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The X-ray structure of Os(CS)(PhC≡CPh)(PPh$_3$)$_2$, a complex containing a four-electron donor acetylene ligand

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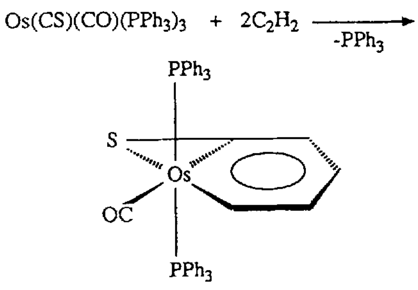
Os(CS)(PhC≡CPh)(PPh$_3$)$_2$ is formed by the treatment of Os(CS)(CO)(PPh$_3$)$_3$ with diphenylacetylene and is an example of a complex containing a four-electron donor acetylene ligand. Os(CS)(PhC≡CPh)(PPh$_3$)$_2$ crystallizes in the monoclinic space group $P2_1/n$ with the cell dimensions $a = 9.028(5)$, $b = 25.256(2)$ and $c = 19.22(2)$ Å with $\beta = 103.8(7)°$, $V = 4260$ Å^3, $Z = 4$ and d(calcd) = 1.461 g cm^{-3} for mol.wt 937.09 g mol^{-1}. Diffraction data were collected with a Nonius CAD-4 diffractometer and refined to $R = 4.05\%$ and $R_w = 4.19\%$ for 1172 independent reflections. The structure can be described as a distorted trigonal bipyramid with the CS ligand occupying an axial position. The two *cis*-PPh$_3$ ligands are in equatorial sites with the acetylene occupying a position between the remaining axial and equatorial sites. The diphenylacetylene is symmetrically bound to the metal with an average Os–C distance of 2.04(3) Å. The Os–CS distance is unusually short at 1.79(2) Å.

Keywords: X-ray structure, osmium, acetylene ligand

INTRODUCTION

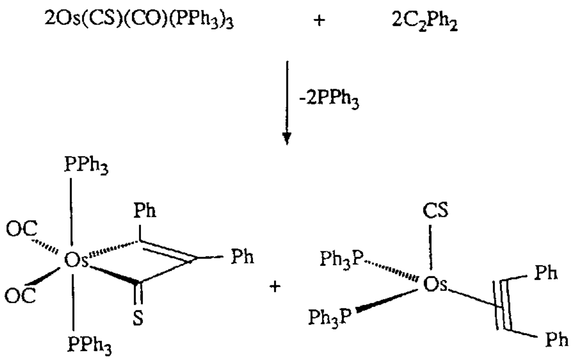
Previously we have described the unusual reactions of acetylenes with Os(CS)(CO)(PPh$_3$)$_3$.[1,2] The reactions of Os(CS)(CO)(PPh$_3$)$_3$ with acetylenes gives rise to some very interesting metallacycles. Reaction of Os(CS)(CO)(PPh$_3$)$_3$ with two molecules of acetylene affords the osmabenzene complex Os(CSCHCHCHCH)(CO)(PPh$_3$)$_2$ which has been structurally characterized.[1] This osmabenzene complex is formed by two successive insertions of C$_2$H$_2$ into osmium carbon bonds (Scheme 1). the complex undergoes several reactions in which the metallacycle is maintained.



Scheme 1

Os(CS)(CO)(PPh$_3$)$_3$ also reacts with disubstituted acetylenes giving rise to products which involve just one acetylene.[2] Treatment of Os(CS)(CO)(PPh$_3$)$_3$ with diphenylacetylene results in two complexes which can be separated by chromatography[2] to give the products Os(PhC≡CPh)(CS)(PPh$_3$)$_2$ and Os(C[S]CPhCPh)(CO)$_2$(PPh$_3$)$_2$ in a 1:1 ratio (Scheme 2) with an overall recoverable return of 80% based on Os(CS)(CO)(PPh$_3$)$_3$.

The reaction must therefore involve some form of bimetallic intermediate, possibly containing



Scheme 2

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Table 1 ^{13}C NMR Data[a] of PhC≡CPh complexes of osmium

Complex	Assignment		δ (ppm)	
Os(PhC≡CPh(CS)L_2	C≡		t, 139.6,	$^2J_{(CP)} = 5.1$ Hz
	CS		m, 170.0	Non-first order
	PPh_3	*ispo*	m, 136.5	Non-first order
		ortho	t, 127.9,	$^2J_{(CP)} = 5.0$ Hz
		meta	t, 133.7,	$^3J_{(CP)} = 6.0$ Hz
		para	s, 129.2	
	Phenyls		s, 126.4	
			s, 127.6	
			s, 128.2	
Os(PhC≡CPh)(CO)$_2L_2$	C≡		t, 109.4,	$^2J_{(CP)} = 3.0$ Hz
	CO		t, 192.6	$^2J_{(CP)} = 9.7$ Hz
	PPh_3	*ipso*	t, 133.9,	$^1J_{(CP)} = 24.7$ Hz
		ortho	t, 127.5,	$^2J_{(CP)} = 4.7$ Hz
		meta	t, 134.1,	$^3J_{(CP)} = 5.7$ Hz
		para	s, 129.5	
	Phenyls		s, 127.0	
			s, 130.1	
			s, 131.3	
			s, 134.3	

[a] Recorded in $CDCl_3$ at 25°C and reported relative to TMS.

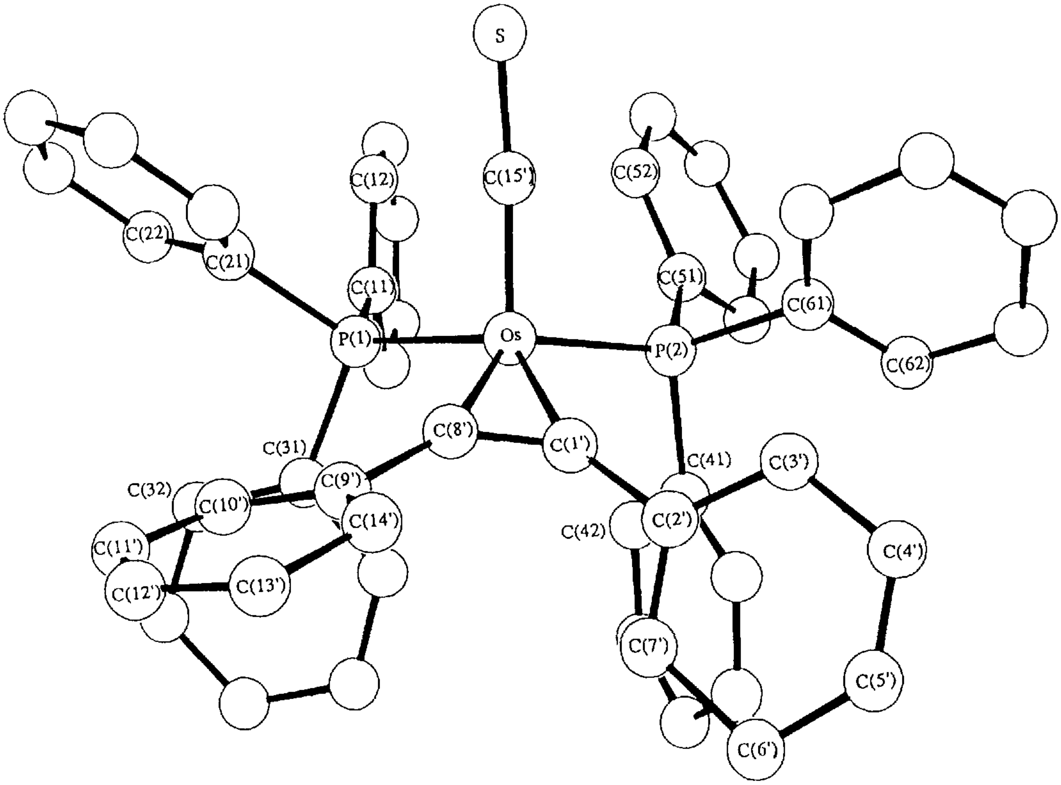


Figure 1 ORTEP representation of the molecular geometry of Os(PhC≡CPh)(CS)$(PPh_3)_2$.

bridging carbonyl and acetylene ligands. $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ is an example of a complex containing a four-electron-donating acetylene. The structure of $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ was previously depicted with *trans*-PPh_3 ligands as in the related $IrCl(PhC{\equiv}CPh)(PPh_3)_2$.[2,3] A re-examination of this complex, described in this paper, indicated that this was not the case. The ^{13}C NMR spectrum indicated that the triphenylphosphine groups were in a *cis* conformation, with the *ipso* carbons of the phenyl rings on the PPh_3 appearing as multiplets. The usual case for *trans* equivalent triphenylphosphine ligands is that the *ipso* carbons appear as triplets due to virtual coupling. The acetylenic carbons resonated at 139.6 ppm (Table 1). Structural examples of four-electron donating acetylene complexes are not common and so an X-ray investigation of $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ was undertaken.

RESULTS AND DISCUSSION

$Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ crystallized in the monoclinic space group $P2_1/n$. The complex geometry can be described as either a distorted tetrahedral or a distorted trigonal bipyramidal complex, with the acetylene occupying a position between an equatorial and axial site. The refinement, with all of the atoms except the phenyl

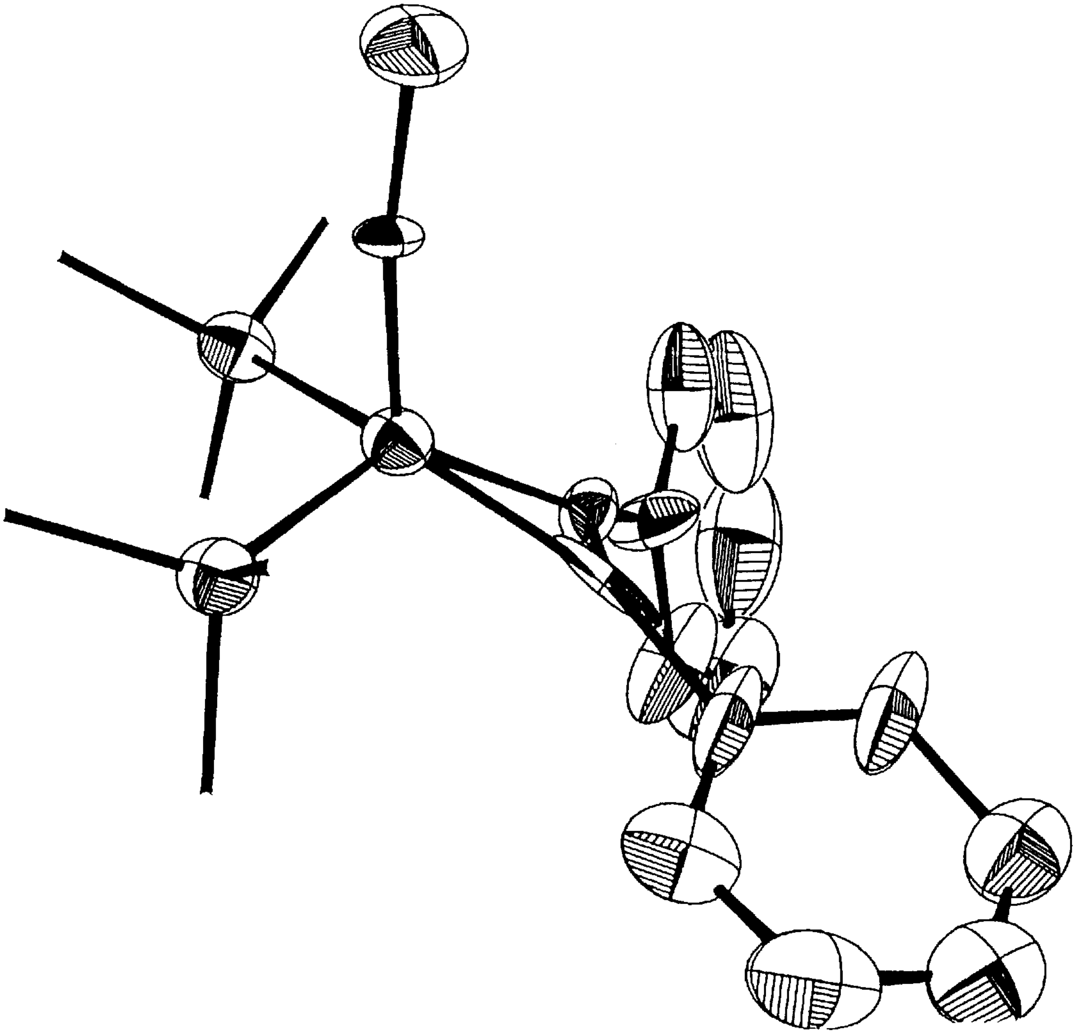


Figure 2 ORTEP representation of the inner coordination sphere of $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$.

Table 2 MPLANE calculation for $Os(C_2Ph_2)(CS)(PPh_3)_2$

Plane Os,P1,P2

Atom	*x*	*y*	*z*	Dev.
Os	−0.1683	3.5089	4.3350	0.0000
P1	0.6932	1.3691	4.4923	0.0000
P2	1.2041	4.7422	2.8804	0.0000
C1	−0.5891	5.0085	5.6799	−1.2305
C8	−0.8918	3.8398	6.1868	−1.1191

Equation for plane:
$(-0.5651)x-(0.2845)y-(0.7744)z+(4.2601)=0$

Plane (C1,C2,C8,C9)

Atom	*x*	*y*	*z*	Dev.
C1	−0.5891	5.0095	5.6799	0.0024
C2	−0.4770	6.3904	6.0848	−0.0010
C8	−0.8918	3.8389	6.1868	−0.0023
C9	−1.3219	3.3432	7.5717	0.0008
Os	−0.1683	3.5089	4.3350	−0.2943

Equation for plane:
$(-0.9589)x+(0.1467)y-(0.2430)z-(0.0832)=0$

carbons of the PPh_3 ligands anisotropic, has converged to give $R=0.041$ and $R_w=0.043$. The molecular geometry (Figs 1 and 2) has two equivalent *cis*-triphenylphosphines bound to the osmium. The PPh_3 ligands could be described as occupying two of the equatorial sites in a trigonal bipyramidal complex. The thiocarbonyl ligand is positioned at approximately 90° to the two phosphorus atoms, and would therefore be in an axial site in a trigonal bipyramid. The remaining two sites of the trigonal bipyramid are bridged by the acetylene ligand. The diphenylacetylene is displaced out of the Os,P1,P2 plane by an average of 1.2 Å (Table 2). Also, the plane of the acetylene (i.e. carbons C1,C2,C8,C9 (Table 2)] is displaced by ≈5° from the osmium P1,P2 plane (Fig. 3). This position and orientation for the acetylene presumably enables overlap of the acetylene π-orbitals with both the d_y and the d_z orbitals on the metal. Selected bond lengths and angles for $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ are given in Tables 3 and 4 respectively.

Of note are the short Os–CS bond and the very long C–S bond. Table 5 lists the bond lengths for some stucturally characterized CS complexes. It can be seen that the C–S bond length in $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ is of comparable length to that of a bridging thiocarbonyl group. A C–S bond of this length indicates that the sulphur should be quite nucleophilic and may be easily alkylated. This was attempted with a number of alkylating reagents under a variety of conditions, but no complex with an alkylated sulphur could be detected. The reaction of $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ with carbon monoxide quantitatively generates $Os(C[S]CPhCPh)(CO)_2(PPh_3)_2$. This complex alkyltes readily and the product,

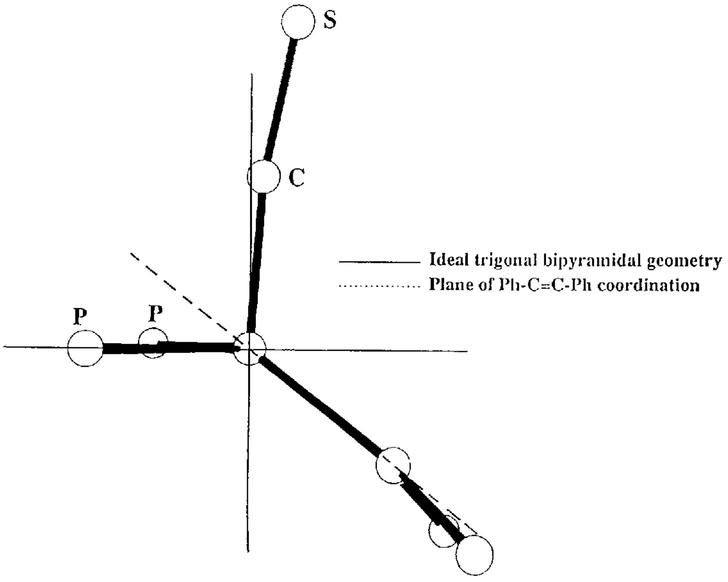


Figure 3 Coordination of the diphenylacetylene in $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$.

Table 3 Selected bond lengths (Å) for $\mathrm{Os(PhC{\equiv}CPh)(CS)(PPh_3)_2}$

Os–P1	2.312(4)
Os–P2	2.350(6)
Os–C1	2.06(2)
Os–C8	2.02(3)
Os–C15	1.79(2)
C15–S	1.59(2)
C1–C8	1.31(3)
C1–C2	1.44(3)
C8–C9	1.53(3)

Table 4 Selected angles (degrees) for $\mathrm{Os(PhC{\equiv}CPh)(CS)(PPh_3)_2}$

P1–Os–P2	108.1(2)
P1–Os–C1	134.9(5)
P1–Os–C8	102.9(4)
P1–Os–C15	91.2(5)
P2–Os–C1	98.1(5)
P2–Os–C8	133.8(7)
P2–Os–C15	93.1(6)
C1–Os–C8	37.5(7)
C1–Os–C15	123.9(7)
C8–Os–C15	119.9(7)
Os–C15–S	170(1)
C1–C8–C9	134(2)
C8–C1–C2	140(2)
Os–C1–C2	150(2)
Os–C8–C9	151(1)

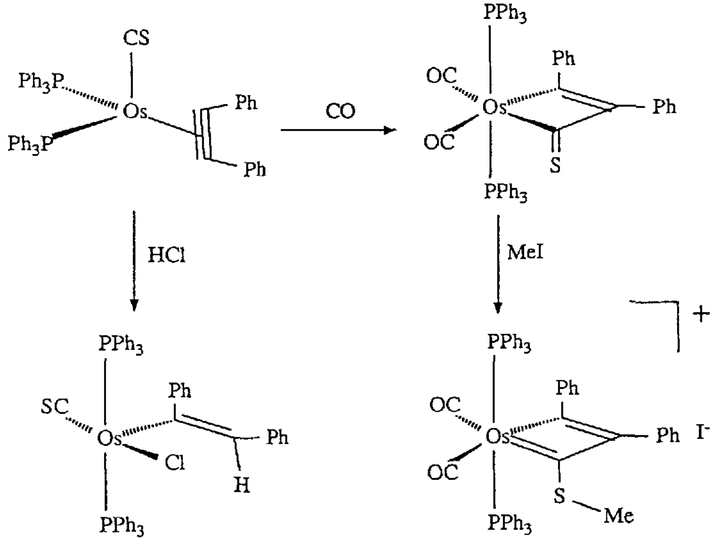
Table 5 Comparison of bonding of the CS ligand

Complex	M–CS (Å)	C–S (Å)	Ref.
$\mathrm{Os(C_2Ph_2)(CS)(PPh_3)_2}$	1.79	1.59	
$\mathrm{(\eta^6\text{-}C_6H_5CO_2Me)Cr(CO)_2(CS)}$	1.80	1.57	4, 5
$\mathrm{W(CO)_4(CS)(CyNC)}$	1.94	1.54	6
$\mathrm{Fe(OEP)(CS)}$[a]	1.66	1.56	7
$\mathrm{[Ir(CO)_2(CS)(PPh_3)_2]PF_6}$	1.87	1.51	8
$\mathrm{RhCl(CS)(PPh_3)_2}$	1.80	1.54	9
$\mathrm{[(Cp)Fe(CO)]_2(\mu\text{-}CS)_2}$	1.90	1.59	10
$\mathrm{[(Cp)Fe(CO)]_2(\mu\text{-}CO)(\mu\text{-}CS)}$	1.89	1.60	11
$\mathrm{[(Cp)Fe(CO)(CNPr^i)]_2\text{-}(\mu\text{-}CO)(\mu\text{-}CS)}$	1.93	1.50	12
$\mathrm{(Cp)Co(PMe_3)(\mu\text{-}CS)Co(Cp)}$	1.81, 1.95	1.57	13

[a] OEP, octaethylporphyrin.

$[\overline{\mathrm{Os(C[SMe]CPhC}}\mathrm{Ph)(CO)_2(PPh_3)_2}]^+$, can be described as a diphenylacetylene adduct of a carbyne complex (Scheme 3). The acetylene ligand is protonated by HCl to give a σ-alkenyl complex, $\mathrm{OsCl(\eta^1\text{-}PhC{=}CHPh)(CS)(PPh_3)_2}$ (Scheme 3).

There appear to be very few structural studies of acetylene complexes of the late transition metals. Two examples are listed in Table 6. No structural comparisons of two-electron- and four-electron-donating acetylenes for late transition metals have been reported. A more useful method of assessing the relative amounts of electron donation (two to four) has been proposed for molybdenum complexes.[16] The ^{13}C chemical shift of the acetylenic carbon is reported to move



Scheme 3

Table 6 Comparison of bonding of the RC≡CR ligand

Complex	M–C (Å)	C–C (Å)	C–C–R (°)	Ref.
$Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$	2.04(3)	1.31(3)	137(3)	
$Pt(PhC{\equiv}CPh)(PPh_3)_2$	2.03	1.32(9)	140	14
$Ni(CNBu^t)_2(PhC{\equiv}CPh)$	1.90(2)	1.28(2)	149	15

towards lower field as the acetylene changes from two- to four-electron bonding. There is a lack of data for the ^{13}C chemical shifts of osmium acetylene complexes. Therefore, the ^{13}C chemical shifts of $Os(PhC{\equiv}CPh)(CO)_2(PPh_3)_2$ and $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ were compared. The acetylenic carbon of $Os(PhC{\equiv}CPh)(CO)_2(PPh_3)_2$ occurred at 109.4 ppm whereas the acetylenic carbon for $Os(PhC{\equiv}CPh)(CS)(PPh_3)_2$ was found at 139.6 ppm.

CONCLUSIONS

This complex provides an example for a four-electron donor acetylene ligand. The effect of four-electron donation can be seen in distortions of the complex geometry and the large downfield shift of the acetylenic carbon resonances in the ^{13}C NMR spectrum. There are very few examples of structurally characterized acetylene complexes of the late transition metals and this makes determination of the effects four-electron donation has on the acetylene ligand in comparison with the more common two-electron donation difficult to determine. A theoretical study of $Os(PhC{=}CPh)(CS)(PPh_3)_2$ along with the structural investigation of other acetylene complexes of osmium is planned to investigate further the bonding in complexes containing this type of ligand.

EXPERIMENTAL

General

Standard Schlenk techniques were used for all manipulations involving $Os(CS)(CO)(PPh_3)_3$. Solvents were purified as follows: benzene and n-hexane were distilled from sodium/benzophenone; dichloromethane was distilled from calcium hydride.

When procedures involved materials that were not air-sensitive, solvents were purified by chromatography on alumina (Spence type H, 100–200 mesh) or filtered prior to use. In these cases, solvent removal under reduced pressure was achieved using a rotary evaporator. Routine recrystallizations were achieved by the following method. The sample was dissolved in a low-boiling point solvent and a higher-boiling-point solvent, in which the compound was insoluble, was added. Evaporation at reduced pressure effected gradual crystallization.

^{13}C NMR were recorded on a Bruker AM-400 spectrometer operating at 100.2 MHz and are quoted in ppm downfield from TMS. Melting points were determined on a Reichert microscope hot stage and are uncorrected. Elemental analyses for carbon and hydrogen were performed by Professor A. D. Campbell and associates of the University of Otago and they are gratefully acknowledged. $Os(CS)(CO)(PPh_3)_3$ was prepared using a literature procedure.[17]

Synthesis

$Os(CS)(PhC{\equiv}CPh)(CS)(PPh_3)_2$ and
$\overline{Os(C[S]CPhC}Ph(CO)_2(PPh_3)_2$

$Os(CO)(CS)(PPh_3)_3$ (1.0 g) and diphenylacetylene (0.17 g) were heated in benzene at reflux temperature for 20 min. The dark green–brown solution was then allowed to cool and the solvent removed at reduced pressure. The resulting oil was dissolved in a minimum of dichloromethane and placed on a 14 cm silica gel column. With dichloromethane as an eluant two bands were observed. The first orange band was collected and ethanol was added. Removal of the dichloromethane at reduced pressure afforded golden–orange crystals of $Os(CS)(PhC{\equiv}CPh)(PPh_3)_2$ (0.35 g, 40%), m.p.205–210°C.

Table 7 Crystal data and details of the structure determination of $\mathrm{Os(C_2Ph_2)(CS)(PPh_3)_2}$

(a) Crystal data	
Formula	$\mathrm{C_{51}H_{40}P_2OsS}$
Molecular weight	937.093 g mol^{-1}
Space group	$P2_1/n$
Crystal system	Monoclinic
a	9.028(5) Å
b	25.256(4) Å
c	19.22(2) Å
β	103.58(7)°
V	4260 Å^3
Z	4
d(calcd)	1.461 g cm^{-3}
F(000)	1872
μ	32.3 cm^{-1}
(b) Data collection and reduction	
Diffractometer	Nonius CAD-4
Radiation	Mo Kα (λ = 0.71069 Å)
Temperature	294–296 K
Scan technique	$2\theta/\omega$
2θ(min–max)	2–48°
Scan speed	2–30° min^{-1}
No. of unique reflections	2647
No. of unique obsd. reflections	1172
σ criterion	3.0
R(MERG)	0.0254
(c) Structure Determination and Refinement.	
R and R_w[a]	0.0405, 0.0419
Weight	$0.7506/(\sigma^2(F)+0.001772F^2)$

[a] $R=\Sigma|(|F_o|-F_c|/\Sigma|F_o|$. $R_w=[\Sigma\omega(|F_o|-|F_c|)^2/\Sigma\omega|F_o|^2]^{1/2}$

Analysis: Found: C, 64.61; H, 4.59%. $\mathrm{C_{51}H_{40}OsP_2S}$ requires: C, 65.37; H 4.30%.

The second band, which appeared red on the column, was collected as a green–yellow fraction. Addition of hexane and removal of the dichloromethane afforded a bright green solid, $\mathrm{Os(C[S]CPhCPh)(CO)_2(PPh_3)_2}$ (0.3 g, 32%), m.p. 225°C.

Analysis: Found: C, 63.34; H, 4.51%. $\mathrm{C_{53}H_{40}O_2OsP_2S}$ requires: C, 64.10; H 4.06%.

Table 8 Atom positions for $\mathrm{Os(C_2Ph_2)(CS)(PPh_3)_2}$

Atom	x/a	y/b	z/c
Os	0.09730(8)	0.13899(3)	0.23200(4)
S	−0.2174(6)	0.1015(2)	0.1091(3)
P1	0.1970(6)	0.0543(2)	0.2404(3)
P2	0.2104(6)	0.1878(2)	0.1542(3)
C1′	0.087(2)	0.1984(7)	0.304(1)
C2′	0.110(3)	0.2531(9)	0.326(1)
C3′	0.031(3)	0.2945(9)	0.281(1)
C4′	0.070(4)	0.350(1)	0.306(2)
C5′	0.181(5)	0.357(2)	0.366(3)
C6′	0.260(4)	0.319(2)	0.414(2)
C7′	0.217(3)	0.2622(8)	0.388(1)
C8′	0.067(2)	0.1521(6)	0.331(1)
C9′	0.056(2)	0.132(1)	0.405(1)
C10′	0.106(2)	0.0814(8)	0.432(1)
C11′	0.076(3)	0.065(1)	0.495(1)
C12′	0.006(2)	0.100(1)	0.534(1)
C13′	−0.032(3)	0.151(1)	0.513(1)
C14′	0.366(3)	−0.0172(8)	0.052(1)
C15′	0.474(2)	0.0017(7)	0.111(1)
C11	0.267(2)	0.0250(7)	0.165(1)
C12	0.161(2)	0.0074(7)	0.106(1)
C13	0.210(2)	−0.0145(7)	0.049(1)
C14	−0.018(3)	0.1683(8)	0.442(1)
C15	−0.061(2)	0.1190(7)	0.162(1)
C16	0.426(2)	0.0246(7)	0.170(1)
C21	0.062(2)	0.0008(7)	0.252(1)
C22	0.105(2)	−0.0529(7)	0.244(1)
C23	−0.001(3)	−0.0928(9)	0.255(1)
C24	−0.135(3)	−0.0793(9)	0.270(1)
C25	−0.175(3)	−0.024(1)	0.283(1)
C26	−0.068(2)	0.0139(7)	0.272(1)
C31	0.358(2)	0.0487(7)	0.317(1)
C32	0.409(2)	0.0005(8)	0.352(1)
C33	0.537(3)	−0.001(1)	0.411(1)
C34	0.619(3)	0.047(1)	0.430(1)
C35	0.577(3)	0.095(1)	0.395(1)
C36	0.449(3)	0.0955(8)	0.339(1)
C41	0.398(2)	0.2080(6)	0.207(1)
C42	0.523(3)	0.1749(8)	0.204(1)
C43	0.666(3)	0.191(1)	0.252(1)
C44	0.677(2)	0.2327(8)	0.300(1)
C45	0.550(2)	0.2637(8)	0.300()
C46	0.412(2)	0.2511(7)	0.254(1)
C51	0.247(2)	0.1624(7)	0.070(1)
C52	0.142(2)	0.1261(7)	0.030(1)
C53	0.159(2)	0.1099(8)	−0.039(1)
C54	0.280(2)	0.1280(8)	−0.064(1)
C55	0.375(3)	0.167(1)	−0.028(1)
C56	0.363(2)	0.1853(8)	0.043(1)
C61	0.102(2)	0.2488(7)	0.120(1)
C62	0.183(2)	0.2941(8)	0.111(1)
C63	0.098(3)	0.342(1)	0.088(2)
C64	−0.065(4)	0.339(1)	0.063(2)
C65	−0.134(3)	0.294(1)	0.072(2)
C66	−0.049(3)	0.2469(9)	0.107(1)

X-ray determination

Crystals suitable for data collection were mounted on glass fibres and positioned on a Nonius CAD-4 diffractometer. Unit cell dimensions were derived from least-squares fits to the observed setting angles of 25 reflections, monochromated Mo Kα (λ = 0.71069 Å) radiation being used. Crystal alignment and decomposition were monitored throughout data collection by measuring three standard reflections every 100 measurements, no non-statistical variation being observed. The data were corrected for Lorentz and polarization effects and equivalent reflections were averaged. Absorption corrections were applied by the empirical azimuthal method,[18] with the maximum and minimum correction factors being 0.9991 and 0.8898 respectively. Computing was carried out by using the SDP suite of programs on a PDP-11 for initial data processing, and SHELX-76 on an IBM 4341 for structure solution and refinement. Details of cyrstal data and intensity data collection parameters are summarized along with atom positions in Tables 7 and 8.

Atomic scattering fators were for neutral atoms. The observed and calculated structure factors are available from the authors as supplementary data.

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