(1)-C(5)	175.94(14)
C(2)-W(1)-C(6)	92.46(13)
C(1)-W(1)-C(6)	174.98(15)
C(3)-W(1)-C(6)	88.17(13)
C(5)-W(1)-C(6)	95.80(14)
C(2)-W(1)-As(1)	174.72(10)
C(1)-W(1)-As(1)	87.20(10)
C(3)-W(1)-As(1)	93.30(10)
C(5)-W(1)-As(1)	87.38(9)
C(6)-W(1)-As(1)	92.61(8)
C(30)-As(1)-C(40)	101.37(13)
C(30)-As(1)-C(20)	101.47(14)
C(40)-As(1)-C(20)	102.89(13)
C(30)-As(1)-W(1)	119.22(9)
C(40)-As(1)-W(1)	119.30(9)
C(20)-As(1)-W(1)	110.05(9)
C(6)-O(6)-C(11)	122.4(3)
C(10)-O(7)-C(7)	107.2(3)
O(1)-C(1)-W(1)	177.4(3)
O(2)-C(2)-W(1)	177.7(4)
O(3)-C(3)-W(1)	176.2(3)
O(5)-C(5)-W(1)	176.2(3)
O(6)-C(6)-C(7)	104.7(3)
O(6)-C(6)-W(1)	130.8(2)
C(7)-C(6)-W(1)	124.3(2)
O(7)-C(7)-C(8)	108.3(3)
O(7)-C(7)-C(6)	118.1(3)
C(8)-C(7)-C(6)	133.5(3)
C(7)-C(8)-C(9)	107.2(3)
C(10)-C(9)-C(8)	106.6(3)

C(9)-C(10)-O(7)	110.7(3)
O(6)-C(11)-C(12)	107.5(3)
C(21)-C(20)-C(25)	119.1(3)
C(21)-C(20)-As(1)	122.8(2)
C(25)-C(20)-As(1)	117.6(2)
C(20)-C(21)-C(22)	120.5(3)
C(23)-C(22)-C(21)	120.0(4)
C(24)-C(23)-C(22)	119.9(3)
C(23)-C(24)-C(25)	120.5(3)
C(24)-C(25)-C(20)	120.0(3)
C(35)-C(30)-C(31)	118.5(3)
C(35)-C(30)-As(1)	120.0(3)
C(31)-C(30)-As(1)	121.5(2)
C(30)-C(31)-C(32)	120.6(3)
C(33)-C(32)-C(31)	119.9(3)
C(34)-C(33)-C(32)	119.9(3)
C(33)-C(34)-C(35)	120.6(4)
C(34)-C(35)-C(30)	120.5(4)
C(45)-C(40)-C(41)	119.7(3)
C(45)-C(40)-As(1)	122.3(2)
C(41)-C(40)-As(1)	117.8(2)
C(42)-C(41)-C(40)	119.8(3)
C(43)-C(42)-C(41)	120.3(3)
C(42)-C(43)-C(44)	120.2(3)
C(43)-C(44)-C(45)	120.3(3)
C(40)-C(45)-C(44)	119.6(3)

Complex **3:**

Identification code	shelx	
Empirical formula	C_{30} H_{26} As N O_5 W	
Formula weight	739.29	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 2_1/n	
Unit cell dimensions	a = 10.3838(10) Å	α= 90°.
	b = 27.751(3) Å	β= 114.966(2)°.
	c = 10.5126(10) Å	γ = 90°.
Volume	2746.3(5) $Å^3$	
Z	4	
Density (calculated)	1.788 Mg/m^3	
Absorption coefficient	5.442 mm^{-1}	
F(000)	1440	
Crystal size	0.299 x 0.248 x 0.029 mm^3	
Theta range for data collection	2.260 to 26.371°.	
Index ranges	-12<=h<=12, -34<=k<=34, -13<=l<=13	
Reflections collected	66642	
Independent reflections	5594 [R(int) = 0.0534]	
Completeness to theta = 25.242°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7471 and 0.4443	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	5594 / 0 / 343	
Goodness-of-fit on F^2	1.268	
Final R indices [I>2sigma(I)]	R1 = 0.0333, wR2 = 0.0788	
R indices (all data)	R1 = 0.0363, wR2 = 0.0798	
Largest diff. peak and hole	1.844 and -1.045 e.$Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for **3**

W(1)-C(2)	1.979(5)
W(1)-C(1)	1.996(5)
W(1)-C(5)	2.035(5)
W(1)-C(3)	2.030(5)
W(1)-C(6)	2.225(5)
W(1)-As(1)	2.6312(5)
As(1)-C(30)	1.951(5)
As(1)-C(20)	1.951(4)
As(1)-C(40)	1.953(4)
N(1)-C(10)	1.361(8)
N(1)-C(7)	1.406(6)
N(1)-C(13)	1.491(7)
O(1)-C(1)	1.158(6)
O(2)-C(2)	1.157(6)
O(3)-C(3)	1.145(6)
O(5)-C(5)	1.142(6)
O(6)-C(6)	1.349(6)
O(6)-C(11)	1.436(6)
C(6)-C(7)	1.431(7)
C(7)-C(8)	1.406(7)
C(8)-C(9)	1.410(7)
C(9)-C(10)	1.363(9)
C(11)-C(12)	1.491(7)
C(20)-C(25)	1.389(7)
C(20)-C(21)	1.387(7)
C(21)-C(22)	1.393(7)
C(22)-C(23)	1.381(9)
C(23)-C(24)	1.396(9)
C(24)-C(25)	1.396(7)
C(30)-C(31)	1.382(7)
C(30)-C(35)	1.390(7)
C(31)-C(32)	1.393(7)
C(32)-C(33)	1.385(8)
C(33)-C(34)	1.378(7)
C(34)-C(35)	1.379(7)
C(40)-C(41)	1.376(7)
C(40)-C(45)	1.393(7)

C(41)-C(42)	1.394(7)
C(42)-C(43)	1.379(8)
C(43)-C(44)	1.390(8)
C(44)-C(45)	1.368(7)

C(2)-W(1)-C(1)	87.6(2)
C(2)-W(1)-C(5)	87.1(2)
C(1)-W(1)-C(5)	87.1(2)
C(2)-W(1)-C(3)	89.78(19)
C(1)-W(1)-C(3)	89.79(19)
C(5)-W(1)-C(3)	175.68(19)
C(2)-W(1)-C(6)	93.16(18)
C(1)-W(1)-C(6)	176.45(19)
C(5)-W(1)-C(6)	89.48(19)
C(3)-W(1)-C(6)	93.68(18)
C(2)-W(1)-As(1)	168.65(14)
C(1)-W(1)-As(1)	83.43(14)
C(5)-W(1)-As(1)	99.32(14)
C(3)-W(1)-As(1)	83.27(13)
C(6)-W(1)-As(1)	96.22(12)
C(30)-As(1)-C(20)	103.74(19)
C(30)-As(1)-C(40)	100.79(19)
C(20)-As(1)-C(40)	100.29(19)
C(30)-As(1)-W(1)	114.97(14)
C(20)-As(1)-W(1)	123.32(14)
C(40)-As(1)-W(1)	110.61(13)
C(10)-N(1)-C(7)	108.5(5)
C(10)-N(1)-C(13)	123.8(5)
C(7)-N(1)-C(13)	127.7(5)
C(6)-O(6)-C(11)	123.6(4)
O(1)-C(1)-W(1)	178.8(4)
O(2)-C(2)-W(1)	176.2(4)
O(3)-C(3)-W(1)	176.8(4)
O(5)-C(5)-W(1)	174.9(4)
O(6)-C(6)-C(7)	108.1(4)
O(6)-C(6)-W(1)	128.2(4)
C(7)-C(6)-W(1)	123.7(3)
N(1)-C(7)-C(8)	105.8(4)
N(1)-C(7)-C(6)	127.3(4)

C(8)-C(7)-C(6)	126.9(4)
C(7)-C(8)-C(9)	108.7(4)
C(10)-C(9)-C(8)	106.4(5)
N(1)-C(10)-C(9)	110.6(5)
O(6)-C(11)-C(12)	107.4(5)
C(25)-C(20)-C(21)	119.7(4)
C(25)-C(20)-As(1)	123.1(4)
C(21)-C(20)-As(1)	117.3(4)
C(20)-C(21)-C(22)	120.5(5)
C(23)-C(22)-C(21)	119.5(5)
C(22)-C(23)-C(24)	120.8(5)
C(25)-C(24)-C(23)	119.1(5)
C(20)-C(25)-C(24)	120.4(5)
C(31)-C(30)-C(35)	119.4(4)
C(31)-C(30)-As(1)	121.5(4)
C(35)-C(30)-As(1)	119.1(4)
C(30)-C(31)-C(32)	119.9(5)
C(33)-C(32)-C(31)	119.8(5)
C(34)-C(33)-C(32)	120.4(5)
C(33)-C(34)-C(35)	119.6(5)
C(34)-C(35)-C(30)	120.8(5)
C(41)-C(40)-C(45)	118.8(4)
C(41)-C(40)-As(1)	122.5(4)
C(45)-C(40)-As(1)	118.4(3)
C(40)-C(41)-C(42)	120.7(5)
C(43)-C(42)-C(41)	119.7(5)
C(42)-C(43)-C(44)	119.7(5)
C(45)-C(44)-C(43)	120.1(5)
C(44)-C(45)-C(40)	120.9(5)

Complex 4:

Identification code	shelx	
Empirical formula	C_{33} H_{25} As O_5 S_2 W	
Formula weight	824.42	
Temperature	150(2) K	
Wavelength	0.71073 Å	
Crystal system	Triclinic	
Space group	P -1	
Unit cell dimensions	a = 9.5332(19) Å	α= 96.17(3)°.
	b = 11.891(2) Å	β= 104.95(3)°.
	c = 16.060(3) Å	γ = 113.40(3)°.
Volume	1568.4(7) $Å^3$	
Z	2	
Density (calculated)	1.746 Mg/m^3	
Absorption coefficient	4.902 mm^{-1}	
F(000)	804	
Crystal size	0.408 x 0.271 x 0.160 mm^3	
Theta range for data collection	2.362 to 26.372°.	
Index ranges	-11<=h<=11, -14<=k<=14, -20<=l<=20	
Reflections collected	9928	
Independent reflections	6106 [R(int) = 0.0196]	
Completeness to theta = 25.242°	95.6 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7485 and 0.5611	
Refinement method	Full-matrix least-squares on F^2	
Data / restraints / parameters	6106 / 0 / 379	
Goodness-of-fit on F^2	1.037	
Final R indices [I>2sigma(I)]	R1 = 0.0214, wR2 = 0.0589	
R indices (all data)	R1 = 0.0225, wR2 = 0.0598	
Largest diff. peak and hole	1.781 and -0.518 $e.Å^{-3}$	

Table 2. Bond lengths [Å] and angles [°] for mo_aj01_0m.

As(1)-C(30)	1.956(3)
As(1)-C(20)	1.961(3)
As(1)-C(40)	1.964(2)
As(1)-W(1)	2.6635(6)
W(1)-C(2)	2.007(3)
W(1)-C(1)	2.023(3)
W(1)-C(3)	2.040(3)
W(1)-C(5)	2.059(3)
W(1)-C(6)	2.192(3)
S(1)-C(10)	1.729(3)
S(1)-C(7)	1.762(3)
S(2)-C(17)	1.726(3)
S(2)-C(14)	1.731(3)
O(1)-C(1)	1.162(3)
O(2)-C(2)	1.149(3)
O(3)-C(3)	1.155(4)
O(5)-C(5)	1.156(4)
O(6)-C(6)	1.342(3)
O(6)-C(11)	1.448(3)
C(6)-C(7)	1.476(4)
C(7)-C(8)	1.374(4)
C(8)-C(9)	1.409(4)
C(9)-C(10)	1.383(4)
C(10)-C(14)	1.457(4)
C(11)-C(12)	1.510(4)
C(14)-C(15)	1.390(4)
C(15)-C(16)	1.429(4)
C(16)-C(17)	1.347(5)
C(20)-C(21)	1.394(4)
C(20)-C(25)	1.403(4)
C(21)-C(22)	1.401(4)
C(22)-C(23)	1.407(5)
C(23)-C(24)	1.381(4)
C(24)-C(25)	1.407(4)
C(30)-C(31)	1.397(4)
C(30)-C(35)	1.405(4)

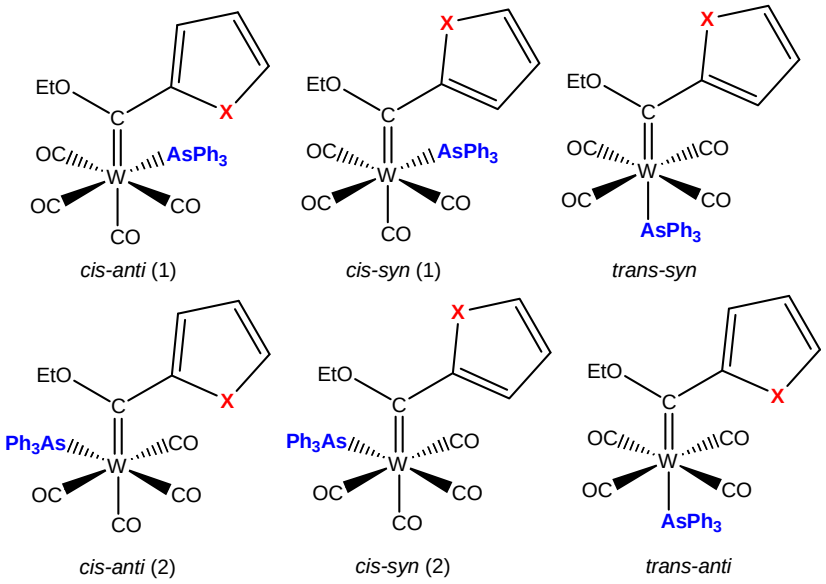
C(31)-C(32)	1.390(4)
C(32)-C(33)	1.402(4)
C(33)-C(34)	1.387(5)
C(34)-C(35)	1.394(4)
C(40)-C(41)	1.394(4)
C(40)-C(45)	1.397(4)
C(41)-C(42)	1.399(4)
C(42)-C(43)	1.383(4)
C(43)-C(44)	1.386(5)
C(44)-C(45)	1.396(4)

C(30)-As(1)-C(20)	101.06(11)
C(30)-As(1)-C(40)	101.08(11)
C(20)-As(1)-C(40)	100.28(11)
C(30)-As(1)-W(1)	121.19(8)
C(20)-As(1)-W(1)	111.86(8)
C(40)-As(1)-W(1)	118.15(8)
C(2)-W(1)-C(1)	89.14(11)
C(2)-W(1)-C(3)	88.88(11)
C(1)-W(1)-C(3)	88.95(12)
C(2)-W(1)-C(5)	90.04(11)
C(1)-W(1)-C(5)	84.10(11)
C(3)-W(1)-C(5)	172.98(10)
C(2)-W(1)-C(6)	88.42(10)
C(1)-W(1)-C(6)	177.55(9)
C(3)-W(1)-C(6)	91.24(11)
C(5)-W(1)-C(6)	95.66(11)
C(2)-W(1)-As(1)	172.97(8)
C(1)-W(1)-As(1)	88.63(8)
C(3)-W(1)-As(1)	84.41(8)
C(5)-W(1)-As(1)	96.36(8)
C(6)-W(1)-As(1)	93.82(7)
C(10)-S(1)-C(7)	92.50(13)
C(17)-S(2)-C(14)	92.29(16)
C(6)-O(6)-C(11)	121.1(2)
O(1)-C(1)-W(1)	177.1(2)
O(2)-C(2)-W(1)	177.6(3)
O(3)-C(3)-W(1)	176.8(3)
O(5)-C(5)-W(1)	174.2(2)

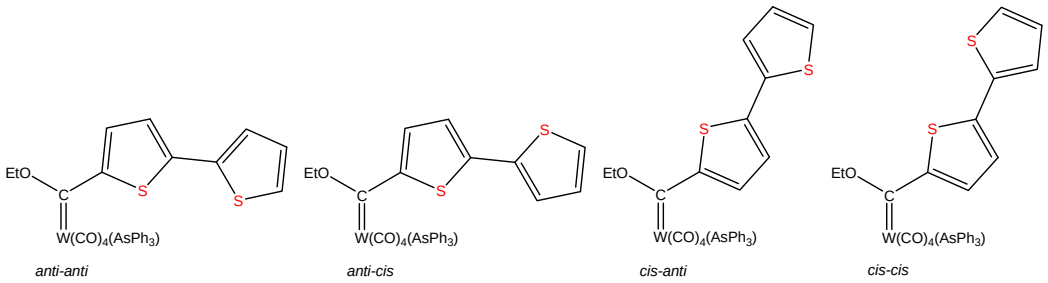
O(6)-C(6)-C(7)	105.2(2)
O(6)-C(6)-W(1)	130.67(19)
C(7)-C(6)-W(1)	124.02(18)
C(8)-C(7)-C(6)	129.6(2)
C(8)-C(7)-S(1)	109.6(2)
C(6)-C(7)-S(1)	120.8(2)
C(7)-C(8)-C(9)	113.8(2)
C(10)-C(9)-C(8)	113.8(3)
C(9)-C(10)-C(14)	128.3(3)
C(9)-C(10)-S(1)	110.3(2)
C(14)-C(10)-S(1)	121.4(2)
O(6)-C(11)-C(12)	106.7(2)
C(15)-C(14)-C(10)	129.5(3)
C(15)-C(14)-S(2)	110.5(2)
C(10)-C(14)-S(2)	120.1(2)
C(14)-C(15)-C(16)	112.0(3)
C(17)-C(16)-C(15)	113.7(3)
C(16)-C(17)-S(2)	111.5(2)
C(21)-C(20)-C(25)	119.4(2)
C(21)-C(20)-As(1)	118.2(2)
C(25)-C(20)-As(1)	122.28(19)
C(20)-C(21)-C(22)	120.1(3)
C(23)-C(22)-C(21)	120.4(3)
C(24)-C(23)-C(22)	119.6(3)
C(23)-C(24)-C(25)	120.3(3)
C(24)-C(25)-C(20)	120.2(3)
C(31)-C(30)-C(35)	120.1(3)
C(31)-C(30)-As(1)	118.9(2)
C(35)-C(30)-As(1)	120.8(2)
C(32)-C(31)-C(30)	119.7(3)
C(31)-C(32)-C(33)	120.3(3)
C(34)-C(33)-C(32)	120.0(3)
C(33)-C(34)-C(35)	120.3(3)
C(34)-C(35)-C(30)	119.7(3)
C(41)-C(40)-C(45)	119.2(2)
C(41)-C(40)-As(1)	118.52(19)
C(45)-C(40)-As(1)	122.3(2)
C(40)-C(41)-C(42)	120.6(3)
C(43)-C(42)-C(41)	120.3(3)

C(42)-C(43)-C(44)	119.1(3)
C(43)-C(44)-C(45)	121.4(3)
C(40)-C(45)-C(44)	119.4(3)

Schemes



Scheme 1. *Cis* and *trans* isomers and possible conformers of [$(AsPh_3)(CO)_4WC(OEt)(Ar)$] (Ar = 2-thienyl (**1**), 2-furyl (**2**) and 2-(N-methyl)pyrrolyl (**3**)). The first term (*cis/trans*) refers to the position of $AsPh_3$ relative to the carbene ligand, the term (*syn/anti*) refers to the orientation of the aryl group relative to OEt and the number in brackets (1 or 2) refers to the orientation of the carbene ligand relative to the *cis* $AsPh_3$ group. Enantiomers exist for each isomer.



Scheme 2. Notation used related to the orientation of the 2,2'-bithienyl group of [$(AsPh_3)(CO)_4WC(OEt)$(2,2'-bithienyl)] (**4**). For each conformation shown, two *cis* and one *trans* isomers are possible, see Scheme 1.

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