Polyhedron 30 (2011) 1250–1257

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Five-coordinate fluorobenzothiolate osmium(IV) complexes $[Os(SR_F)_4(PR_3)]$ ($R_F = C_6F_4H$-4, $R_3 = Ph_2(C_6F_5)$; $R_F = C_6F_4H$-4, $R_3 = (OPh)_3$; $R_F = C_6F_5$, $R_3 = (OPh)_3$): Single-crystal structures and solution structural characterization

Margarita Cerón [a], Verónica Cortina [a], Armando Ramírez-Monroy [a], Sylvain Bernès [b], Hugo Torrens [c], Maribel Arroyo [a,*]

[a] *Centro de Química del Instituto de Ciencias de la Benemérita Universidad Autónoma de Puebla, Edificio 193 del Complejo de Ciencias, Ciudad Universitaria, San Manuel 72571, Puebla, Pue., Mexico*
[b] *DEP, Facultad de Ciencias Químicas, UANL, Guerrero y Progreso S/N, Col. Treviño 64570, Monterrey, N.L., Mexico*
[c] *División de Estudios de Posgrado, Facultad de Química, UNAM, Cd. Universitaria, 04510 México D.F., Mexico*

ARTICLE INFO

Article history:
Received 1 December 2010
Accepted 2 February 2011
Available online 4 March 2011

Keywords:
Five-coordinate osmium
Fluorinated thiolates
Phosphines
Fluxional processes

ABSTRACT

Reactions of OsO_4 with excess of HSR_F and PR_3 in ethanol afford five-coordinate compounds $[Os(SR_F)_4(PR_3)]$ ($R_F = C_6F_4H$-4, $R_3 = Ph_2(C_6F_5)$ (**1**); $R_F = C_6F_4H$-4, $R_3 = (OPh)_3$ (**2**); and $R_F = C_6F_5$, $R_3 = (OPh)_3$ (**3**)). Single crystal X-ray diffraction studies of **1–3** exhibit a common pattern with an osmium center in a trigonal-bipyramidal coordination arrangement. Axial positions are occupied by mutually *trans* thiolate and phosphine or phosphite ligands, while the remaining three equatorial positions are occupied by thiolate ligands. In compound **1** the tetrafluorophenyl rings of the equatorial ligands are directed away from the axial phosphine ligand in a "3-up" arrangement. In contrast, a "2-up, 1-down" arrangement was found in compounds **2** and **3**, where only two of the fluorinated rings from the equatorial thiolates are directed towards the axial thiolate, while the fluorinated substituent of the third equatorial thiolate is directed towards the phosphine ligand. Structural characterization in solution by ^1H, $^{31}P\{^1H\}$ and ^{19}F NMR, variable temperature and COSY ^{19}F–^{19}F NMR studies are discussed.

1. Introduction

The first examples of five-coordinate ruthenium and osmium complexes bearing a formal +4 oxidation state, $[M(SR)_4(CH_3CN)]$ (M = Ru, Os; R = C_6HMe_4-2,3,5,6 or $C_6H_2{}^iPr_3$-2,4,6), were reported by Koch and Millar in 1983 [1]. In these complexes two of the aromatic rings of equatorial thiolates are projected towards the axial CH_3CN ligand and the other one is directed towards the axial sulfur ("2-up, 1-down" arrangement). In 1985, these authors reported [2] the compounds, $[M(SR)_4(CO)]$, where the overall structure is similar to that of $[M(SR)_4(CH_3CN)]$, with the CO occupying an axial position in the trigonal bipyramidal coordination arrangement, however the three substituents of equatorial thiolates are oriented in the direction of the CO ("3-up" arrangement). Other five-coordinate ruthenium and osmium compounds with these sterically hindered aromatic thiolate ligands were reported [3,4].

On the other hand, restricted rotation of polyfluoro-phenyl/alkyl groups has been observed in a variety of coordination and organometallic compounds [5–14]. The corresponding fluxional processes can be accompanied by conformational changes in the molecules and dynamic ^{19}F NMR studies of fluoro-thiolate complexes have revealed that isomeric forms exist due to different orientations of the SR_F ligands and that such isomers can undergo positional exchange as a result of rotations about $M—SR_F$ bonds.

For a long time, we have also been involved in the synthesis and reactivity studies of five-coordinate Os^{IV}–polythiolate-complexes [6,15–23] of general formula $[OsX(SR_F)_3(PR_3)]$ (X = Cl, SR_F; $SR_F = SC_6F_5$, SC_6F_4H-4, SC_6H_4F-4, SC_6H_5; PR_3 = tertiary phosphine). Up to now, all members of these series characterized by X-ray crystallography had shown, invariably, the "3-up" orientation for the substituents of equatorial thiolates, probably because of the axial tertiary phosphine hinders that a R_F group lie near of such axial position. Interestingly, on the recently reported systems $[Os(SC_6F_5)_4(P(C_6H_4X\text{-}4)_3)]$, where X = OCH_3, CH_3, F, Cl or CF_3, [21] the X-ray diffraction studies showed a configuration "3-up", although exhaustive NMR studies revealed the presence of the "3-up" and "2-up, 1-down" isomers in solution. Now, we used these fluorinated ligands, which offer the possibility to distinguish clearly the structural details of these types of molecules, to investigate how the variations in PR_3 ligands influence the configuration of the complexes. Thus, we report here the preparation of analogous compounds $[Os(SR_F)_4(PR_3)]$ ($R_F = C_6F_4H$-4, $R_3 = Ph_2(C_6F_5)$ (**1**); $R_F = C_6F_4H$-4, $R_3 = (OPh)_3$ (**2**); and $R_F = C_6F_5$, $R_3 = (OPh)_3$ (**3**)) and

---

* Corresponding author. Tel.: +52 222 2295500; fax: +52 222 2295551.
E-mail address: slarroyo@siu.buap.mx (M. Arroyo).

0277-5387/$ - see front matter © 2011 Elsevier Ltd. All rights reserved.
doi:10.1016/j.poly.2011.02.001

discuss their structural characterization both in the solid-state and in solution by ^{1}H, ^{31}P{^{1}H} and ^{19}F NMR studies.

2. Results and discussion

Reactions of OsO_4 with excess of HSR_F and PR_3 in refluxing ethanol afford the five-coordinated compounds $[Os(SR_F)_4(PR_3)]$ ($R_F = C_6F_4H$-4, $R_3 = Ph_2(C_6F_5)$ (**1**); $R_F = C_6F_4H$-4, $R_3 = (OPh)_3$ (**2**); and $R_F = C_6F_5$, $R_3 = (OPh)_3$ (**3**)).

$$OsO_4 + HSR_F + PR_3 \overset{\text{Ethanol}}{\rightarrow} \underset{\mathbf{1-3}}{[Os(SR_F)_4(PR_3)]}$$

$$R_F = C_6F_4H\text{-4},\ R_3 = Ph_2(C_6F_5)\ (\mathbf{1});\ R_F = C_6F_4H\text{-4},\ R_3 = (OPh)_3\ (\mathbf{2});$$
$$R_F = C_6F_5,\ R_3 = (OPh)_3\ (\mathbf{3})$$

The osmium(IV) diamagnetic complexes **1–3** were isolated by column chromatography and characterized by elemental analyses, FAB$^+$-mass spectrometry, single crystal X-ray structure determinations and ^{1}H, ^{31}P{^{1}H} and ^{19}F NMR studies.

The FAB-mass spectra show low intensity signals for M^+ (**1** and **2**) or $[M^+{-}H]$ (**3**), $[M^+{-}F]$ (**1**, **2** and **3**), $[M^+{-}Ph]$ (**1**) or $[M^+{-}OPh]$ (**2** and **3**). A common high intensity signal on all the spectra is that corresponding to $[Os(SR_F)_3(PR_3)]^+$. Compounds **2** and **3** also show low intensity signals corresponding to $[M^+{-}H{-}2SR_F]$, $[M^+{-}3SR_F{-}3H]$, $[M^+{-}2SR_F{-}P(OPh)_3]$ and more considerable intensity signals of $[P(OPh)_2{}^+]$.

The solid-state structures of complexes **1**–**3** were determined by X-ray diffraction (Table 1). The trigonal-bipyramidal coordination geometry is consistent with all the five-coordinated Os(IV) complexes $[OsX(SR_F)_3(PR_3)]$ (X = Cl, SC_6F_5, SC_6F_4H; $R_F = C_6F_5$, C_6F_4H; PR_3 = tertiary phosphine) previously reported [15–17,19,21]. In all the X-ray characterized structures **1–3**, the axial positions are occupied by thiolate and P-containing ligands, with *trans* S4–Os1–P1 angles in the range 172.40(6)–177.10(5)°. In the case of compounds **2** and **3** bearing axial triphenylphosphite ligands, S4–Os1–P1 angles are closer to linearity than the corresponding angle in compound **1**, probably as a result of the smaller cone angle of the ligand triphenylphosphite (128°) compared to the cone angle of diphenyl(pentafluorophenyl)phosphine (158°) [24]. This difference in the cone angle allows a relaxed arrangement around the metal center, minimizing the steric hindrance for the aryl groups in the molecule. Regardless of the lower basicity of the phosphite compared to that of phosphine ligands, Os1–P1 bond lengths for complexes **2** and **3** are shorter by ca. 0.1 Å than the Os1–P1 bond distance in **1** (Table 2), corroborating the low steric requirement of the triphenylphosphite ligand. The bonds *trans* to the phosphine or phosphite ligands vary in the opposite way, albeit spanning a short range.

As for all the complexes $[OsX(SR_F)_3(PR_3)]$ where PR_3 is a phosphine, compound **1** exhibits a hemidirected arrangement for the equatorial SR_F substituents, which are oriented toward the axial thiolate (arrangement referred to "3-up", see Fig. 1). In contrast, the equatorial substituents in compounds **2** and **3** show a "2-up, 1-down" arrangement (Fig. 2), with two R_F rings directed toward the axial thiolate while the third is found in the phosphite hemisphere. The observed distribution for R_F groups within the coordination spheres in **1**–**3** is thus consistent with the different steric requirement of the P-containing ligands. Interestingly, the "2-up, 1-down" arrangement had been detected in solution for complexes $[Os(SC_6F_5)_4(P(C_6H_4X\text{-}4)_3)]$ (X = CF_3, Cl, F, H, CH_3, OCH_3), on the basis of variable-temperature ^{19}F NMR experiments [21]. However, this arrangement accounted only for the minor isomer in solution, while the major isomer in solution and all crystal structures were invariably found to correspond to the "3-up" isomer.

No significant intermolecular contacts like π–π or C–H–π interactions seem to help in crystal structures stabilization. For instance, in the case of **3**, π–π contacts are limited to two S1-benzene rings related by inversion, the centroid–centroid separation being 3.82 Å. Indeed, a stronger π–π intramolecular interaction is present in **1**, with a distance of 3.54 Å, because of the claw like geometry of the thiolates hemisphere. A consequence of the poor packing in this family of compounds is that very small change in formula may induce crystal symmetry modification, even if molecules are almost isostructural. This is the case for **2** and **3**, which, in spite of being chemically closely related and having similar molecular structures (r.m.s. for the best fit on non-H atoms: 0.82 Å), crystallize in different space groups (see Table 1).

Table 1
Summary of data collection and refinement[a] for complexes **1**–**3**.

Complex	**1**	**2**	**3**
Chemical formula	$C_{42}H_{14}F_{21}OsPS_4$	$C_{42}H_{19}F_{16}O_3OsPS_4$	$C_{42}H_{15}F_{20}O_3OsPS_4$
Formula weight	1266.94	1224.98	1296.95
Crystal size (mm^3)	0.46 × 0.40 × 0.06	0.62 × 0.28 × 0.14	0.42 × 0.32 × 0.24
T (K)	298(2)	298(2)	298(2)
Crystal system	monoclinic	monoclinic	triclinic
Space group	$P2_1/c$	$P2_1/n$	$P\bar{1}$
a (Å)	10.7253(8)	11.0196(16)	9.8938(6)
b (Å)	17.7966(12)	10.4846(9)	12.9027(12)
c (Å)	23.2151(18)	37.795(3)	19.3854(12)
α (°)	90.00	90.00	100.836(6)
β (°)	96.446(7)	92.974(9)	97.643(4)
γ (°)	90.00	90.00	109.169(5)
V (Å^3)	4403.1(6)	4360.8(8)	2244.6(3)
Z, *Z*′	4, 1	4, 1	2, 1
μ (mm^{-1})	3.244	3.261	3.186
$D_{calc.}$(g cm^{-3})	1.911	1.866	1.919
2θ Range (°)	3–52	4–55	3–60
Completeness (%)	100	99.9	99.4
R_1, wR_2 [$I > 2\sigma(I)$]	0.049, 0.113	0.041, 0.079	0.035, 0.071
R_1, wR_2 (all data)	0.079, 0.129	0.069, 0.091	0.050, 0.077
Reflections collected/unique	15 273/8672	12 782/10 010	15 093/13 006
R_{int}	0.051	0.037	0.021
Data/parameters ratio	8672/623	10 010/605	13 006/641
Goodness of fit (GOF) on F^2	1.015	1.034	1.043

[a] Formula used for computing R_1, wR_2, R_{int} and *S* indices are those applied by SHELXL [25].

Table 2
Coordination bond lengths (Å) and angles (°) for complexes **1**, **2**, and **3**.

	1	**2**	**3**
Bond lengths (Å)			
Os1–S1	2.1990(17)	2.2103(13)	2.2402(9)
Os1–S2	2.2170(18)	2.2051(15)	2.1872(9)
Os1–S3	2.2362(18)	2.2195(14)	2.2352(9)
Os1–S4	2.4001(17)	2.4433(13)	2.4404(8)
Os1–P1	2.4031(18)	2.3031(13)	2.2954(8)
Bond angles (°)			
S1–Os1–S2	114.77(7)	118.62(6)	117.51(4)
S1–Os1–S3	124.35(8)	120.09(6)	126.60(4)
S2–Os1–S3	119.14(8)	121.28(6)	115.82(4)
S1–Os1–S4	96.13(6)	91.98(5)	91.02(3)
S2–Os1–S4	88.81(6)	93.18(5)	95.99(3)
S3–Os1–S4	97.67(7)	85.39(5)	86.10(3)
S1–Os1–P1	87.20(6)	86.72(5)	84.78(3)
S2–Os1–P1	83.60(6)	85.18(5)	87.58(3)
S3–Os1–P1	85.97(7)	97.51(5)	94.93(3)
S4–Os1–P1	172.40(6)	177.10(5)	175.42(3)

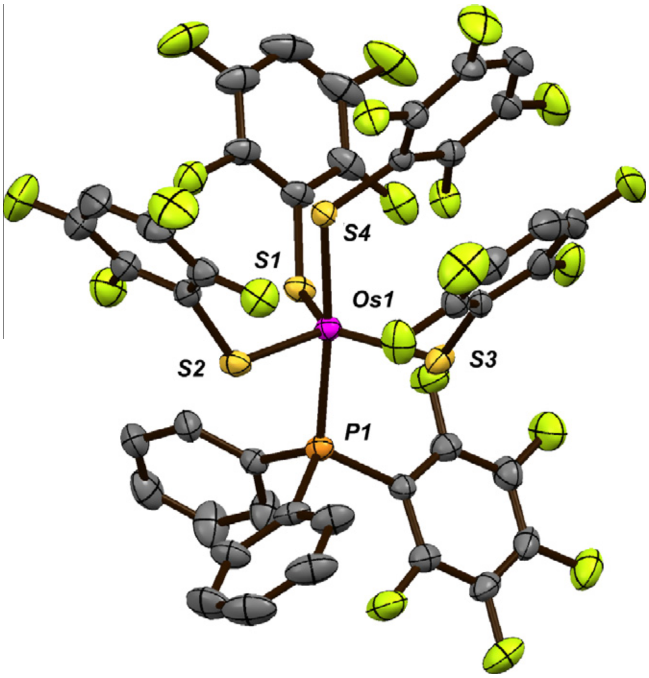


Fig. 1. Molecular structure of complex [Os(SC_6F_4H-4)$_4$(PPh$_2$(C_6F_5))] **1** with displacement ellipsoids drawn at the 25% probability level. H atoms have been omitted.

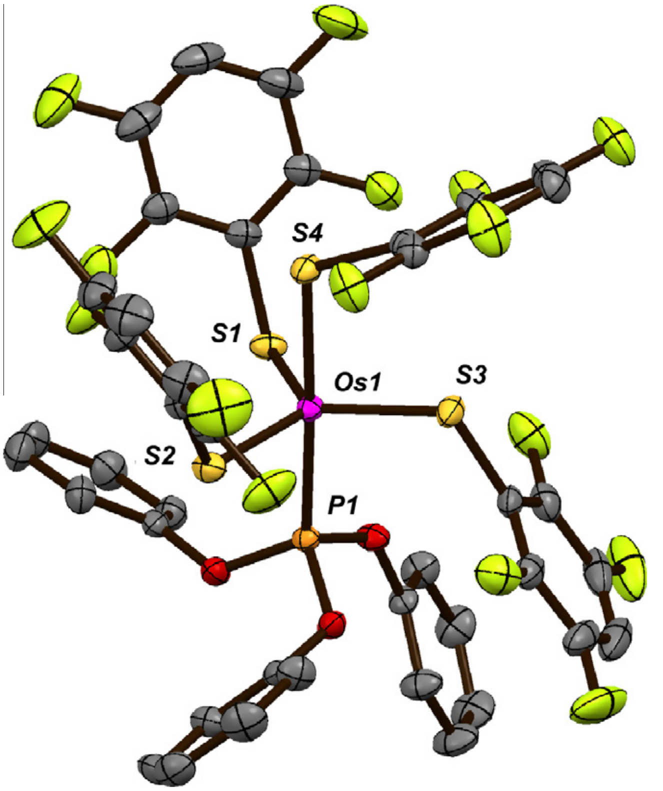
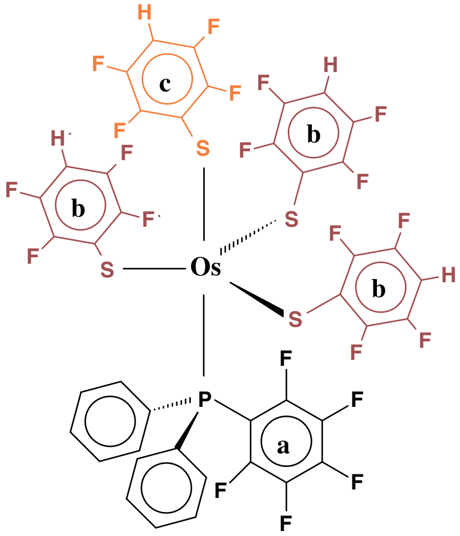


Fig. 2. Molecular structure of complex [Os(SC_6F_4H-4)$_4$(P(OPh)$_3$)] **2** with displacement ellipsoids drawn at the 25% probability level. H atoms have been omitted.



Scheme 1. Drawing of [Os(SC_6F_4H-4)$_4$(PPh$_2$(C_6F_5))] **1** showing the different fluorinated phenyl rings as in the X-ray structure.

2.1. NMR studies

2.1.1. [Os(SC_6F_4H-4)$_4$(PPh$_2$(C_6F_5))] **1**

At room temperature the $^{31}P\{^1H\}$ NMR spectrum of compound **1** (Scheme 1) shows one multiple signal corresponding to the phosphorous coupled to the fluorine atoms of the ring C_6F_5 (**a**), while the ^1H NMR spectrum exhibits: at low field three signals corresponding to the *ortho*, *meta* and *para* hydrogen atoms of two equivalent C_6H_5 rings (relative intensities 4:4:2). Yet on the aromatic region, at higher field, the spectrum exhibits a broad singlet from three equatorial $^-SC_6F_4H$ ligands (rings **b**, relative intensity 3, Scheme 1), and a triplet of triplets corresponding to the axial $^-SC_6F_4H$ (ring **c**, relative intensity 1, Scheme 1). The ^{19}F NMR spectra of **1**, from +80 °C to room temperature, show: a group of three signals corresponding to *ortho*, *para* and *meta* fluorine atoms of the C_6F_5 group (ring **a**, Scheme 1), at low, medium and high field, respectively (A_2BC_2 spin system, relative integrals 2:1:2); a group of two signals from *ortho* and *meta*-fluorine atoms of three equivalent equatorial $^-SC_6F_4H$-4 ligands (rings **b**, Scheme 1) (A_2B_2 spin system, relative integrals 6:6); and a group of another two signals corresponding to *ortho* and *meta*-fluorine atoms of an axial $^-SC_6F_4H$-4 ligand (ring **c**, Scheme 1) (A_2B_2 spin system, relative integral 2:2). ^{19}F–^{19}F NMR experiments were used to unambiguously identify each set of signals. All these NMR spectra are consistent with a configuration "3-up" of three equivalent C_6F_4H-substituents of the equatorial thiolates. However, as the temperature is decreased (Fig. 3) the original sharp singlets 6:6 from *ortho* and

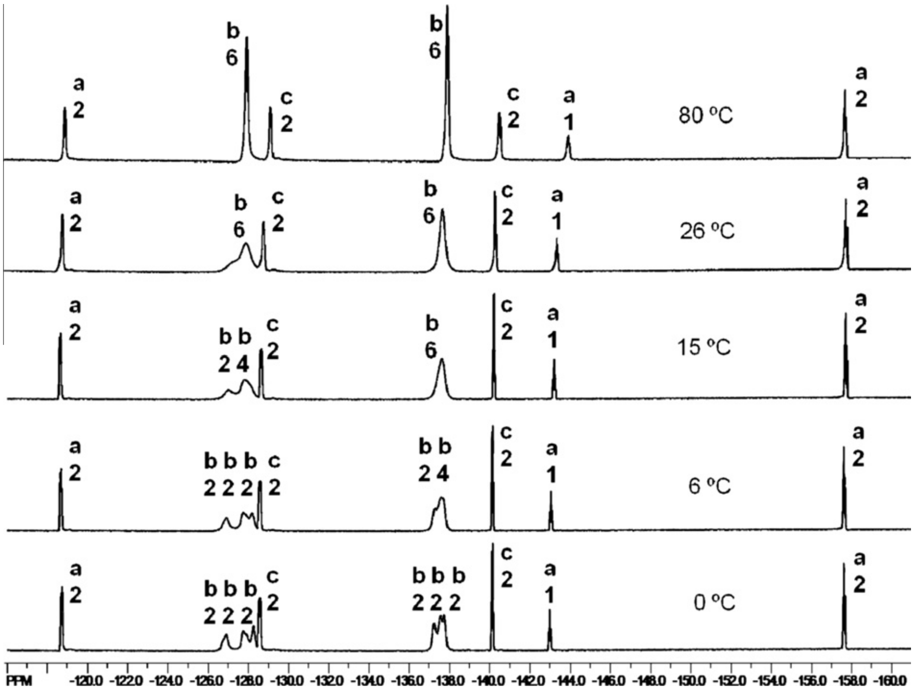


Fig. 3. Variable temperature ^{19}F NMR spectra of $[Os(SC_6F_4H\text{-}4)_4(PPh_2(C_6F_5))]$ **1** in $C_6D_5CD_3$.

meta-fluorine atoms of the equatorial thiolates broaden and each one eventually collapses giving rise to two signals [relative integrals ca. 2:4 (*ortho*) and 2:4 (*meta*)], a fact which is congruent with a set of equatorial thiolates where one substituent is non-equivalent respect to the other two. On additional decreasing of temperature, each signal integrating four experiences a second collapse giving two signals 2:2. In contrast, the absorptions from the rings **a** and **c** remain unaltered along the full range of temperatures studied. At low temperatures, the spectrum is consistent with the "2-up, 1-down" isomer (with the two 2-up equivalent C_6F_4H groups restricted to rotate about their C—S bonds) without evidence of an equilibrium between the two different molecular species. The fact that the "3-up" isomer suddenly disappear to produce the "2-up, 1-down" isomer is not probable at all. For these reasons we ruled out the "2-up, 1-down" configuration. We think that the "3-up" configuration remains in all the range of temperatures analyzed and propose as a more congruent possibility that, as the temperature decreases, the equatorial thiolates are gradually frozen (two sequential collapses) giving a configuration probably nearly to that found in the X-ray diffraction structure.

2.1.2. $[Os(SC_6F_4H\text{-}4)_4(P(OPh)_3)]$ 2

At room temperature, the $^{31}P\{^1H\}$ NMR spectrum of compound **2** shows a singlet, consistent with the presence of one species in solution, as found above for the product **1**. The room temperature ^1H NMR spectrum exhibits (Fig. 4), at low field, the signals corresponding to the *ortho*, *meta* and *para* hydrogen atoms of the C_6H_5 rings of the $P(OPh)_3$ ligand, along the residual protio atoms of the solvent. Also on the aromatic region, at higher field, the spectrum shows a broad singlet (relative integral 2) attributable to the *para* hydrogen atoms of two equivalent equatorial $^-SC_6F_4H$ ligands in the orientation "2-up" (rings **b**, Scheme 2) and two triplets of triplets (relative integrals 1:1) attributable to the *para*-hydrogen atoms of two non-equivalent equatorial "1-down" and axial $^-SC_6F_4H$ ligands (rings **a** and **c**, Scheme 2). The ^{19}F NMR spectrum, at room temperature, shows eight signals of the same integral, four of these at low field in the *ortho* fluorine region and the other four, at higher field, in the *meta* fluorine region. This spectrum is consistent with two equivalent equatorial $^-SC_6F_4H$ ligands in the orientation "2-up" (rings **b**), in which each ring has non-equivalent *ortho* fluorine atoms and non-equivalent *meta* fluorine atoms (*ortho*, *ortho′*, *meta*, *meta′*; 1:1:1:1) (AA′BB′ spin systems), one equatorial $^-SC_6F_4H$ ligand in the orientation "1-down" (ring **a**) with equivalent *ortho* fluorines and equivalent *meta* fluorines (*ortho*, *meta*; 2:2; A_2B_2 spin system), and one axial $^-SC_6F_4H$ ligand (ring **c**) also with equivalent *ortho* fluorines and equivalent *meta* fluorines (*ortho*, *meta*; 2:2; A_2B_2 spin system). The COSY ^{19}F–^{19}F NMR spectra confirm these three sets of signals. At lower temperatures the number of signals and their integrals remain constant. However, when the temperature is increased (Fig. 5) the two *ortho* and *ortho′* signals and the two *meta* and *meta′* signals from the rings **b** coalesce, confirming a fluxional process that involves the two equivalent equatorial $^-SC_6F_4H$ ligands in the orientation "2-up" (rings **b**, Scheme 2). This is congruent with two C_6F_4H rings (**b**) exhibiting restricted rotation about their C—S bonds at low temperatures but becoming free to rotate as the temperature increases.

Thus, as seen in the ^1H NMR studies, the ^{19}F NMR spectra are also consistent with the conformation "2-up, 1-down" for the substituents of the equatorial thiolates in solution.

2.1.3. $[Os(SC_6F_5)_4(P(OPh)_3)]$ 3

As for the complex **2**, the room temperature $^{31}P\{^1H\}$ NMR spectrum of compound **3** shows a singlet, while the ^1H NMR spectrum only exhibits the signals corresponding to the aromatic-hydrogen atoms of the three C_6H_5 rings of the $P(OPh)_3$ ligand. The room temperature ^{19}F NMR spectrum shows four signals at low field on the *ortho* region (relative integrals 2:2:2:2), three well defined triplets (relative integrals 1:2:1) at medium field on the *para* region, and three additional multiplets (relative integrals 2:4:2) at high field on the *meta* region. These results can be rationalized with the conformation "2-up, 1-down" for the substituents of the equatorial thiolates, and a restricted rotation about the C—S bonds of the two equivalent equatorial thiolates "2-up" to make thus non-equivalent *ortho* fluorine and non-equivalent *meta* fluorine atoms in each of the rings **b**, although *meta* and *meta′* fluorine atoms

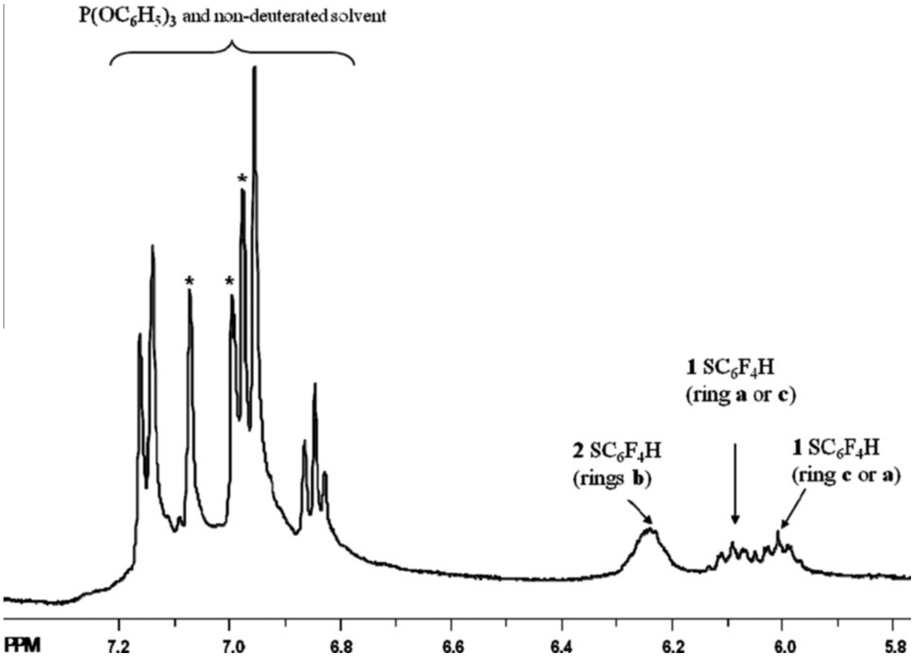
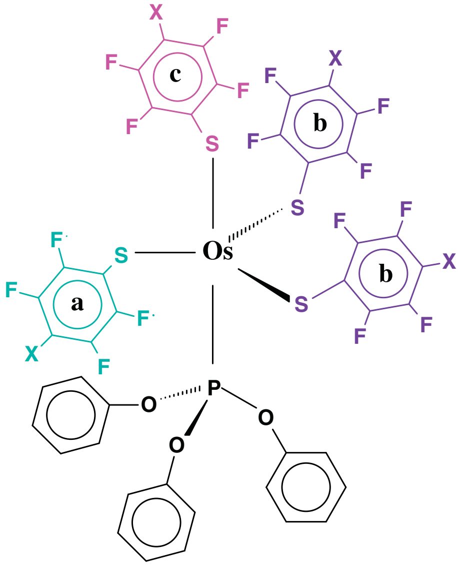


Fig. 4. ^1H NMR spectrum of $[Os(SC_6F_4H\text{-}4)_4(P(OC_6H_5)_3)]$ **2** at RT, in $C_6D_5CD_3$.



Scheme 2. Drawing of $[Os(SC_6F_4X\text{-}4)_4(P(OPh)_3)]$ **2** (X = H) or **3** (X = F) showing the different fluorinated phenyl rings as in the X-ray structures. The ^{19}F NMR signals of rings **b**, could be assigned, while those for **a** and **c** remain interchangeable.

would be both coupled to only one *para* fluorine atom. It is worth to notice that, although the *meta* region does not exhibit four signals 2:2:2:2 but three signals 2:4:2, the signal integrating four is broad by the overlap of two *meta* signals 2:2. This interpretation is corroborated by the COSY ^{19}F–^{19}F NMR spectra (Fig. 6).

3. Conclusion

As all the members of the series $[OsX(SR_F)_3(PR_3)]$, where X is a Cl^- or ^-SR_F ligand (R_F is a fluorinated phenyl group), and PR_3 is a tertiary phosphine [15,16,19–23], in the solid state the compound $[Os(SC_6F_4H)_4(PPh_2(C_6F_5))]$ **1** presents the conformation "3-up" for the equatorial thiolate-substituents in a trigonal bipyramidal geometry. In solution, the NMR spectra are consistent with this conformation. However, in the solid state, the presence of one oxygen atom in the P—C_6H_5 bonds of the compounds **2** and **3**, related to compounds $[Os(SC_6F_4H\text{-}4)_4(PPh_3)]$ **4** [16,20] and $[Os(SC_6F_5)_4(PPh_3)]$ **5** [19], causes a conformational change, thus **2** and **3** show the conformation "2-up, 1-down" while **4** and **5** exhibit the conformation "3-up". In solution, **2** and **3** also exhibit the conformation "2-up, 1-down", while **5** shows both of these conformations, being more abundant the isomer "3-up" [21].

4. Experimental

All reactions were carried out under argon atmospheres using conventional Schlenk-tube techniques. Thin-layer chromatography (Merck, silica gel 60 F_{254}) was used to monitor the progress of the reactions under study with hexane–dichloromethane (4:1) as eluent. The starting materials: osmium tetraoxide, pentafluorobenzenethiol, 2,3,5,6-tetrafluorobenzenethiol, triphenylphosphite and pentafluorophenyldiphenylphosphine were used as received from Aldrich Chemical Co.

Melting points were obtained on a Fisher-Johns apparatus and are uncorrected.

Infrared spectra were recorded on a 750 Nicolet Fourier Transform Magna-IR Spectrometer as KBr pellets. Data are expressed in wavenumbers (cm^{-1}) with relative intensities (vs = very strong, s = strong, m = medium, w = weak).

^1H, $^{31}P\{^1H\}$, ^{19}F, and COSY ^{19}F–^{19}F NMR spectra were recorded using a Varian Mercury VX400 spectrometer. ^1H NMR data (400 MHz) were referenced internally using the residual protio solvent resonance ($PhCHD_2$, quintuplet, 2.08 ppm or $CHCl_3$, singlet, 7.26 ppm) relative to $SiMe_4$ ($\delta = 0$), ^{19}F (376 MHz) externally to $CFCl_3$ ($\delta = 0$) and ^{31}P (162 MHz) externally to 85% H_3PO_4 ($\delta = 0$). Data are given as chemical shifts (δ) using the high positive convention [multiplicity, relative intensity, assignment, J/Hz]; s, singlet; d, doublet; t, triplet; m, multiplet; br, broad.

Positive ion FAB mass spectra were recorded on a Jeol JMS-SX102A mass spectrometer operated at an accelerating voltage of

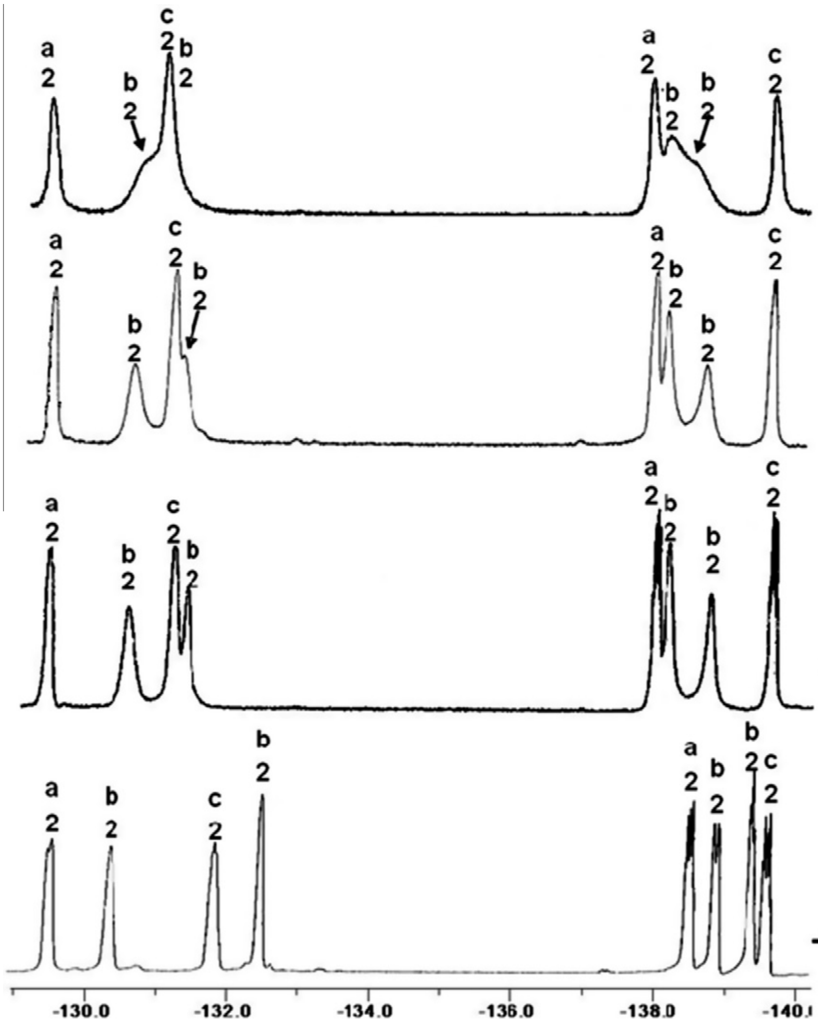


Fig. 5. Variable temperature ^{19}F NMR spectra of $[Os(SC_6F_4H)_4(P(OC_6H_5)_3)]$ **2** in $C_6D_5CD_3$.

10 kV. Samples were desorbed from a 3-nitrobenzyl alcohol (NOBA) matrix using 3 keV xenon atoms. Mass measurements in FAB are performed at a resolution of 3000 using magnetic field scans and the matrix ions as the reference material.

Elemental analyses were determined by Galbraith Laboratories Inc.

4.1. [Os(SC$_6$F$_4$H-4)$_4$(PPh$_2$(C$_6$F$_5$))] **1**

2,3,5,6-Tetrafluorofluorobenzenethiol (0.8 mL, 6.0 mmol) was dissolved in ethanol (25 mL), then osmium tetraoxide (0.25 g, 1.0 mmol) was added. The mixture rapidly turned black, $PPh_2(C_6F_5)$ (2.11 g, 6.0 mmol) was added and the mixture refluxed for 3 h turning green. The solvent was distilled off under vacuum and the solid product was purified through a silica gel chromatographic column eluted with hexane–dichloromethane 4:1. Compound **1** was isolated as a green microcrystalline powder (0.265 g, 21% yield). Dark green single crystals of **1** were obtained by slow evaporation of the eluent. *Anal.* Calc. for $C_{42}H_{14}F_{21}OsPS_4$: C, 39.82; H, 1.11; S, 10.12. Found: C, 39.63; H, 1.14; S, 10.30%. Mp: 175 °C decomposes. IR (KBr, cm^{-1}): ν_{thiolate} 1492(vs), 1431(m), 1228(m), 1177(m), 918(vs), 712(m); $\nu_{\text{phosphine}}$ 1521(m), 1474(s), 1097(m), 985(w), 747(w), 693(w). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$, RT): δ 3.23 (br s, $PPh_2(C_6F_5)$). ^{19}F NMR ($C_6D_5CD_3$, 80 °C): ring **a** of $PPh_2C_6F_5$, δ −119.06 (br s, 2F*o*, C_6F_5), −144.32 (br s, 1F*p*, C_6F_5), −158.21 (m, 2F*m*, C_6F_5); rings **b** of the *equatorial* SC_6F_4H ligands, δ −128.19 (br s, 6F*o*, 3SC_6F_4H-*eq*), −138.26 (br s, 6F*m*, 3SC_6F_4H-*eq*); ring **c** of the *axial* SC_6F_4H ligand, δ −129.38 (br s, 2F*o*, 1SC_6F_4H-*ax*), −140.87 (m, 2F*m*, 1SC_6F_4H-*ax*). ^{1}H NMR ($C_6D_5CD_3$, RT): δ 7.96 (dd, 4H*o*, $PPh_2C_6F_5$, $^3J_{Ho-Hm}$ = 7.6 Hz, $^3J_{Ho-P}$ = 12.2 Hz), 7.22 (td, 4H*m*, $PPh_2C_6F_5$, $^3J_{Hm-Ho/p}$ = 7.6 Hz, $^4J_{Hm-P}$ = 2.8 Hz), 7.17–7.13 (m, 2H*p*, $PPh_2C_6F_5$,), 6.02 (br s, 3H*p*, 3SC_6F_4H-*eq* (rings **b**)), 5.85 (tt, H*p*, 1SC_6F_4H-*ax*, $^3J_{Hp-Fm}$ = 10.0 Hz, $^4J_{Hp-Fo}$ = 7.2 Hz (ring **c**)). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 1268 (5) M$^+$, 1249 (1) [M$^+$−F], 1191 (1) [M$^+$−Ph], 1087 (100) [M$^+$−(SC_6F_4H)], 938 (3) [M$^+$−(SC_6F_4H)−(C_6F_4H)].

4.2. [Os(SC$_6$F$_4$H-4)$_4$(P(OPh)$_3$)] **2**

The procedure is analogous to that for **1**. Dark green single crystals of **2** were obtained by slow evaporation of a hexane–dichloromethane 4:1 solution of the compound (0.208 g, 17% yield). *Anal.* Calc. for $C_{42}H_{19}F_{16}O_3OsPS_4$: C, 41.18; H, 1.56; S, 10.47. Found: C, 41.37; H, 1.73; S, 10.65%. Mp: 110 °C decomposes. IR (KBr, cm^{-1}): ν_{thiolate} 1492(vs), 1432(w), 1229(m), 1181(s), 924(vs), 713(m); $\nu_{\text{thriphenylphosphite}}$ 1591(w), 1204(m), 1181(s), 1158(s), 763(m), 692(w). ^{31}P{^{1}H} NMR ($C_6D_5CD_3$, RT): δ −12.0 (s, $P(OC_6H_5)_3$). ^{19}F NMR ($C_6D_5CD_3$, RT): ring **a** of the *equatorial* 1-down-SC_6F_4H ligand, δ −129.34 (m, 2F*o*, 1SC_6F_4H-*eq*-“1-down”), −138.84 (pq, 2F*m*, 1SC_6F_4H-*eq*-“1-down”, $^3J_{Fm-Fo}$ = 12.4 Hz, $^3J_{Fm-H}$ = 10.9 Hz); rings **b** of the *equatorial* 2-up-SC_6F_4H ligands, δ −130.48 (br s, 2F*o*, ½(2SC_6F_4H)-*eq*-“2-up”), −131.73 (br s, 2F*o*′,

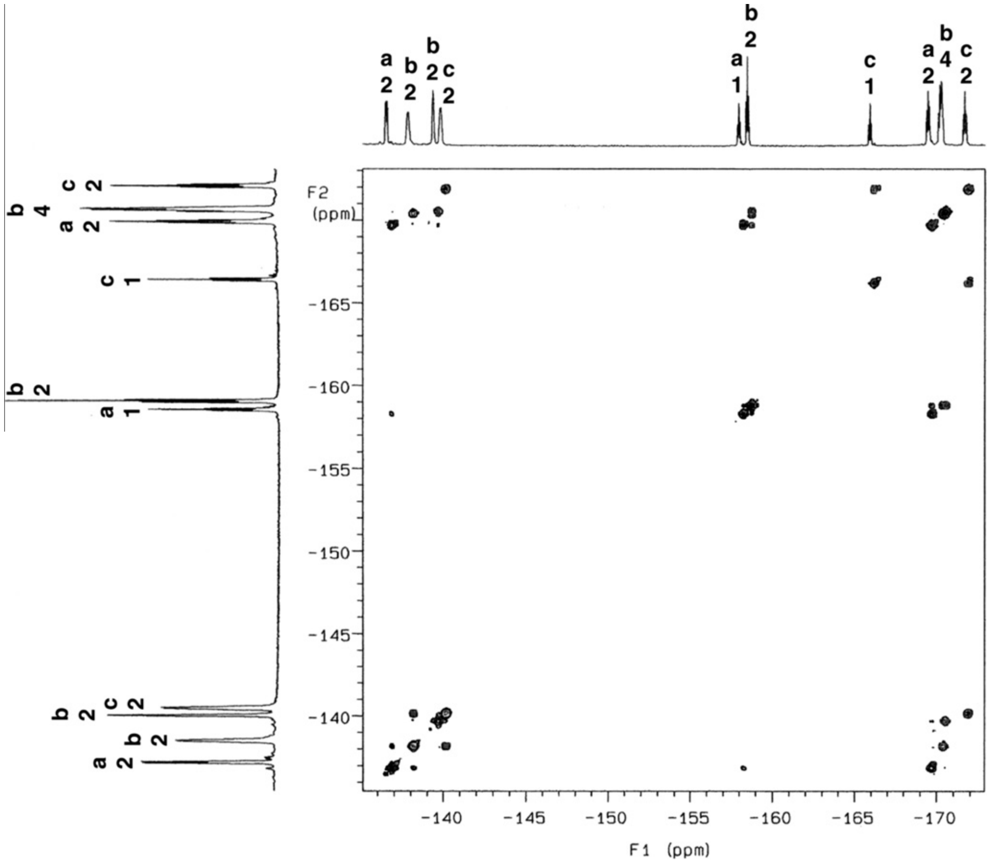


Fig. 6. COSY ^{19}F–^{19}F NMR spectrum of $[Os(SC_6F_5)_4(P(OC_6H_5)_3)]$ **3** in $CDCl_3$ at room temperature.

½($2SC_6F_4H$)-*eq*-“2-up”), −139.06 (m, 2F*m*, ½($2SC_6F_4H$)-*eq*-“2-up”), −139.71 (m, 2F*m*′, ½($2SC_6F_4H$)-*eq*-“2-up”); ring **c** of the *axial* SC_6F_4H ligand, δ −131.42 (m, 2F*o*, $1SC_6F_4H$-*ax*), −140.51 (m, 2F*m*, $1SC_6F_4H$-*ax*). ^1H NMR ($C_6D_5CD_3$, RT): δ 7.17–6.83 (m, $P(OC_6H_5)_3$; and aromatic protio atoms of residual non-deuterated solvent), 6.24 (br s, 2H*p*, $2SC_6F_4H$)-*eq*-“2-up”), 6.09 (tt, 1H*p*, $1SC_6F_4H$, $^3J_{Hp-Fm} = 9.6$ Hz, $^3J_{Hp-Fo} = 7.2$ Hz), 6.00 (tt, 1H*p*, $1SC_6F_4H$, $^3J_{Hp-Fm} = 9.6$ Hz, $^3J_{Hp-Fo} = 7.2$ Hz). The FAB$^+$-MS {*m*/*z* (%) [fragment]}: 1226 (2) M^+, 1207 (1) $[M^+–F]$, 1133 (2) $[M^+–(OPh)]$, 1045 (92) $[M^+–(SC_6F_4H)]$, 863 (3) $[M^+–H–2(SC_6F_4H)]$, 680 (4) $[M^+–3(SC_6F_4H)–3H]$, 554 (3) $[M^+–2(SC_6F_4H)–(P(OPh)_3)]$, 217 (23) $[P(OPh)_2^+]$.

4.3. $[Os(SC_6F_5)_4(P(OPh)_3)]$ 3

The procedure is analogous to that for **1** and **2**. Deep green single crystals of **3** were obtained by slow evaporation of a hexane–dichloromethane 4:1 solution of the compound (0.259 g, 20%). *Anal.* Calc. for $C_{42}H_{15}F_{20}O_3OsPS_4$: C, 38.83; H, 1.16; S, 9.85. Found: C, 38.70; H, 1.22; S, 9.85%. Mp: 160 °C. IR (KBr, cm^{-1}): $\nu_{thiolate}$ 1509(vs), 1488(vs), 1086(vs), 982(vs), 849(s); $\nu_{triphenylphosphite}$ 1589(m), 1203(s), 1178(s), 1156(s), 765(vs), 686(m). ^{19}F NMR ($CDCl_3$, RT): ring **a** of the *equatorial* 1-down-SC_6F_5 ligand, δ −128.5 (d, 2F*o*, $1SC_6F_5$-*eq*-“1-down”, $^3J_{Fo-Fm} = 23.7$ Hz), −149.9 (t, 1F*p*, $1SC_6F_5$-*eq*-“1-down”, $^3J_{Fp-Fm} = 20.7$), −161.4 (m, 2F*m*, $1SC_6F_5$-*eq*-“1-down”); rings **b** of the *equatorial* 2-up-SC_6F_5 ligands, δ −129.9 (br s, 2F*o*, ½($2SC_6F_5$)-*eq*-“2-up”), −131.4 (br s, 2F*o*′, ½($2SC_6F_5$)-*eq*-“2-up”), −150.5 (t, 2F*p*, ($2SC_6F_5$)-*eq*-“2-up”, $^3J_{Fp-Fm} = 20.7$), −162.1 (br m, 2F*m* and 2F*m*′, $2SC_6F_5$-*eq*-“2-up”); ring **c** of the *axial* SC_6F_5 ligand, δ −131.9 (br d, 2F*o*, $1SC_6F_5$-*ax*), −157.8 (t, 1F*p*, $1SC_6F_5$-*ax*, $^3J_{Fp-Fm} = 20.7$ Hz); −163.5 (m, 2F*m*, $1SC_6F_5$-*ax*). ^1H NMR ($CDCl_3$, RT): δ 7.35 (t, 6H*m*, $P(OC_6H_5)_3$, $^3J_{Hm-Ho/p} = 7.8$ Hz), 7.26 (t, 3H*p*, $P(OC_6H_5)_3$, $^3J_{Hp-Hm} = 9$ Hz; and aromatic protio atoms of residual non-deuterated solvent), 7.15 (d, 6H*o*, $P(OC_6H_5)_3$, $^3J_{Ho-Hm} = 8.1$ Hz). FAB$^+$-MS {*m*/*z* (%) [fragment]}: 1297 (1) $[M^+–H]$, 1279 (1) $[M^+–F]$, 1205 (1) $[M^+–(OPh)]$, 1099 (100) $[M^+–(SC_6F_5)]$, 1051 (10) $[M^+–(OPh)–2Ph)]$, 899 (5) $[M^+–H–2(SC_6F_5)]$, 698 (3) $[M^+–3(SC_6F_5)–3H]$, 590 (4) $[M^+–2(SC_6F_5)–(P(OPh)_3)]$, 217 (30) $[P(OPh)_2^+]$.

4.4. X-ray diffraction data

Air stable single-crystals of complexes **1** (dark green), **2** (dark green) and **3** (deep green) were obtained by slow evaporation of the corresponding solutions in hexane–dichloromethane 4:1. X-ray diffraction data were measured at 298(2) K, using a Bruker P4 diffractometer [26] equipped with the Mo Kα radiation ($\lambda = 0.71073$ Å). Data were corrected for absorption effects on the basis of ψ-scans (**1–2**) or crystal faces indexation (**3**). The structures were solved and refined using SHELX software [25]. In all cases, final refinements were carried out without neither restraints nor constraints for non-H-atoms. H atoms were placed in idealized positions and refined as riding on their C atoms with fixed isotropic *U*. Data collection parameters and structure refinement are summarized in Table 1. Details may be found in the deposited CIF along with full geometric parameters.

Acknowledgements

We are grateful to VIEP (ARCS-NAT-09-G) and PROMEP for financial support. S.B. acknowledges BUAP for the use of diffraction facilities.

Appendix A. Supplementary data

CCDC 802483, 802484, and 802485 contain the supplementary crystallographic data for **1–3**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

References

[1] S.A. Koch, M. Millar, J. Am. Chem. Soc. 105 (1983) 3362.
[2] M.M. Millar, T. O'Sullivan, N. de Vries, S.A. Koch, J. Am. Chem. Soc. 107 (1985) 3714.
[3] S.-L. Soong, J.H. Hain Jr., M. Millar, S.A. Koch, Organometallics 7 (1988) 556.
[4] S.P. Satsangee, J.H. Hain Jr., P.T. Cooper, S.A. Koch, Inorg. Chem. 31 (1992) 5160.
[5] C.J. Bourgeois, H. Huang, R.B. Larichev, L.N. Zakharov, A.L. Rheingold, R.P. Hughes, Organometallics 26 (2007) 264.
[6] M. Arroyo, S. Bernès, M. Cerón, V. Cortina, C. Mendoza, H. Torrens, Inorg. Chem. 46 (2007) 4857.
[7] M.C. Carrión, A. Guerrero, F.A. Jalón, B.R. Manzano, A. de la Hoz, R.M. Claramunt, V. Milata, J. Elguero, Inorg. Chem. 42 (2003) 885.
[8] L.R. Falvello, J. Forniés, C. Fortuño, A. Martín, A.P. Martínez-Sariñena, Organometallics 16 (1997) 5849.
[9] M. Arroyo, S. Bernès, J.L. Briansó, E. Mayoral, R.L. Richards, J. Rius, H. Torrens, J. Organomet. Chem. 599 (2000) 170.
[10] J. Forniés, M.A. Gómez-Saso, A. Martín, F. Martínez, B. Menjón, J. Navarrete, Organometallics 16 (1997) 6024.
[11] A. Gelling, M.D. Olsen, K.G. Orrell, A.G. Osborne, V. Sik, Inorg. Chim. Acta 264 (1997) 257.
[12] J.A. Casares, S. Coco, P. Espinet, Y.-S. Lin, Organometallics 14 (1995) 3058.
[13] W.A.W.A. Bakar, J.L. Davidson, W.E. Lindsell, K.J. McCullough, J. Chem. Soc., Dalton Trans. (1990) 61.
[14] W.A.W.A. Bakar, J.L. Davidson, W.E. Lindsell, K.J. McCullough, K.W. Muir, J. Chem. Soc., Dalton Trans. (1989) 991.
[15] A. Hills, D.L. Hughes, R.L. Richards, M. Arroyo, D. Cruz-Garritz, H. Torrens, J. Chem. Soc., Dalton Trans. (1991) 1281.
[16] M. Arroyo, J.A. Chamizo, D.L. Hughes, R.L. Richards, P. Román, P. Sosa, H. Torrens, J. Chem. Soc., Dalton Trans. (1994) 1819.
[17] M.-L. Abasq, C.J. Pickett, R.L. Richards, M. Arroyo, J.A. Chamizo, A. Calderón, P. Sosa, H. Torrens, Polyhedron 15 (1996) 3623.
[18] M. Arroyo, C. Mendoza, E. Mayoral, H. Torrens, R.L. Richards, Rev. Mex. Fís. 46 (Suppl. 2) (2000) 120.
[19] C. Mendoza, S. Bernès, M. Arroyo, Acta Crystallogr. C62 (2006) m201.
[20] M. Cerón, M. Arroyo, S. Bernès, Acta Crystallogr. E62 (2006) m2167.
[21] M. Arroyo, C. Mendoza, S. Bernès, H. Torrens, H. Morales-Rojas, Polyhedron 28 (2009) 2625.
[22] A. Arias, L. Meléndez, S. Bernès, M. Arroyo, Acta Crystallogr. E66 (2010) m477.
[23] C. Mendoza, S. Bernès, H. Torrens, M. Arroyo, Organometallics 29 (2010) 2646.
[24] C.A. Tolman, Chem. Rev. 77 (1977) 313.
[25] G.M. Sheldrick, Acta Crystallogr. A64 (2008) 112.
[26] XSCAnS (Release 2.21) Users Manual, Siemens Analytical X-ray Instruments Inc., Madison, WI, USA, 1996.