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Registry No. $[(PMePh_2)CuI]_4$, 64024-83-5.

Supplementary Material Available: A listing of structure factor amplitudes (22 pages). Ordering information is given on any current masthead page.

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Structure of Hydrido(dithiomethyl ester)bis(carbonyl)bis(triphenylphosphine)osmium–Hemibenzene, $OsH(CS_2(CH_3))(CO)_2(P(C_6H_5)_3)_2\cdot{}^1/_2C_6H_6$

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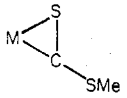
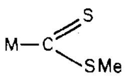
The structure of $OsH(CS_2Me)(CO)_2(PPh_3)_2\cdot{}^1/_2C_6H_6$ has been determined by single-crystal x-ray methods. The compound crystallizes with two formula units in space group C_i^1-$P\bar{1}$ of the triclinic system in a cell of dimensions a = 12.217 (4) Å, b = 15.129 (9) Å, c = 11.241 (4) Å, α = 106.23 (3)°, β = 93.97 (3)°, γ = 101.57 (3)°, V = 1936.9 Å^3, ρ_{calcd} = 1.546 g/cm^3, and ρ_{obsd} = 1.56 (2) g/cm^3. The structure has been refined by least-squares methods to a final R index on F of 0.036 for the 182 variables and 7005 data. Included in the refinement was the hydrido ligand. The coordination about the Os atom is approximately octahedral with trans phosphine groups and with the dithiomethyl ester group trans to a carbonyl and the hydrido ligand trans to the other carbonyl group. The Os–H distance is 1.64 (6) Å. The dithiomethyl ester ligand is bound in a monodentate fashion through the C atom. The Os–C(3), C(3)–S(1), and C(3)–S(2) bond lengths of 2.137 (5), 1.724 (5), and 1.648 (4) Å, respectively, suggest that stabilization of the donor C atom is by π interaction between it and the two adjacent sulfur atoms and not with the metal.

Introduction

Recent reports describe the preparation of complexes involving the dithiomethyl ester group (SCSMe) as a ligand.[3,4] On the basis of IR evidence, two coordination modes are suggested for it. The group can either behave in a bidentate fashion with carbon and sulfur atoms acting as donors (A) or, alternatively, a monodentate attachment is possible with coordination occurring via the central carbon atom (B).



A



B

The first bonding mode is found in the complexes $Os(SCSMe)(CO)_2(PPh_3)_2^+$ and $Ru(SCSMe)(CO)_2(PPh_3)_2^+$ for which IR bands, attributed to ν_{CS}, have been observed at 1070 and 1115 cm^{-1}, respectively.[3,5] Confirmation of such an arrangement has been obtained from a crystal-structure analysis of the latter compound.[5] For the complexes $OsH(CS_2Me)(CO)_2(PPh_3)_2$ and $IrHCl(CS_2Me)(CO)(PPh_3)_2$,[4] however, bidentate coordination is not possible if octahedral geometry is to be maintained. The shift in the ν_{CS} bands to 1005 and 985 cm^{-1}, respectively, is consistent with the alternative monodentate attachment. The present crystal structure of $OsH(CS_2Me)(CO)_2(PPh_3)_2$ confirms this mode of attachment and provides insight into the stabilization of this ligand.

Experimental Details

The compound $OsH(CS_2Me)(CO)_2(PPh_3)_2$ was prepared as described previously.[4] Suitable crystals as the hemibenzene solvate were obtained by recrystallization from benzene.

On the basis of morphology and an extensive series of photographs the material was assigned to the triclinic system. Cell dimensions, obtained by hand centering[6] of 11 reflections in the region $75 \leq 2\theta$(Cu Kα_1) $\leq 90°$ on a Picker FACS-I diffractometer, are a = 12.217 (4) Å, b = 15.129 (9) Å, c = 11.241 (4) Å, α = 106.23 (3)°, β = 93.97 (3)°, and γ = 101.57 (3)° (t = 23.5 °C, λ(Cu Kα_1) 1.540562 Å). For a cell volume of 1936.9 Å^3 and a molecular weight of 902.95 amu ($C_{43}H_{37}O_2OsP_2S_2$) the density of 1.546 g/cm^3 calculated for two formula units in the cell agrees well with that of 1.56 (2) g/cm^3 measured by flotation methods. A Delaunay reduction failed to reveal any hidden symmetry in the cell. Space group C_i^1-$P\bar{1}$ was assumed and was ultimately shown to be correct on the basis of the excellent agreement between observation and model.

A crystal of prismatic habit was mounted in air roughly along [010]. The crystal, which displayed faces of the forms {010}, {100}, {001}, and {01$\bar{1}$}, had a calculated volume of 0.00662 mm^3 and was approximately 0.37-mm long and of cross section 0.18 × 0.12 mm. Data were collected in shells of 2θ by methods standard in this laboratory.[6,7] The scan speed was 2°/min from 0.75° below the Cu Kα_1 peak to 0.75° above the Cu Kα_2 peak. The takeoff angle was 4.5° and the

Table I. Positional and Thermal Parameters for the Nongroup Atoms of $OsH(CS_2Me)(CO)_2(PPh_3)_2 \cdot {}^1/_2C_6H_6$

ATOM	X[A]	Y	Z	B11 OR B,A^2 [B]	B22	B33	B12	B13	B23
OS	-0.134728(13)	0.228950(13)	-0.162787(15)	46.17(15)	37.96(13)	67.03(20)	9.32(9)	11.19(11)	16.45(11)
S(1)	-0.24352(12)	0.021316(97)	-0.35198(12)	94.0(10)	49.68(72)	82.5(11)	10.03(68)	10.00(84)	11.12(70)
S(2)	-0.24443(12)	0.03135(10)	-0.08699(13)	99.0(11)	53.22(76)	105.3(13)	8.66(73)	27.93(96)	35.26(80)
P(1)	0.046526(84)	0.194233(80)	-0.177558(96)	49.72(65)	42.03(59)	66.33(87)	11.41(48)	10.20(59)	17.31(56)
P(2)	-0.317763(86)	0.257458(83)	-0.18600(10)	47.55(66)	42.52(62)	74.66(93)	8.60(50)	8.80(61)	17.50(60)
O(1)	-0.12602(41)	0.25998(32)	0.12139(35)	130.5(49)	80.6(29)	74.8(36)	27.9(30)	18.6(32)	24.4(25)
O(2)	-0.03432(36)	0.43514(30)	-0.14446(41)	114.4(36)	45.8(25)	138.3(47)	6.7(24)	32.0(33)	29.7(27)
C(1)	-0.12944(40)	0.24665(33)	0.01553(44)	66.6(34)	43.0(25)	83.6(43)	14.0(23)	12.4(29)	14.9(25)
C(2)	-0.07089(37)	0.35817(36)	-0.14950(43)	61.3(30)	48.0(29)	85.1(42)	9.5(23)	14.5(28)	22.1(27)
C(3)	-0.21226(35)	0.08307(34)	-0.19503(42)	52.9(28)	45.2(27)	86.9(40)	12.6(21)	17.6(27)	22.5(26)
C(4)	-0.31677(68)	-0.09670(48)	-0.36146(63)	175.7(76)	46.3(37)	140.7(66)	-0.7(41)	11.9(55)	2.3(39)
H	-0.1541(51)	0.2039(44)	-0.3155(55)	4.1(15)					

[A] ESTIMATED STANDARD DEVIATIONS IN THE LEAST SIGNIFICANT FIGURE(S) ARE GIVEN IN PARENTHESES IN THIS AND ALL SUBSEQUENT TABLES. [B] THE FORM OF THE ANISOTROPIC THERMAL ELLIPSOID IS: $EXP[-(B11H^2+B22K^2+B33L^2+2B12HK+2B13HL+2B23KL)]$. THE QUANTITIES GIVEN IN THE TABLE ARE THE THERMAL COEFFICIENTS X 10^4.

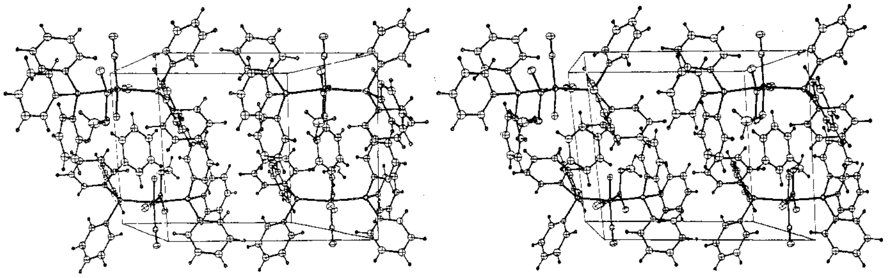


Figure 1. Unit cell of $OsH(CS_2Me)(CO)_2(PPh_3)_2 \cdot {}^1/_2C_6H_6$. In this figure the atoms have been drawn at their 50% probability levels, except for the methyl and phenyl hydrogen atoms which have been drawn artificially small.

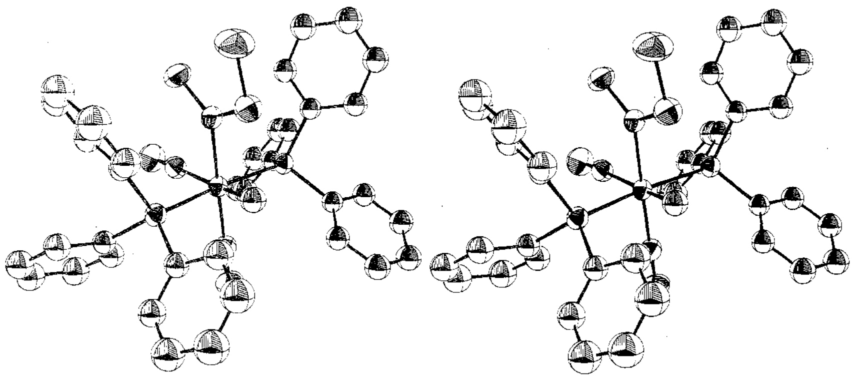


Figure 2. A stereoview of the $OsH(CS_2Me)(CO)_2(PPh_3)_2$ molecule. The hydride hydrogen atom is included, but other hydrogen atoms have been omitted. The 50% probability ellipsoids are shown.

counter aperture, positioned 32 cm from the crystal, was 4.7-mm wide by 4.0-mm high. Background counts were for 10 s at each end of the scan range, unless the rescan option was invoked in which case total background counts at each end were for 30 s. A total of 7502 reflections were examined out to $2\theta \leq 150°$. Of these the 7005 unique data having $F_o^2 > 3\sigma(F_o^2)$ were used in subsequent calculations. These data were processed in the usual way using a value of p of 0.04.[6] An absorption correction[8] was applied to these data; minimum and maximum transmission factors were 0.208–0.446.

The structure was solved from an origin-removed Patterson function. In all calculations the phenyl rings were treated as rigid groups of D_{6h} symmetry with a C–C bond distance of 1.395 Å. Similarly the benzene solvate molecule, whose center is at a center of symmetry, was treated as a three-atom group. In a difference Fourier map computed after anisotropic refinement of the nongroup atoms the hydrido ligand as well as the methyl and phenyl hydrogen atoms were the main features. While the hydrido ligand was subsequently refined as an isotropic atom, the positions of the methyl and phenyl hydrogen atoms were idealized using a C–H distance of 0.95 Å. The final least-squares cycle converged to values of R and R_w of 0.036 and 0.053, respectively, for the 182 variables and 7005 data. The error in an observation of unit weight is 2.09 electrons. Of the 348 reflections having $F_o < 3\sigma(F_o)$ omitted from the refinement only four have $|F_o^2 - F_c^2| > 4\sigma(F_o^2)$. An analysis of $\sum w(|F_o| - |F_c|)^2$ as a function of $|F_o|$, setting angles, and Miller indices reveals no trends. The final values of the parameters are given in Table I, while in Table II the positional coordinates of the group atoms are presented. Table III[9] presents the values of $10|F_o|$ vs. $10|F_c|$ in electrons for the reflections used in the refinements. Table IV[9] gives the calculated positions of the methyl and phenyl hydrogen atoms.

Description of the Structure and Discussion

The crystal structure consists of the packing of discrete monomeric units of the Os complex and benzene solvent

Table II. Derived Parameters for the Rigid Group Atoms of $OsH(CS_2Me)(CO)_2(PPh_3)_2\cdot{}^1/_2C_6H_6$

ATOM	X	Y	Z	B, $Å^2$	ATOM	X	Y	Z	B, $Å^2$
C(11)	0.14146(26)	0.24083(24)	-0.02764(25)	3.42(7)	C(43)	-0.60051(30)	0.03682(27)	-0.31633(28)	6.00(14)
C(12)	0.21435(30)	0.18948(20)	0.00689(30)	4.58(10)	C(44)	-0.62319(27)	0.01421(25)	-0.20707(36)	5.47(12)
C(13)	0.28433(29)	0.22654(27)	0.12106(34)	5.39(11)	C(45)	-0.55345(30)	0.06369(27)	-0.09482(28)	5.17(11)
C(14)	0.28142(31)	0.31496(28)	0.20068(27)	5.44(12)	C(46)	-0.46103(26)	0.13579(24)	-0.09182(23)	4.32(9)
C(15)	0.20852(35)	0.36631(22)	0.16615(32)	5.82(13)	C(51)	-0.34520(29)	0.29746(24)	-0.32309(26)	3.55(8)
C(16)	0.13854(30)	0.32925(24)	0.05199(33)	4.89(11)	C(52)	-0.33440(32)	0.24030(21)	-0.44077(32)	4.74(10)
C(21)	0.13216(21)	0.24680(21)	-0.27958(25)	3.20(6)	C(53)	-0.35863(36)	0.26706(27)	-0.54697(24)	6.02(13)
C(22)	0.24626(22)	0.24557(23)	-0.27239(27)	3.89(8)	C(54)	-0.39366(39)	0.35098(30)	-0.53549(29)	6.22(14)
C(23)	0.31367(18)	0.28319(26)	-0.34975(31)	4.28(9)	C(55)	-0.40446(37)	0.40814(24)	-0.41780(36)	5.78(13)
C(24)	0.26697(25)	0.32204(26)	-0.43429(30)	4.64(10)	C(56)	-0.38023(31)	0.38138(23)	-0.31160(26)	4.42(9)
C(25)	0.15287(26)	0.32327(26)	-0.44148(29)	4.53(10)	C(61)	-0.35022(26)	0.34879(23)	-0.05496(27)	3.55(8)
C(26)	0.08546(18)	0.28565(23)	-0.36412(28)	3.73(8)	C(62)	-0.46253(23)	0.34937(24)	-0.04017(30)	4.54(9)
C(31)	0.05144(26)	0.06957(16)	-0.23371(26)	3.19(7)	C(63)	-0.48851(23)	0.41462(29)	0.06244(35)	5.15(11)
C(32)	0.08140(27)	0.03026(20)	-0.35115(25)	3.75(8)	C(64)	-0.40219(33)	0.47930(26)	0.15026(31)	5.75(13)
C(33)	0.07929(30)	-0.06607(21)	-0.39277(24)	4.38(9)	C(65)	-0.28989(28)	0.47872(26)	0.13547(31)	5.74(12)
C(34)	0.04724(32)	-0.12310(16)	-0.31694(31)	4.69(11)	C(66)	-0.26390(20)	0.41346(27)	0.03286(33)	4.55(10)
C(35)	0.01728(30)	-0.08379(20)	-0.19949(29)	4.61(10)	C(71)	0.00372(38)	0.53192(32)	0.629588(53)	5.61(12)
C(36)	0.01939(27)	0.01254(21)	-0.15788(22)	3.90(8)	C(72)	-0.08116(30)	0.45516(31)	0.55851(35)	5.66(12)
C(41)	-0.43835(24)	0.15840(22)	-0.20108(29)	3.42(7)	C(73)	-0.08488(30)	0.42325(24)	0.42892(33)	5.70(12)
C(42)	-0.50809(30)	0.10892(27)	-0.31333(24)	4.50(10)					

RIGID GROUP PARAMETERS

GROUP	X_C [A]	Y_C	Z_C	DELTA [B]	EPSILON	ETA
PH(1)	0.21144(20)	0.27790(18)	0.08652(22)	1.0232(27)	2.5351(21)	0.8539(28)
PH(2)	0.19957(17)	0.28442(15)	-0.35693(18)	0.9766(20)	2.8330(18)	-0.7881(22)
PH(3)	0.04934(17)	-0.02676(15)	-0.27532(20)	0.2011(29)	-2.3248(17)	1.9971(29)
PH(4)	-0.53077(20)	0.08631(17)	-0.20407(22)	-1.0592(26)	-2.7215(19)	1.2669(26)
PH(5)	-0.36943(21)	0.32422(19)	-0.42929(23)	0.2871(30)	-2.4890(19)	-1.6064(29)
PH(6)	-0.37621(21)	0.41404(18)	0.04765(23)	-2.1030(28)	2.4783(21)	2.3128(30)
PH(7)	0	1/2	1/2	-0.9552(39)	-3.1950(30)	1.5915(39)

[A] X_C, Y_C, AND Z_C ARE THE FRACTIONAL COORDINATES OF THE ORIGIN OF THE RIGID GROUP. [B] THE RIGID GROUP ORIENTATION ANGLES DELTA, EPSILON, AND ETA(RADIANS) HAVE BEEN DEFINED PREVIOUSLY: S.J. LA PLACA AND J.A. IBERS, ACTA CRYSTALLOGR., 18, 511(1965).

molecules. The benzene molecules occupy centers of symmetry in the cell. A stereoview of the contents of the unit cell is given in Figure 1. There are no unusual intermolecular contacts. The shortest calculated H···H interaction is 2.60 Å.

The geometry about the central Os atom is approximately octahedral. The two phosphine groups are trans to one another. One of the carbonyl groups is trans to the hydrido ligand while the other carbonyl group is trans to the dithiomethyl ester group. Consistent with the infrared evidence[4] this group is bonded to the Os atom in a monodentate fashion through the C atom. There is some distortion from the ideal octahedral geometry as the bulky triphenylphosphine ligands bend toward the hydrido ligand so that the angle P(1)–Os–P(2) is 170.14 (4)°. This bending is mainly in the plane containing the hydrido ligand since the angles subtended at Os by the P atoms and the two C atoms (C(2) and C(3)) differ little from their ideal values of 90°. The widening of the angle C(1)–Os–C(2) to 96.3° presumably also results from a small ligand tilt toward the hydrido ligand. Selected bond distances and angles are given in Table V.

The Os–C(3) bond distance of 2.137 (5) Å is a little larger than the 2.06 Å predicted from the sum of covalent radii[10,11] and suggests that the dithiomethyl ester ligand exhibits little or no π-acceptor behavior in this complex. The value lies within the range of distances observed (2.06–2.16 Å) for

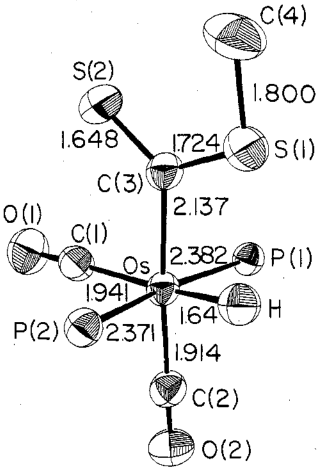


Figure 3. Inner-coordination sphere of the $OsH(CS_2Me)(CO)_2(PPh_3)_2$ molecule with some distances presented. The 50% probability ellipsoids are shown.

Table V. Bond Distances (Å) and Angles (deg) in $OsH(CS_2Me)(CO)_2(PPh_3)_2 \cdot {}^1/_2C_6H_6$

Bond Distances

Os-P(1)	2.382 (1)	P(1)-C(11)	1.849 (3)
Os-P(2)	2.371 (1)	P(1)-C(21)	1.840 (3)
Os-C(1)	1.941 (5)	P(1)-C(31)	1.829 (3)
Os-C(2)	1.914 (5)	P(2)-C(41)	1.839 (3)
Os-C(3)	2.137 (5)	P(2)-C(51)	1.840 (4)
Os-H	1.64 (6)	P(2)-C(61)	1.844 (3)
S(1)-C(3)	1.724 (5)	C(1)-O(1)	1.146 (6)
S(1)-C(4)	1.800 (7)	C(2)-O(2)	1.144 (6)
S(2)-C(3)	1.648 (4)		

Nonbonded Distance

S(1)-H	2.66 (6)

Bond Angles

P(1)-Os-P(2)	170.14 (4)	Os-P(1)-C(11)	113.6 (1)
P(1)-Os-C(1)	95.5 (1)	Os-P(1)-C(21)	115.7 (1)
P(1)-Os-C(2)	90.2 (1)	Os-P(1)-C(31)	117.2 (1)
P(1)-Os-C(3)	91.2 (1)	C(11)-P(1)-C(21)	101.4 (1)
P(1)-Os-H	89 (2)	C(11)-P(1)-C(31)	104.3 (2)
P(2)-Os-C(1)	94.3 (1)	C(21)-P(1)-C(31)	102.7 (1)
P(2)-Os-C(2)	89.6 (1)	Os-P(2)-C(41)	117.4 (1)
P(2)-Os-C(3)	88.2 (1)	Os-P(2)-C(51)	112.9 (1)
P(2)-Os-H	82 (2)	Os-P(2)-C(61)	115.7 (1)
C(1)-Os-C(2)	96.3 (2)	C(41)-P(2)-C(51)	104.6 (2)
C(1)-Os-C(3)	88.7 (2)	C(41)-P(2)-C(61)	100.5 (1)
C(1)-Os-H	173 (2)	C(51)-P(2)-C(61)	104.0 (2)
C(2)-Os-C(3)	174.7 (2)	Os-C(3)-S(1)	112.5 (2)
C(2)-Os-H	90 (2)	Os-C(3)-S(2)	126.1 (3)
C(3)-Os-H	85 (2)	S(1)-C(3)-S(2)	121.4 (3)
Os-C(1)-O(1)	177.9 (4)	C(3)-S(1)-C(4)	106.3 (3)
Os-C(2)-O(2)	178.2 (4)		

σ-bonded carbon in some other complexes[12-18] of third-row transition metals. The bond length of 1.64 (6) Å determined for Os–H also lies within the range of values (1.5–1.7 Å)[19] found in a number of x-ray studies, e.g., 1.66 (5) Å in $RhH(N_2)(PPh\text{-}t\text{-}Bu_2)_2$.[20]

The two Os–C(O) bond distances (1.941 (5), 1.914 (5) Å), although differing from one another, are normal and agree with those found in second- and third-row transition metal carbonyl complexes (1.81–2.08 Å).[21] They are consistent with the π interaction which is expected for this ligand and their differences reflect the differing trans-directing capacities of the hydrido and dithiomethyl ester ligands. The C–O distances of 1.146 (6) and 1.144 (6) Å are also in accord with previously reported values.

Normal Os–P bond distances of 2.382 (1) and 2.371 (1) Å are observed for the two trans PPh_3 groups. These values lie within the range found in other Os complexes (2.32–2.44 Å).[22-24]

Of particular interest is the geometry of the dithiomethyl ester group. This group is essentially planar and is coplanar with the Os and H atoms. The atoms Os, S(1), S(2), and C(3) lie in the plane $11.863x - 6.474y + 0.286z = 3.127$ with atom C(3) being the farthest (0.015 (4) Å) from this plane. Interestingly, the dithiomethyl ester group is oriented along the H, Os, C(3) plane with the H atom being only 0.11 Å out of the plane of the ester. Some deviations from the ideal trigonal angles are observed at atom C(3). The angle Os–C(3)–S(2) has increased to 126.1 (3)° and Os–C(3)–S(1) decreased to 112.5 (2)° suggesting that the ligand has tilted slightly toward the hydrido ligand. The S(1)···H distance is only 2.66 (6) Å, a feature consistent with the ready loss of methylthiol observed when the complex is refluxed in 2-methoxyethanol.[4]

The C(4)–S(1) distance of 1.800 (7) Å agrees well with the C–S single bond length determined for the molecules $(CH_3)_2S$ (1.81 Å)[25] and $(CH_3)_2SO$ (1.80 Å).[26] However, the distances 1.724 (5) and 1.648 (4) Å observed for C(3)–S(1) and C(3)–S(2), respectively, are both shorter than this and indicate some multiple bonding. The latter bond involves the nonsubstituted sulfur atom; the distance is close to that observed (1.64 Å)[27] for the C–S bond in the first excited state of the CS_2 molecule. These distances and angles in the dithiomethyl ester ligand are consistent with a trigonally hybridized donor carbon atom in which the unhybridized p_z orbital has little, if any, interaction with orbitals on the metal. On the other hand this orbital does interact with appropriate orbitals on both sulfur atoms so that considerable π-electron delocalization occurs over the three atoms and especially between atoms C(3) and S(2). This is a similar pattern to that observed in a number of other carbenoid complexes where the major π interaction is between the donor carbon and its adjacent heteroatoms, with the π contribution from the metal being small.

Data for a number of carbenoid complexes,[5,30-39] in which at least one of the heteroatoms is sulfur, are given in Table VI. The Os–C distance of I is the longest in this list but it is not possible to determine any correlation with the C–S distances because of the differing nature of the second heteroatom and the coordination mode. Of the bidentate complexes, V–XII, the most obvious comparison with I is V. In this complex the M–C distance (2.03 Å) is shorter, as is the C–S bond to the substituted sulfur atom (1.65 Å), but no significant difference is observed for the coordinated C–S value when measured against C(3)–S(2). Such bond distance differences between similar molecules can be seen in many of the examples of Table VI but no discernible pattern relating bond order in the carbene ligand with chemical or structural features is obvious. A difficulty lies in the degree of accuracy attained in some analyses. Thus for compounds V, VI, and VII, where comparison with the present work might be deemed to be fruitful, one report is a preliminary communication and the other two quote large standard deviations. On the whole, π interaction between the metal and carbene carbon atom is negligible but there are exceptions, the most notable occurring in the two manganese complexes (X and XI) where changes

Table VI. Structural Data for Some Carbenoid Complexes Where Sulfur is One of the Heteroatoms[a]

	Complex	M–C, Å	C–S, Å	C–X, Å	X	Ref
I	$OsH(CS_2Me)(CO)_2(PPh_3)_2$	2.137 (5)	1.724 (5)	1.648 (4)	S	*b*
II	$[Pt(CH_3NC)_2\{C(NHCH_3)(SCH_2CH_3)\}_2][PF_6]_2$	2.058 (7)	1.681 (8)	1.300 (10)	N	30
III	$[Cl(PPh_3)_2Pt(CS_2)Pt(PPh_3)_2][BF_4]$	1.950 (15)	1.709 (21)	1.692 (20)	S	31
IV	$Cr(CO)_5[C(CH_3)(SC_6H_5)]$	2.020 (3)	1.690 (3)	1.490 (4)	C	32
V	$[Ru(SCSMe)(CO)_2(PPh_3)_2][ClO_4]$	2.03	1.66	1.65	S	5
VI	$Pt(CS_2)(PPh_3)_2$	2.063 (46)	1.72 (5)	1.54 (5)	S	33
VII	$Pd(CS_2)(PPh_3)_2$	2.00 (3)	1.63 (3)	1.65 (3)	S	34
VIII	$RhCl(S_2CN(CH_3)_2)(SCN(CH_3)_2)(PPh_3)$	1.895 (16)	1.64 (2)	1.31 (2)	N	35
IX	$[MoS(SCN(C_3H_7)_2)(S_2CN(C_3H_7)_2)]_2$	2.069 (7)	1.683 (8)	1.298 (10)	N	36
X	$Mn(CO)_3(SCN(CH_3)_2)(PPh_3)_2$	1.924 (6)	1.682 (6)	1.294 (8)	N	37
XI	$[Mn(CO)_3(C(SCH_3)N(CH_3)_2)(PPh_3)_2][BF_4]$	1.843 (17)	1.784 (16)	1.279 (20)	N	37
XII	$[PdCl(P(OMe)_3]_2(CSNMe)_2$	1.99 (1)	1.72 (1)	1.30 (1)	N	38
XIII	$\{Fe(CO)_3\}_2((C_6H_5)_2C_2S)$	2.061 (6)	1.756 (6)			39

[a] Absence of standard deviations occurs only where these values are omitted in the original reference. [b] This work.

Table VII. Structural Data for Some Carbenoid Complexes Where There Is a Chloro Group Trans to the Carbene Carbon but No Sulfur Heteroatom

Complex	M–C, Å	Ref
cis-$PdCl_2(Me_2C_2N_4H_4)$	1.948 (5)	40
cis-$PtCl_2[C(NPhCH_2)_2](PEt_3)$	2.009 (13)	41
cis-$[PtCl_2\{C(Cl\text{-}C_6H_3\text{-}NH)(NHMe)\}(PEt_3)_2][ClO_4]$	1.973 (11)	42
$RuCl_2(caffeine)(NH_3)_3$	2.03 (1)	43
cis-$PdCl_2(C(NMe)(OMe))_2$	1.953 (8) 1.972 (10)	44
cis-$PtCl_2(C(N\text{-}Ph)(OEt))(PEt_3)$	1.962 (18)	45

in bond length follow changes to the carbene ligand in a predictable way.[37] The remaining examples of a short metal–carbon bond (compounds III, VIII, and XII) are those in which a chloro ligand is trans to the carbene ligand. It could be argued that the presence of the chloro group aids double bond formation with the carbene carbon atom to bring about the shortening effect noted. It is interesting that of six carbene complexes which do not have a sulfur heteroatom but which feature a trans chloro group[40–45] (Table VII) at least four have a metal to carbon distance clearly indicative of some double bonding. However, the two borderline values, and the fact that some manganese complexes[46,47] (including X and XI) have short M–C(carbene) distances despite the presence of a trans-carbonyl group, highlight the difficulty in proposing simple electronic explanations and emphasize the need for further structural data especially for compounds of selected chemical composition.

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Supplementary Material Available: Table III, the structure amplitudes, and Table IV, the calculated hydrogen atom positions (49 pages). Ordering information is given on any current masthead page.

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