Inorganic Chemistry

pubs.acs.org/IC

Communication

Unequivocal Characterization of an Osmium Complex with a Terminal Sulfide Ligand and Its Transformation into Hydrosulfide and Methylsulfide

María L. Buil, Miguel A. Esteruelas,* Enrique Oñate, and Nieves R. Picazo

Cite This: *Inorg. Chem.* 2024, 63, 5779−5782

Read Online

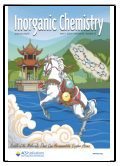
ACCESS | Metrics & More | Article Recommendations | Supporting Information

ABSTRACT: Deprotonation of the thioamidate group of [OsH{κ^2-*N*,*S*-[NHC(CH_3)S]}(≡CPh)(IPr)(P^iPr_3)]OTf [**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene; OTf = CF_3SO_3] results in the release of acetonitrile and formation of the terminal sulfide complex OsH(S)(≡CPh)(IPr)(P^iPr_3) (**2**), which has been transformed into the hydrosulfide [OsH(SH)(≡CPh)(IPr)(P^iPr_3)]OTf (**3**) and the methylsulfide [OsH(SMe)(≡CPh)(IPr)(P^iPr_3)]OTf (**4**) through protonation and methylation reactions, respectively. The structure, spectroscopic characteristics, and reactivity of these compounds are compared. Reactions of **3** and **4** with 2-hydroxypyridine and 2-mercaptopyridine afford [OsH{κ^2-*X*,*N*-[X-py]}(≡CPh)(IPr)(P^iPr_3)]OTf [X = O (**5**), S(**6**)].

Metal sulfides have attracted great attention in recent years. The interest is mainly motivated by the relevance of these types of compounds in biological systems and by the role they can play in the metal-catalyzed hydrodesulfurization of fossil fuels.[1] Sulfur is larger and softer than oxygen. Its 3p orbitals are more diffuse, and therefore it forms weaker π interactions with other atoms. Thus, sulfur tends to form bridging rather than terminal interactions. As a consequence, the terminal sulfide compounds of transition metals are difficult to stabilize and the number of these compounds is significantly much less than that of the terminal oxo derivatives.[2] Ruthenium and osmium are overwhelming pieces of evidence of this. Both elements form numerous terminal oxo complexes, which play important roles in stoichiometric and catalytic oxidations.[3] In contrast, no terminal sulfide derivatives are known for ruthenium, although they have been proposed as intermediates in the formation of polymetallic derivatives,[4] while the existence of a single such osmium complex has been suggested based on very little evidence. In 1994, Shapley and co-workers reported the presence of a terminal sulfide ligand in a salt of stoichiometry [N(*n*-Bu)$_4$][Os(N)(S)(CH_2SiMe_3)$_2$], according to a band at 613 cm^{-1} on the IR spectrum. The salt was obtained in low yield from the reaction crude resulting from the treatment of [N(*n*-Bu)$_4$][Os(N)(CH_2SiMe_3)$_2$$Cl_2$] with Li_2S. The crude containing mainly binuclear species.[5] Like terminal oxo compounds, terminal sulfide complexes are frequent for iron[6] and the transition elements found on the left side of Group 8,[7] while they are very rare for the 3d metals on the right side[8] and practically unknown for the platinum group metals.[9] Some terminal sulfide derivatives of these elements have been proposed as transient species for the formation of condensed metal frameworks.[4,10] In two cases, the coordination of a terminal sulfur atom to a platinum group metal has been suggested, but they are controversial: the osmium salt mentioned above and a [Ru_2Pd] cluster containing a Pd−S terminal bond.[11] Although the latter has been characterized by X-ray diffraction analysis, the structural parameters obtained and therefore the validity of the structure seem to raise doubts.[9] This Communication shows the stabilization and complete and unequivocal characterization of an osmium terminal sulfide complex, which represents a rare example within the chemistry of platinum group elements. In addition, its transformation into hydrosulfide and methylsulfide derivatives and a comparative study of the structures, spectroscopic characteristics, and reactivity of the three compounds are included.

We recently reported the preparation of the first aromatic metallathiazole derivative of a transition metal. The procedure involves an intramolecular expansion of the four-membered metalladiheterocycle ring that forms the thioamidate group and the osmium atom of the alkylidyne complex [OsH{κ^2-*N*,*S*-[NHC(CH_3)S]}(≡CPh)(IPr)(P^iPr_3)]OTf (**1**; IPr = 1,3-bis(2,6-diisopropylphenyl)imidazolylidene; OTf = CF_3SO_3), with the C sp atom of the alkylidyne ligand. The process was carried out in two steps. The expansion initially generated an osmathiazolium derivative, which upon subsequent deprotonation produced osmathiazole.[12] In the search to simplify and generalize the procedure, we attempted to perform a "one-pot" transformation from amidatoosmium alkylidyne to osmathiazole. To do this, we decided to use potassium *tert*-butoxide as a deprotonating agent. To our surprise, the addition of the base to solutions of **1** in tetrahydrofuran at room temperature produced an instantaneous color change from red to green, which is associated with formation of the unexpected osmium terminal sulfide derivative OsH(S)(≡CPh)(IPr)(P^iPr_3) (**2**).

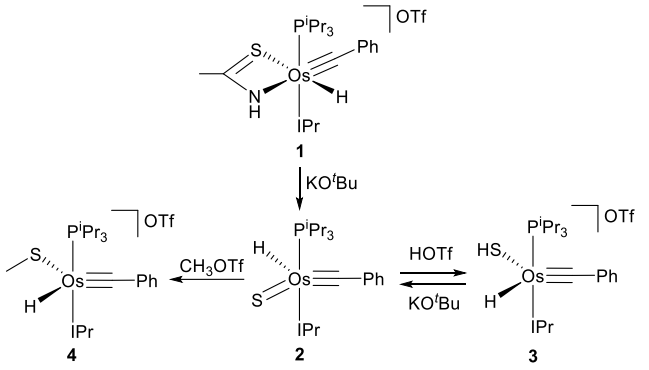
Received: February 9, 2024
Revised: March 8, 2024
Accepted: March 12, 2024
Published: March 15, 2024



https://doi.org/10.1021/acs.inorgchem.4c00596
Inorg. Chem. 2024, 63, 5779−5782

This compound was isolated as green crystals in 66% yield (Scheme 1). Its formation involves deprotonation of the

Scheme 1



coordinated thioamidate and the subsequent release of acetonitrile. The process in the opposite direction resembles formation of the amidate group of the amidate intermediates [OsH{κ^2-*N*,*O*-[NHC(R)O]}(≡CPh)(IPr)(P^{i}Pr$_3$)]OTf, which are the key to formation of the oxazolium derivatives [OsH{κ^2-*C*,*O*-[C(Ph)NHC(R)O]}(NCR)(IPr)(P^{i}Pr$_3$)]OTf. These salts are precursors of the oxazole complexes OsH{κ^2-*C*,*O*-[C(Ph)NC(R)O]}(IPr)(P^{i}Pr$_3$). Amidate intermediates result from the addition of the hydroxide group of [OsH(OH)(≡CPh)(IPr)(P^{i}Pr$_3$)]OTf to nitriles.[13]

The terminal sulfur atom is a nucleophilic center that is susceptible to protonation and methylation. Thus, the addition of a stoichiometric amount of HOTf to **2** in toluene results in precipitation of the salt [OsH(SH)(≡CPh)(IPr)(P^{i}Pr$_3$)]OTf (**3**), the sulfur counterpart of [OsH(OH)(≡CPh)(IPr)(P^{i}Pr$_3$)]OTf.[14] It contains a cation bearing a terminal hydrosulfide group,[15] an uncommon ligand in osmium chemistry.[16] This salt was isolated as a brown solid in about 50% yield. The yellow methylsulfide analogue [OsH(SMe)(≡CPh)(IPr)(P^{i}Pr$_3$)]OTf (**4**) was similarly prepared by reaction with MeOTf, also in approximately 50% yield. Sulfide protonation of **2** is reversible despite the presence of hydride and its expected Brønsted acid character.[17] Treatment of **3** in tetrahydrofuran with potassium *tert*-butoxide regenerates **2**.

The steric requirement of the bulky ligands P^{i}Pr$_3$ and IPr is probably the reason for the surprising stability of these five-coordinate compounds. The hindrance experienced when two molecules or cations approach each other prevents their condensation through the use of sulfur-donor groups as bridging ligands. The three compounds were characterized by X-ray diffraction analysis. Figure 1 shows the structures (a–c),[18] whereas Table 1 summarizes the most relevant bond lengths and angles. The geometry around the osmium atoms can be rationalized as distorted trigonal bipyramids, with the phosphine and IPr ligands in apical positions and inequivalent angles within the Y-shaped equatorial plane. The Os–S distance is shortened in the sequence **2** < **4** < **3**. The reduction of approximately 0.05 Å observed upon going from **3** to **2** suggests a significant degree of double character for the Os–S bond in **2**, which was confirmed by NBO calculations.[19] The replacement of SH by SMe produces a shortening of the length of the Os–S bond of about 0.03 Å, which can be attributed to an increase in the σ-donor character of the SMe group with respect to the SH ligand as a consequence of the donor ability of the methyl substituent. Unlike the Os–S

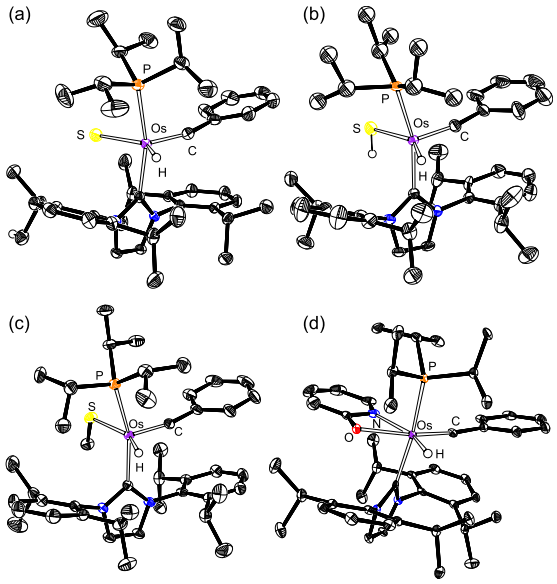


Figure 1. Molecular diagrams of complexes **2** (a), **3** (b), **4** (c), and **5** (d). Hydrogen atoms, except hydrides and S–H, and the [OTf]$^-$ anions of **3**–**5** have been omitted for clarity.

Table 1. Selected Distances (Å) and Angles (deg) for 2–5

	2	3	4	5
		Distances		
Os–S	2.2774(7)	2.3296(18)	2.2988(9)	
Os–C	1.741(3)	1.712(6)	1.717(3)	1.736(5)
		Angles		
S–Os–C	123.15(10)	114.0(3)	112.55(12)	
O–Os–C				169.21(19)
N–Os–C				109.8(2)
S–Os–H	135.9(11)	145(3)	151(2)	
Os–S–R[a]		102(5)	114.74(13)	

[a]R = H (**3**), CH$_3$ (**4**).

distance, the Os–CPh bond length is approximately 0.03 Å longer in **2** than in **3** and **4**. The contraction observed in **3** and **4** is consistent with the presence of a multiple Os–S bonding in **2**. Competition for π-bonding orbitals between the sulfide and alkylidyne in the latter leads to a longer Os–C bond. Protonation and methylation of the sulfur atom reduce the S–Os–C angle by about 10°, approximately the same as the S–Os–H angle increase. The Os–S–R angles of 102(5)° in **3** and 114.74(13)° in **4** are as expected and suggest a low degree of π-donor character for the SR ligand, although the Os–S distances in these compounds are especially short compared to those previously reported for neutral related Os–SR derivatives (2.39–2.45 Å).[16b,c] Given the cationic nature of **3** and **4**, the electrostatic component of the Os–S bond likely contributes significantly to their shortening.

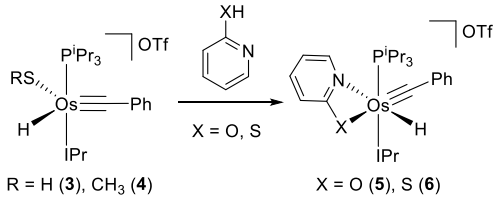
The ^{1}H, ^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra of these compounds are consistent with those of the structures shown in Figure 1. In the ^{1}H NMR spectra, the most notable resonance is a doublet ($^2J_{H-P}$ ≈ 17 Hz), due to the hydride ligand, which appears in the high-field region displaced toward the low field according to the sequence **2** (−15.13 ppm) < **3** (−2.02 ppm) < **4** (−0.62 ppm). The ^{13}C{^{1}H} NMR spectrum of **2** shows the resonance corresponding to the alkylidyne C$_{Os}$ atom at 275.5 ppm, as a doublet ($^2J_{C-P}$ = 16.3 Hz), while this signal appears at approximately 266 ppm, with a lower C–P

https://doi.org/10.1021/acs.inorgchem.4c00596
Inorg. Chem. 2024, 63, 5779–5782

coupling constant of approximately 6 Hz, in the $^{13}C\{^1H\}$ NMR spectra of **3** and **4**. The $^{31}P\{^1H\}$ NMR spectra contain a singlet at 35.2 ppm for **2** and close to 46 ppm for **3** and **4**. In contrast to the NMR spectra, a comparison of the IR spectra of the three complexes is poorly informative because the region between 800 and 500 cm^{-1} of the three is similar, including a band around that reported by the Shapley group [689 (**2**), 636 (**3**), and 635 (**4**) cm^{-1}].

There is a marked difference in the reactivity between **2** and salts **3** and **4**. Complex **2** does not react with 2-hydroxypyridine and 2-mercaptopyridine. Unlike the sulfur atom of **2**, the SR ligand of the cation of the salts is capable of deprotonating the substituents of these pyridines. Thus, their addition to solutions of **3** and **4**, in dichloromethane, at room temperature results in displacement of the SR ligand, leading to salts [OsH{κ^2-*X*,*N*-[X-py]}(≡CPh)(IPr)(P^iPr_3)]OTf [X = O (**5**), S(**6**)] containing a six-coordinate cation (Scheme 2).[20]

Scheme 2



These compounds were isolated as orange solids in high yield, about 80%. The six-coordinate number for the metal center of cations was confirmed by the X-ray diffraction analysis structure of **5**. As revealed in Figure 1d, the coordination geometry around the osmium atom is a distorted octahedron with the phosphine and IPr ligands arranged trans. The incoming ligand lies in a plane perpendicular to the $^iPr_3P$–Os–IPr direction with the pyridyl group disposed trans to the hydride ligand and the oxygen atom located trans with respect to the alkylidyne. Noticeable NMR spectroscopic features of these salts are a doublet ($^2J_{H-P} \approx 18$ Hz) at about −3.5 ppm, in the ^1H NMR spectra, due to the hydride ligand, a doublet ($^2J_{C-P} \approx 10$ Hz) around 270 ppm in the $^{13}C\{^1H\}$ NMR spectra, corresponding to the alkylidyne C_{Os} atom, and a singlet at 30.4 ppm for **5** and 20.0 ppm for **6** in the $^{31}P\{^1H\}$ NMR spectra.

Alternative synthetic procedures to the known ones usually give rise to different compounds; this Communication is clear evidence of this. Transition-metal sulfide complexes have traditionally been prepared by a metathesis reaction on halide precursors with ionic sulfides and by the reductive addition of elemental sulfur.[7] We conclude, on the basis of the results of this Communication, that the deprotonation of NH-thioamidate groups in cationic complexes is also a useful method to obtain complexes of this interesting class. Probably due to the relatively poor nucleophilicity of the coordinated sulfide ligand, such deprotonation results in the release of the nitrile fragment, which implies the liberation of a neutral sulfide complex. This discovery allows us to here show the preparation of an unusual sulfide derivative of a platinum group metal and its transformation to hydrosulfide and methylsulfide and to compare the structures, spectroscopic characteristics, and reactivities of the three new complexes.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.inorgchem.4c00596.

General information, experimental details (no uncommon hazards are noted), and NMR, IR, and UV–vis spectra and structural analysis of complexes **2**–**5** (PDF)

Accession Codes

CCDC 2331421–2331424 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

■ AUTHOR INFORMATION

Corresponding Author

Miguel A. Esteruelas − *Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea, Centro de Innovación en Química Avanzada, Universidad de Zaragoza-CSIC, Zaragoza 50009, Spain;* orcid.org/0000-0002-4829-7590; Email: maester@unizar.es

Authors

María L. Buil − *Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea, Centro de Innovación en Química Avanzada, Universidad de Zaragoza-CSIC, Zaragoza 50009, Spain;* orcid.org/0000-0002-3284-1053

Enrique Oñate − *Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea, Centro de Innovación en Química Avanzada, Universidad de Zaragoza-CSIC, Zaragoza 50009, Spain;* orcid.org/0000-0003-2094-719X

Nieves R. Picazo − *Departamento de Química Inorgánica, Instituto de Síntesis Química y Catálisis Homogénea, Centro de Innovación en Química Avanzada, Universidad de Zaragoza-CSIC, Zaragoza 50009, Spain*

Complete contact information is available at: https://pubs.acs.org/10.1021/acs.inorgchem.4c00596

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

Financial support from MICIN/AEI/10.13039/501100011033 (PID2020-115286GB-I00 and RED2022-134287-T), Gobierno de Aragón (E06_23R), FEDER, and the European Social Fund is acknowledged. N.R.P. acknowledges support via a predoctoral fellowship from the DGA.

■ REFERENCES

(1) (a) Stiefel, E. I. Transition Metal Sulfur Chemistry: Biological and Industrial Significance and Key Trends. In *Transition Metal Sulfur Chemistry: Biological and Industrial Significance*; Stiefel, E. I., Matsumoto, K., Eds.; American Chemical Society: Washington, DC, 1996; Vol. 652, pp 2–39. (b) Donahue, J. P. Thermodynamic Scales for Sulfur Atom Transfer and Oxo-for-Sulfido Exchange Reactions. *Chem. Rev.* **2006**, *106*, 4747–4783. (c) Sanchez-Delgado, R. A. Hydrodesulfurization and Hydrodenitrogenation. In *Comprehensive Organometallic Chemistry III*; Crabtree, R. H., Mingos, D. M. P., Eds.; Elsevier: Amsterdam, The Netherlands, 2007; Chapter 702, pp 121–

https://doi.org/10.1021/acs.inorgchem.4c00596
Inorg. Chem. 2024, 63, 5779–5782

236. (d) Can, M.; Armstrong, F. A.; Ragsdale, S. W. Structure, Function, and Mechanism of the Nickel Metalloenzymes, CO Dehydrogenase, and Acetyl-CoA Synthase. *Chem. Rev.* **2014**, *114*, 4149−4174. (e) Tonzetich, Z. J. H_2S and Bioinorganic Metal Complexes. In *Hydrogen Sulfide: Chemical Biology Basics, Detection Methods, Therapeutic Applications, and Case Studies*; Pluth, M. D., Ed.; Wiley, 2022.

(2) (a) Ray, K.; Heims, F.; Pfaff, F. F. Terminal Oxo and Imido Transition-Metal Complexes of Groups 9−11. *Eur. J. Inorg. Chem.* **2013**, 3784−3784. (b) Liu, Y.; Lau, T.-C. Activation of Metal Oxo and Nitrido Complexes by Lewis Acids. *J. Am. Chem. Soc.* **2019**, *141*, 3755−3766. (c) Shimoyama, Y.; Kojima, T. Metal−Oxyl Species and Their Possible Roles in Chemical Oxidations. *Inorg. Chem.* **2019**, *58*, 9517−9542. (d) Larson, V. A.; Battistella, B.; Ray, K.; Lehnert, N.; Nam, W. Iron and manganese oxo complexes, oxo wall and beyond. *Nat. Chem. Rev.* **2020**, *4*, 404−419.

(3) Ishizuka, T.; Sugimoto, H.; Itoh, S.; Kojima, T. Recent progress in oxidation chemistry of high-valent ruthenium-oxo and osmium-oxo complexes and related species. *Coord. Chem. Rev.* **2022**, *466*, 214536.

(4) Shaver, A.; El-Khateeb, M.; Lebuis, A.-M. C−S Bond Cleavage in $CpRu(PPh_3)_2SCH_2CH{=}CH_2$ To Give the Trimer $(CpRu)_3(\mu_3\text{-}S)_2(\mu\text{-}SCH_2CH{=}CH_2)$. *Inorg. Chem.* **1999**, *38*, 5913−5915.

(5) Shapley, P. A.; Liang, H.-C.; Shusta, J. M.; Schwab, J. J.; Zhang, N.; Wilson, S. R. Synthesis and Reaction Chemistry of New, High-Oxidation-State Ruthenium and Osmium Sulfido Complexes. *Organometallics* **1994**, *13*, 3351−3359.

(6) (a) Larsen, P. L.; Gupta, R.; Powell, D. R.; Borovik, A. S. Chalcogens as Terminal Ligands to Iron: Synthesis and Structure of Complexes with Fe^{III}-S and Fe^{III}-Se Motifs. *J. Am. Chem. Soc.* **2004**, *126*, 6522−652310. (b) Dey, A.; Hocking, R. K.; Larsen, P.; Borovik, A. S.; Hodgson, K. O.; Hedman, B.; Solomon, E. I. X-ray Absorption Spectroscopy and Density Functional Theory Studies of $[(H_3buea)\text{-}Fe^{III}\text{-}X]^{n-}$ ($X = S^{2-}$, O^{2-}, OH^-): Comparison of Bonding and Hydrogen Bonding in Oxo and Sulfido Complexes. *J. Am. Chem. Soc.* **2006**, *128*, 9825−9833. (c) Valdez-Moreira, J. A.; Wannipurage, D. C.; Pink, M.; Carta, V.; Moënne-Loccoz, P.; Telser, J.; Smith, J. M. Hydrogen atom abstraction by a high-spin $[Fe^{III}{=}S]$ complex. *Chem.* **2023**, *9*, 2601−2609.

(7) Seo, W. T. M.; Tsui, E. Y. Structural and Redox Interconversions of Sulfur Ligands of Transition Metal Complexes. *Comments Inorg. Chem.* **2024**, *44*, 55.

(8) Hartmann, N. J.; Wu, G.; Hayton, T. W. Synthesis of a "Masked" Terminal Nickel(II) Sulfide by Reductive Deprotection and its Reaction with Nitrous Oxide. *Angew. Chem.* **2015**, *127*, 15169−15172.

(9) Baeza Cinco, M. A.; Hayton, T. W. Progress toward the Isolation of Late Metal Terminal Sulfides. *Eur. J. Inorg. Chem.* **2020**, 3613−3626.

(10) (a) Dobbs, D. A.; Bergman, R. G. Late Transition-Metal Sulfido Complexes: Reactivity Studies and Mechanistic Analysis of Their Conversion into Metal-Sulfur Cubane Complexes. *Inorg. Chem.* **1994**, *33*, 5329−5336. (b) Novio, F.; González-Duarte, P.; Lledós, A.; Mas-Ballesté, R. Reaction Chemistry of Complexes Containing Pt−H, Pt−SH, or Pt−S Fragments: From Their Apparent Simplicity to the Maze of Reactions Underlying Their Interconversion. *Chem. Eur. J.* **2007**, *13*, 1047−1063.

(11) Takei, I.; Kobayashi, K.; Dohki, K.; Hidai, M. Synthesis and Reactivity of a Bis(disulfide)-Bridged $RuMo_3S_4$ Double-Cubane Cluster: A New Family of Nona- or Decanuclear Mixed-Metal Sulfide Clusters with Two $RuMo_3S_4$ Units. *Inorg. Chem.* **2007**, *46*, 1045−1047.

(12) Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Picazo, N. R. Osmathiazole Ring: Extrapolation of an Aromatic Purely Organic System to Organometallic Chemistry. *Organometallics* **2023**, *42*, 327−338.

(13) Buil, M. L.; Esteruelas, M. A.; Oñate, E.; Picazo, N. R. Dissimilarity in the Chemical Behavior of Osmaoxazolium Salts and Osmaoxazoles: Two Different Aromatic Metalladiheterocycles. *Organometallics* **2021**, *40*, 4150−4162.

(14) Buil, M. L.; Cardo, J. J. F.; Esteruelas, M. A.; Fernández, I.; Oñate, E. Hydroboration and Hydrogenation of an Osmium−Carbon Triple Bond: Osmium Chemistry of a Bis-σ-Borane. *Organometallics* **2015**, *34*, 547−550.

(15) Pluth, M. D.; Tonzetich, Z. J. Hydrosulfide complexes of the transition elements: diverse roles in bioinorganic, cluster, coordination, and organometallic chemistry. *Chem. Soc. Rev.* **2020**, *49*, 4070−4134.

(16) (a) Buil, M. L.; Elipe, S.; Esteruelas, M. A.; Oñate, E.; Peinado, E.; Ruiz, N. Five-Coordinate Complexes $MHCl(CO)(P^iPr_3)_2$ (M = Os, Ru) as Precursors for the Preparation of New Hydrido− and Alkenyl−Metallothiol and Monothio−β-Diketonato Derivatives. *Organometallics* **1997**, *16*, 5748−5755. (b) Esteruelas, M. A.; López, A. M.; Mora, M.; Oñate, E. B−H activation and H−H formation: two consecutive heterolytic processes on an osmium−hydrogensulfide bond. *Chem. Commun.* **2013**, *49*, 7543−7545. (c) Esteruelas, M. A.; Fernández, I.; García-Yebra, C.; Martín, J.; Oñate, E. Cyclo-osmathioborane Compounds: Other Manifestations of the Hückel Aromaticity. *Inorg. Chem.* **2019**, *58*, 2265−2269.

(17) Morris, R. H. Brønsted−Lowry Acid Strength of Metal Hydride and Dihydrogen Complexes. *Chem. Rev.* **2016**, *116* (15), 8588−8654.

(18) The rotation of the SMe group around the Os−S bond appears to be hindered in solution. Thus, complex **4** exists as an 80:20 mixture of two conformers (Figures S8−S11) at 243 K. At temperatures above 340 K, coalescence occurs between the resonances of both (Figure S9).

(19) Calculated Wiberg bond indexes: 2.11 [NBO(3)] and 1.81 [NBO(7)] on the density-functional-theory-optimized structure at the B3LYP(D3)/SDD(f)-631G** level.

(20) Complex **6** was obtained doped with approximately 10% of an isomer containing the chelate ligand coordinated with a sulfur atom arranged trans with respect to the hydride ligand and a nitrogen atom located trans with respect to the alkylidyne group (Figures S15−S17).

https://doi.org/10.1021/acs.inorgchem.4c00596
Inorg. Chem. 2024, 63, 5779−5782