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Metallacycles

Access to Metal-Bridged Osmathiazine Derivatives by a Formal [4+2] Cyclization

Jinhua Li,[a] Yu-Mei Lin,*[a] Hong Zhang,[a] Yuan Chen,[a] Zhenyang Lin,[b] and Haiping Xia*[a]

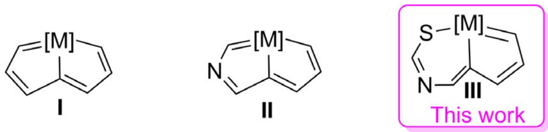
Abstract: Treatment of osmacyclopentadiene derivatives **1** with phenyl or isopropyl isothiocyanate gave the fused five and six-membered osmacycles **2**–**5** by a formal [4+2] cyclization. The facile protonation of the newly generated exocyclic imine in complexes **2**–**5** afforded conjugation-extended osmacycle derivatives **6**–**9**. Compounds **2**–**9** each contain two main-group heteroatoms (N and S) in the fused six-membered ring located at the *ortho* (for S) and *para* (for N) positions relative to the osmium centre; these species can be regarded as rare osma-1,3-thiazine derivatives and represent the first fused metallathiazine derivatives. In contrast to the non-planar organic 6*H*-1,3-thiazine, nearly coplanar metallathiazines **8** and **9** can be achieved by tuning the groups on the two nitrogen atoms. These unique metal-bridged osma-1,3-thiazine derivatives exhibit remarkable stabilities, broad spectral absorptions spanning the visible spectra, and considerable photothermal properties, which suggests their potential applications in material science.

Introduction

The chemistry of transition-metal-containing metallacycles with conjugated carbon skeletons is currently attracting widespread attention. The past decades have witnessed the rapid development in the chemistry of metallabenzenes,[1] metallabenzynes,[2] metallaannulenes,[3] and other metallacycles.[4] Most of the well-characterized conjugated metallacycles feature participation of the transition metal in one ring.[1–3,5] In contrast, the metal-bridged metallacycles, in which the metal is shared by the fused rings, have been much less exploited.[6] In 2013, a family of highly conjugated metal-bridged metallacycles, namely, osmapentalynes[7] and osmapentalenes,[8] in which the metal is chelated by a "carbolong ligand",[9] have been discovered. Lately, by extension of the carbon chain in the "carbolong ligands", a series of "carbolong complexes" composed of 7–12 carbon atoms have been synthesized.[10] Some interesting phenomena, such as single-molecular conductivity,[11] *J*-aggregates behavior,[12] and photothermal conversion,[9,12,13] were observed for these complexes with fine-tuned structures, which enabled their potential future applications. Developing a new strategy for modification or construction of these metallacyclic derivatives is a continuous, interesting subject.

The incorporation of main-group heteroatoms into metallacycles can produce new compounds with distinctive chemical and physical properties.[4e] Various metallacycles that contain one or two main-group heteroatoms have been isolated, such as metallapyridines,[6k,14] metallapyridynes,[6k] metallathiobenzenes,[15] metallabenzothiophenes,[16] metallabenzofurans,[17] metallabenzothiazoles,[6j,18] metallabenzoxazoles,[18] metallabenzoxathialoes,[19] and metallabenzoxolones.[20] This strategy significantly enriches the structural and compositional varieties of metallacycles.

Based on the unique structure of metallapentalene (Scheme 1, type **I**), we have recently reported an aza-metallapentalene (Scheme 1, type **II**), in which a carbon atom was replaced by a nitrogen atom.[21] In this respect, we are interested to investigate whether more main-group heteroatoms can be embedded in this system. Herein, we present the synthesis and characterization of novel metal-bridged metallathiazine derivatives that contain two main-group heteroatoms (N and S) at *ortho* (for S) and *para* (for N) positions relative to metal center in the fused six-membered ring (Scheme 1, type **III**). The new metallabicyclic species were realized by a formal [4+2] cyclization that invovles the osmacyclopentadiene derivatives and isothiocyanates. In addition, the fused osma-1,3-thiazine derivatives exhibit remarkable stabilities, broad absorptions, and considerable photothermal properties.



Scheme 1. The skeleton structures of metallapentalene (I), aza-metallapentalene (II) and metallathiazine derivatives (III).

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[a] J. Li, Dr. Y.-M. Lin, Dr. H. Zhang, Y. Chen, Prof. Dr. H. Xia
State Key Laboratory of Physical Chemistry of Solid Surfaces and Department of Chemistry, College of Chemistry and Chemical Engineering
Xiamen University, Xiamen 361005 (P. R. China)
E-mail: linyum@xmu.edu.cn
hpxia@xmu.edu.cn

[b] Prof. Dr. Z. Lin
Department of Chemistry, The Hong Kong University of Science & Technology, Clear Water Bay, Kowloon, Hong Kong (P. R. China)

Supporting information and the ORCID identification number(s) for the author(s) of this article can be found under: https://doi.org/10.1002/chem.201806354.

Results and Discussion

Synthesis and characterization

The previously reported aza-osmapentalene[21] was synthesized by reaction of osmacyclopentadiene derivative **1a** with propynol as the new carbon source. To extend the strategy, we envisioned that heterocumulenes may be an appropriate candidate for introducing new heteroatoms into the metallacycles. Phenyl isothiocyanate was selected and reacted with compound **1a** in the presence of silver oxide and triethylamine, which gave rise to complex **2** in 73% yield. The removal of iodine by silver oxide facilitated the coordination of isothiocyanate to the osmium center through the sulfur atom. Triethylamine was used to abstract the proton of the exocyclic imine to promote the nucleophilic addition to the C=S bond, which resulted in the formation of a six-membered ring (Scheme 2). Treatment of compound **1a** with isopropyl isothiocyanate under similar conditions led to the formation of the analogue **3** in 62% yield.

The structure of complex **2** was determined by single-crystal X-ray diffraction. The selected bond lengths are given in Table 1, and the crystallographic details are summarized in Table 2. As shown in Figure 1, complex **2** contained a bicyclic skeleton with the osmium center shared by the fused five and six-membered rings. The metallabicycle was non-planar, which was indicated by the large mean deviation of the least-squares plane that consisted of Os1, C1–C5, N1, C6, and S1 atoms (0.126 Å) and the significant displacement (out of the equatorial plane) of the C6 atom (0.285 Å). The bond length of Os1–S1 (2.4748(13) Å) and the single-bond character of C6–S1 (1.750(5) Å), which fall in the ranges of the previously reported sulfur-bonded mononuclear osmacycles (2.445–2.513 Å for Os–S bond and 1.689–1.763 Å for C–S bond),[22] indicate that the C=S bond in phenyl isothiocyanate participated in the cyclization reaction to form the six-membered ring. A new exocyclic imine was formed, as indicated by the bond length of C6–N2 (1.274(6) Å). Notably, the phenyl group on N2 displayed a *Z* configuration to reduce the steric hindrance of the phenyl substituent on N1. The bond length of C5–N1 (1.336(6) Å) suggested that it maintained the C=N double bond character as it was shorter than the single bond of C6–N1 (1.460(6) Å). The bond lengths of Os1–C1 (2.005(5) Å) and Os1–C4 (2.103(5) Å) were comparable with those observed in typical osmacyclopentadienes.[23] All of the carbon–carbon bond lengths in the metallabicycle fall in the range of 1.385(7)–1.425(7) Å, which were between the typical single and double C–C bond lengths.

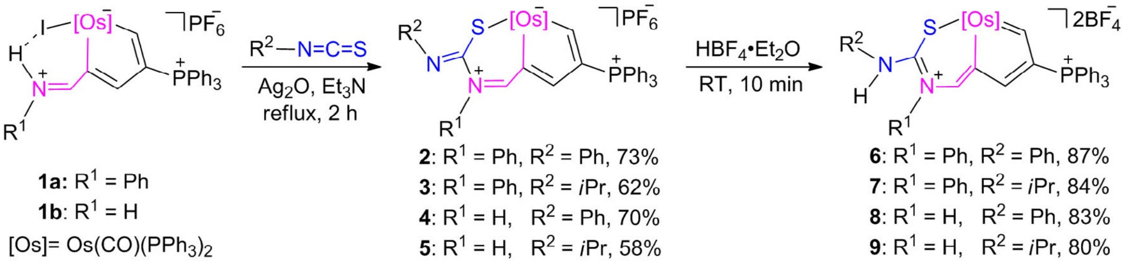
Table 1. Selected bond lengths (Å) for complexes **2**, **7**, **8**, and **9**.

Bond	**2**	**7**	**8**	**9**
Os1–C1	2.005(5)	1.976(3)	1.980(8)	2.007(7)
Os1–C4	2.103(5)	2.110(3)	2.105(9)	2.105(7)
Os1–S1	2.4748(13)	2.4528(9)	2.444(2)	2.4576(18)
C1–C2	1.394(7)	1.417(5)	1.404(11)	1.407(11)
C2–C3	1.425(7)	1.396(5)	1.391(11)	1.403(11)
C3–C4	1.385(7)	1.402(5)	1.400(12)	1.403(10)
C4–C5	1.405(6)	1.371(5)	1.384(13)	1.373(11)
C5–N1	1.336(6)	1.372(5)	1.347(15)	1.345(10)
C6–N1	1.460(6)	1.407(5)	1.375(18)	1.392(10)
C6–N2	1.274(6)	1.305(5)	1.414(16)	1.319(10)
C6–S1	1.750(5)	1.695(4)	1.668(16)	1.686(8)

In accordance with the solid-state structure, complex **2** was further characterized by NMR spectroscopy. The ^1H NMR spectrum showed a characteristic phosphorus-coupled OsC*H* doublet signal at $\delta = 11.97$ ppm. The signals of other protons of the metallabicycle were observed at $\delta = 7.99$ (*H*5) and 7.79 (*H*3) ppm. In the ^{31}P NMR spectrum, the two signals at $\delta =$ 14.02 and −6.21 ppm were attributed to C*P*Ph_3 and Os*P*Ph_3 nuclei, respectively. With the aid of ^1H–^{13}C HSQC and ^{13}C-DEPT-135 spectrum, the chemical shifts for metal-bonded carbon atoms were observed at $\delta = 240.1$ (C1) and 157.5 (C4) ppm. The other four carbon atom signals were observed at $\delta = 181.8$ (C3), 169.9 (C5), 152.9 (C6), and 120.5 (C2) ppm.

When the phenyl group on the exocyclic C=N bond in complex **1a** was changed to a hydrogen atom, analogues **4** and **5** were obtained by treatment of complex **1b**[24] with phenyl or isopropyl isothiocyanate, respectively. The NMR spectra showed that a mixture of isomers **4a** and **b** or **5a** and **b** were formed (see the Experimental Section and the Supporting Information), which were attributed to the *E/Z* configurational mixture of the newly generated exocyclic C=N bond. Unlike the exclusive formation of *Z* products for complexes **2** and **3**, the small hydrogen atom on the N1 atom in complexes **4** and **5** eliminated the steric hindrance and resulted in the formation of both the *Z* and *E* species.

Metallacycles **2**–**5** each contain a fused five and six-membered ring with the osmium center at the bridged position. Two main-group heteroatoms (N and S) were incorporated into the fused six-membered ring at the *ortho* (for S) and *para*



Scheme 2. Synthesis of osma-1,3-thiazine derivatives **2**–**9**.

Table 2. Crystal data and structure refinement for complexes **2**, **7**, **8**, and **9**.

	2·CH_2Cl_2	**7**	**8**·3 H_2O	**9**·H_2O·0.5 CH_2Cl_2
formula	$C_{74}H_{60}Cl_2F_6N_2OOsP_4S$	$C_{70}H_{61}B_2F_8N_2OOsP_3S$	$C_{67}H_{61}B_2F_8N_2O_4OsP_3S$	$C_{64.5}H_{60}B_2ClF_8N_2O_2OsP_3S$
M_r	1524.28	1434.99	1446.97	1419.38
temperature [K]	173(2)	100(10)	100(10)	173(2)
crystal system	triclinic	triclinic	monoclinic	triclinic
space group	*P*-1	*P*-1	*C*2/*c*	*P*-1
a [Å]	11.8604(5)	11.9105(10)	29.1344(4)	12.1498(4)
b [Å]	14.1459(7)	14.9267(10)	20.6127(3)	16.3228(6)
c [Å]	19.9037(9)	20.5465(2)	21.7045(3)	17.1862(7)
α [°]	99.790(4)	96.3770(10)	90	94.025(3)
β [°]	91.163(4)	93.3840(10)	107.642(2)	106.181(3)
γ [°]	93.295(4)	103.4650(10)	90	99.109(3)
V [Å^3]	3283.8(3)	3516.81(5)	12421.4(3)	3208.5(2)
Z	2	2	8	2
ρ_{calcd} [g cm^{-3}]	1.542	1.355	1.541	1.468
μ [mm^{-1}]	2.217	4.871	5.558	2.203
F(000)	1532.0	1444.0	5776.0	1424.0
crystal size [mm^3]	0.20×0.10×0.05	0.20×0.10×0.10	0.30×0.10×0.05	0.40×0.30×0.10
radiation (Å)	$Mo_{K\alpha}$ (λ = 0.71073)	$Cu_{K\alpha}$ (λ = 1.54184)	$Cu_{K\alpha}$ (λ = 1.54184)	$Mo_{K\alpha}$ (λ = 0.71073)
θ range [°]	2.879 to 25.000	3.526 to 64.996	3.71 to 64.999	2.341 to 25.000
reflns collected	25337	42030	38928	22587
independent reflns	11556	11901	10545	11302
observed reflns [$I \geq 2\sigma$]	9621	37716	18478	6454
Data/restraints/params	11556/6/832	11901/0/771	10545/108/790	11302/62/663
GOF on F^2	1.014	1.063	1.019	1.069
$R_1/wR_2[I \geq 2\sigma(I)]$	0.0465/0.0803	0.0324/0.0863	0.0689/0.1887	0.0590/0.1628
R_1/wR_2 (all data)	0.0613/0.0854	0.0361/0.0890	0.0767/0.1972	0.0667/0.1687
Largest peak/hole [e Å^{-3}]	1.41/−1.54	1.60/−1.51	2.07/−1.96	2.01/−1.66
CCDC no.[a]	1878322	1878382	1878383	1878392

[a] CCDC contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre

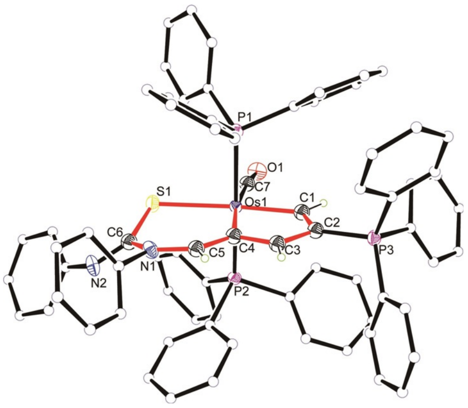


Figure 1. X-ray molecular structure for the cation of complex **2** (thermal ellipsoids set at 50 % probability, the hydrogen atoms of the phenyl moieties and counter anions have been omitted for clarity).

(for N) positions relative to osmium atom. Such heteroatom-containing metallacycles can be recognized as metalla-1,3-thiazine derivatives. Several examples of monocyclic metallathiazine have been reported;[25] however, the osmathiazine derivatives **2**–**5** are the first cases of metal-bridged fused metallathiazine derivatives, which enrich the varieties of metallathiazines.

The formation of complexes **2**–**5** were realized by the nucleophilic addition of the exocyclic imine to the C=S double bond, which can be viewed as a formal [4+2] cyclization that invovles the Os1–C4–C5–N1 fragment of complex **1** and the C6–S1 moiety of the isothiocyanates. The formal [4+2] cyclization has been a practical strategy to construct heteroatom-containing metallacycles. For example, titanocene vinylimido complexes reacted readily with unsaturated organic substrates (ketones, nitriles, and imines) to form titana-2,5-dihydropyrimidines.[26] In our previous work, we showed that osmapyridinium[14b] and iso-osmapyridinium[27] were obtained by reactions between osmium hydrido alkenylcarbynes and nitriles. In the present case, heterocumulene was used as the precursor in the formal [4+2] cyclization to access the metal-bridged osmacycles that contain main-group heteroatoms.

The newly generated exocyclic imine in complexes **2**–**5** can be readily protonated with acid. Treatment of complexes **2**–**5** with three equivalents of HBF_4·Et_2O at room temperature led to the formation of complexes **6**–**9**, respectively, which were isolated in yields of 80–87 % (Scheme 2). All the compounds have been characterized by NMR spectroscopy and the structures of complexes **7**–**9** were further confirmed by single-crystal X-ray diffraction.

The ^1H NMR spectrum of complex **7** displayed a downfield-shifted doublet signal at δ = 12.88 ppm for OsC*H*. The signals of *H*3 and *H*5 were observed at δ = 8.17 and 7.82 ppm, respectively. A broad signal at δ = 1.26 ppm was assigned to the proton at N2. The ^{31}P NMR spectrum showed two signals at δ = 14.76 (C*P*Ph$_3$) and −6.70 ppm (Os*P*Ph$_3$). In the ^{13}C NMR spectrum, the chemical shift of C1 (δ = 265.5 ppm) was shifted significantly downfield than that of complex **3** (δ = 236.6 ppm), which indicates its carbene character. C6 ($\delta=164.0$ ppm) and C5 ($\delta=164.6$ ppm) have nearly identical chemical shifts. The remaining carbon signals of the metallacycle were observed at $\delta=118.1$ (C2), 196.9 (C3), 157.5 (C4), and 188.1 ppm (C7).

Compound **7** was further characterized by single-crystal X-ray diffraction (Figure 2, Tables 1 and 2). It showed that the metallabicycle is retained and the geometry around the Os center can be viewed as octahedral with three carbon atoms (C1, C4, C7), one sulfur atom in the equatorial plane, and two PPh_3 ligands in the axial coordination sites. The metallabicycle was also nonplanar, as reflected by the large mean deviation of the least-squares plane (0.103 Å), and the C6 atom was displaced out of the plane by 0.224 Å. The bond length of Os1–C1 (1.976(3) Å) was much shorter than that of Os1–C4 (2.110(3) Å), which was consistent with the downfield carbon chemical shift of C1 ($\delta=265.5$ ppm) and suggests its significant carbene character. The C–C bond lengths in the chain C1–C5 (1.371(5)–1.417(5) Å) showed no significant alternations. In addition, the comparable bond lengths of C6–N1 (1.407(5) Å), C6–N2 (1.305(5) Å), and C5–N1 (1.372(5) Å) showed delocalization across the C–N bonds, which indicate the N1–C6–N2 fragment could be regarded as an amidinium ion with the positive charge delocalized on both nitrogen atoms. The observations regarding bond lengths indicated that the resonance form **7′** contributed to the structure (Scheme 3). Alternatively, another resonance structure **7″** should be taken into consideration owing to the relatively short bond length of C6–S1 (1.695(4) Å) (Scheme 3).[6k, 22c, 28]

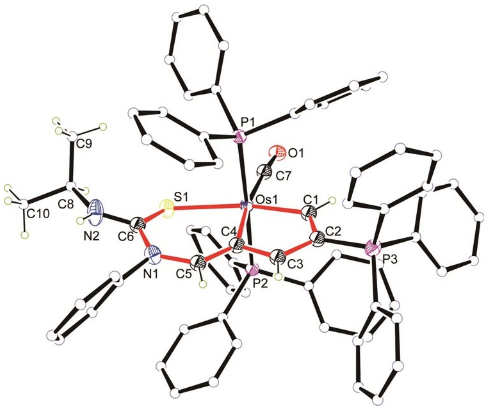
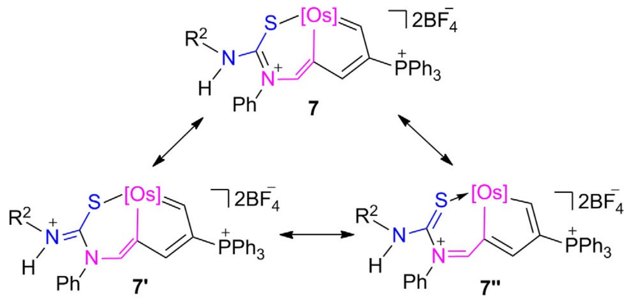


Figure 2. X-ray molecular structure for the cation of complex **7** (thermal ellipsoids set at 50 % probability, the hydrogen atoms of the phenyl moieties and counter anions have been omitted for clarity).

Notably, treatment of the mixture of isomers **4a** and **b** with acid led to the exclusive formation of product **8**. The protonation process made the exocyclic imine into an amine, thus eliminating the conformation isomerism as a result of the exocyclic C=N double bond and resulting in a conjugation-extended osmacycle. As reflected by in situ NMR spectroscopy, the ^{31}P NMR spectrum showed one set of signals at $\delta=14.58$ (CPPh_3) and -0.54 ppm (OsPPh_3). A doublet proton signal at $\delta=12.75$ ppm (C1H) was observed in the ^{1}H NMR spectrum. The carbon chemical shifts of complex **8** were observed at $\delta=$ 260.2 (C1), 118.4 (C2), 193.3 (C3), 159.4 (C4), 160.4 (C5), 163.7 (C6), and 188.0 ppm (C7), which were very close to those of complex **7**. Complex **9** can be obtained under similar conditions, and it's structure was confirmed by NMR spectroscopy (see the Supporting Information).



$[Os] = Os(CO)(PPh_3)_2$, $R^2 = i$Pr

Scheme 3. The resonance structures of complex **7**.

Suitable crystals for X-ray diffraction analysis of complexes **8** and **9** were obtained. As shown in Figures 3 and 4, the essential structure parameters (bond lengths and bond angles) of

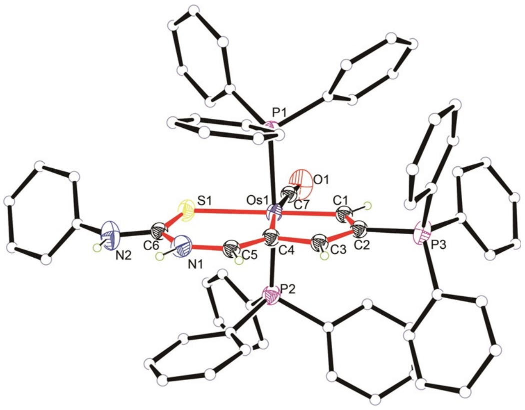


Figure 3. X-ray molecular structure for the cation of complex **8** (thermal ellipsoids set at 50 % probability, the hydrogen atoms of the phenyl moieties and counter anions have been omitted for clarity).

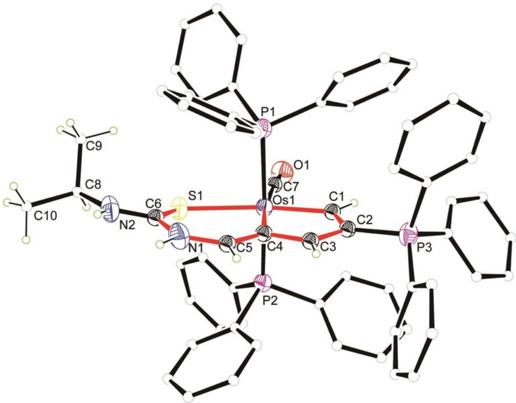
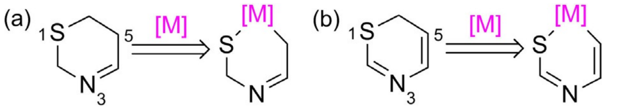


Figure 4. X-ray molecular structure for the cation of complex **9** (thermal ellipsoids set at 50 % probability, the hydrogen atoms of the phenyl moieties and counter anions have been omitted for clarity).

complexes **8** and **9** were comparable with those of complex **7**, which indicates that they form delocalization structures similar to those of complex **7**. The metallabicyclic units in complexes **8** and **9** were almost coplanar, as reflected by the small mean deviation from the least-squares planes (0.021 Å for **8** and 0.073 Å for **9**) that consisted of Os1, C1–C5, N1, C6, and S1. These values were much smaller than that of complex **7** (0.103 Å). Replacement of the phenyl substituent on N1 in complex **7** by a hydrogen atom reduced the steric effect and thus allowed the formation of the more planar complexes **8** and **9**. The substituents on N2 also have an impact on the planarity, as evidenced by the fact that the bulkier isopropyl group led to formation of the less planar metallabicycle **9**.

Various metallacycles have been realized by incoporation of a transition-metal fragment into the traditional organic molecules.[1–2,5] Compexes **2**–**9**, which have a six-membered ring, can be recognized as metallacyclic analogues of 5,6-dihydro-2*H*-1,3-thiazine[29] (for complexes **2**–**5**) and 6*H*-1,3-thiazine[29] (for complexes **6**–**9**) (Scheme 4), in which one sp^3 hybridized carbon atom was replaced by the osmium counterpart. In contrast to the nonplanar organic 6*H*-1,3-thiazine,[30] nearly coplanar metallathiazines **8** and **9** can be obtained by changing the groups on the two nitrogen atoms. We documented here a new type of metalla-1,3-thiazine derivative, which represents an important supplement to the rare metal-bridged metallacycles that contain two main-group heteroatoms.



Scheme 4. a) 5,6-Dihydro-2*H*-1,3-thiazine and its metallacyclic analogue; b) 6*H*-1,3-thiazine and its metallacyclic analogue.

Thermal stabilities of complexes 2–9

Solid-state thermal stability analysis of the metal-bridged osma-1,3-thiazine derivatives **2**–**9** has been performed in air by heating for 5 h. Complexes **2**–**5** were stable under 100 °C (Table 3). The stabilities of conjugation-extended osma-1,3-thiazine derivatives **6**–**9** are related to the electron-donating abilities of the groups attached to the N1 and N2 atoms. As shown in Table 4, complexes **8** and **9** exhibit higher thermal stabilities than complexes **6** and **7**. Complex **6** is more liable to decompose than **7**, whereas complex **9** is more stable than **8**. A strong electron-donating group could balance the positive charge on the amidinium ion and thus improve its stability. In this regard, complex **9** shows the highest thermal stability, whereas complex **6** is the most unstable under the given conditions. This observation is in accordance with the electron-donating ability order of isopropyl > H > phenyl.

Table 3. Thermal decomposition data for complexes **2**–**5** in the solid state.[a]

	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C
2	●[b]	●	▲[c]	ν[e]	–	–
3	●	●	▲	ν	–	–
4	●	●	◆[d]	▲	▲	ν
5	●	●	▲	ν	–	–

[a] All reactions were carried out for 5 hours in air. [b] ● = Stable. [c] ▲ = Partly decomposed. [d] ◆ = Slightly decomposed. [e] ν = Completely decomposed.

Table 4. Thermal decomposition data for complexes **6**–**9** in the solid state.[a]

	80 °C	100 °C	120 °C	140 °C	160 °C	180 °C
6	●[b]	▲[c]	ν[d]	–	–	–
7	●	●	▲	ν	–	–
8	●	●	●	▲	ν	–
9	●	●	●	●	▲	ν

[a] All reactions were carried out for 5 hours in air. [b] ● = Stable. [c] ▲ = Partly decomposed. [d] ν = Completely decomposed.

UV/Vis/NIR absorption spectra and photothermal properties

The UV/Vis absorptions of complexes **2**–**9** were examined (Figure 5). In the range of 300–500 nm, the absorption band for complex **4** is red-shifted by approximately 40 nm compared to that of complex **5**. The red-shifted behavior was also observed for complex **8** compared to that of complex **9**. The phenomena were probably due to the participation of the phenyl

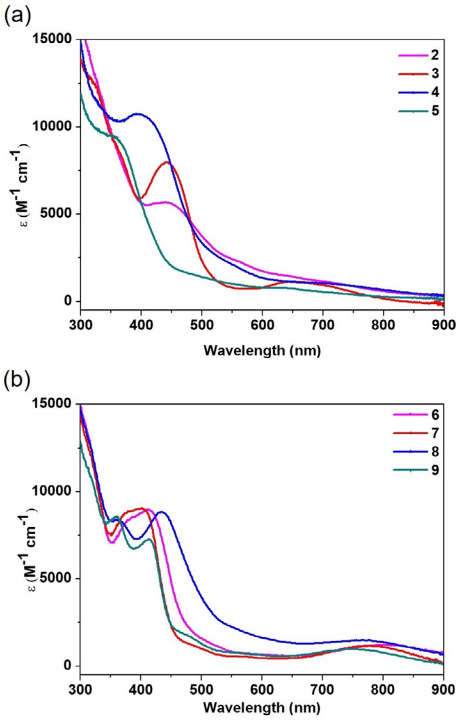


Figure 5. UV/Vis/NIR absorption spectra of a) complexes **2**–**5** and b) complexes **6**–**9**. Measured in CH_2Cl_2 (1.0×10^{-4} M) at room temperature.

group attached to N2 in the conjugation of complexes **4** and **8**. Notably, the metal-bridged metallacycles **6**–**9** exhibited broad absorption bands that ranged from the ultraviolet to the visible region and extended to the near-infrared region (NIR) (Figure 5b). Thus, the photothermal conversion abilities of complexes **6**–**9** were further examined by measuring the temperature of their solutions under NIR laser irradiation (808 nm, 1.0 W cm^{-2}).[9,12–13] As shown in Figure 6, all the samples exhibited photothermal properties. The temperature of the 1,2-dichloroethane solution containing complex **9** (0.5 mg mL^{-1}) significantly increased from 26 to 58 °C within 4 min, whereas the solvent alone (without **6**–**9**) showed a negligible temperature change (< 4 °C) under similar conditions.

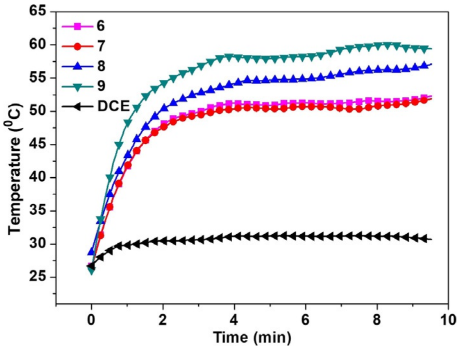


Figure 6. Temperature curves of 1,2-dichloroethane solutions of complexes **6**–**9** (0.50 mg mL^{-1}) irradiated with an 808 nm laser at a power density of 1.0 W cm^{-2}.

Conclusion

We have described the synthesis and characterization of a new type of metal-bridged osma-1,3-thiazine derivatives. The generation of the metal-bridged fused metallathiazine derivatives were realized by a formal [4+2] cyclization between osmacyclopentadiene derivatives and heterocumulenes, which can be extended to construct other metal-bridged metallacycles containing main-group atoms. The resulting bicyclic metallacycles are interesting and enrich the varieties of metal-bridged metallacycle species. The unique structures, broad absorption, and considerable stabilities together with photothermal properties enable the potential applications of these osmacycles in material science.

Experimental Section

All syntheses were performed under an N_2 atmosphere by using standard Schlenk techniques, unless otherwise stated. Diethyl ether was distilled from sodium/benzophenone and dichloromethane from calcium hydride under N_2 prior to use. The starting materials, osmacyclopentadiene derivative **1a** and osmabenzene, were synthesized according to previously published procedures.[31] Other reagents were used as received from commercial sources without further purification. Column chromatography was performed on neutral alumina (200–300 mesh) in air. NMR spectroscopic experiments were performed on a Bruker AVIII-400 (^{1}H: 400.0, ^{13}C: 100.6, ^{31}P: 161.9 MHz) spectrometer, a Bruker AVIII-500 (^{1}H: 500.2, ^{13}C: 125.8, ^{31}P: 202.5 MHz) spectrometer, or a Bruker Ascend III 600(^{1}H: 600.1, ^{13}C: 150.9, ^{31}P: 242.9 MHz) spectrometer at room temperature. The ^{1}H and ^{13}C NMR chemical shifts (δ) are reported relative to tetramethylsilane, and the ^{31}P NMR chemical shifts are relative to 85 % H_3PO_4. The absolute values of the coupling constants are given in hertz (Hz). Multiplicities are abbreviated as singlet (s), doublet (d), triplet (t), multiplet (m), and broad (br). HRMS experiments were performed on a Bruker En Apex Ultra 7.0T FTMS. Elemental analyses were performed on a Vario EL III elemental analyser. Absorption spectra were recorded on a UV-2550 UV/Vis spectrophotometer. The STL808T1-15W fiber-coupled laser system (Stone Company) was used in photothermal experiments and the temperature data were collected by using an FLIR A35 FOV 24 thermal imaging camera.

Synthesis

Synthesis of complex 1b: CH_2Cl_2 (10 mL) was added to a mixture of osmabenzene (300 mg, 0.21 mmol), NH_4HCO_3 (82 mg, 1.04 mmol), and $NaPF_6$ (175 mg, 1.04 mmol), and the mixture was heated at reflux overnight to give a brown solution. After it was cooled to RT, the mixture was filtered, and the filtrate was reduced to approximately 2 mL under vacuum. The residue was purified by the column chromatography (neutral alumina, acetone/dichloromethane, 1:15) to give product **1b** as a brown solid (177 mg, 63 %). ^{1}H NMR (500.2 MHz, CD_2Cl_2/CD_3COCD_3, 1:4): $\delta = 11.63$ (dd, 1 H, J(PH) = 16, 2 Hz), 8.98 (br, 1 H, NH), 8.14 (br, 1 H, NH), 7.88–6.97 (m, 47 H, PPh_3 and C3H, C5H), 7.85 (br, 1 H, C5H), 7.83 ppm (br, 1 H, C3H); ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2/CD_3COCD_3, 1:4): $\delta = 12.73$ (s, CPPh$_3$), −2.84 (s, OsPPh$_3$), −144.22 ppm (septet, PF_6); ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2/CD_3COCD_3, 1:4, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): $\delta = 223.7$ (br, C1), 191.0 (t, J(PC) = 10.6 Hz, C6), 181.7 (t, J(PC) = 18.6 Hz, C5), 174.8 (d, J(PC) = 20.1 Hz, C3), 160.3 (td, J(PC) = 21.7, 10.9 Hz, C4), 136.1–121.3 (m, Ph), 121.0 ppm (d, J(PC) = 81.8 Hz, C2); HRMS (ESI): m/z calcd for $C_{60}H_{50}INOOsP_3^+$: 1212.1759 $[M-PF_6]^+$; found: 1212.1745; elemental analysis calcd (%) for $C_{60}H_{50}F_6INOOsP_4$: C 53.14, H 3.72, N 1.03; found: C 53.01, H 4.11, N 0.61.

Synthesis of complex 2: Et_3N (146 μL, 1.05 mmol) was added to a mixture of complex **1a** (300 mg, 0.21 mmol) and silver oxide (146 mg, 0.63 mmol) in CH_2Cl_2 (10 mL) followed by phenyl isothiocyanate (125 μL, 1.05 mmol), and the mixture was heated at reflux for about 2 h to give a yellow-green suspension. The mixture was filtered through a Celite pad to remove the silver salt, and the filtrate was reduced to approximately 2 mL under vacuum. The residue was then purified by column chromatography (neutral alumina, acetone/dichloromethane, 1:15) to give product **2** as a yellow-green solid (220 mg, 73 %).^{1}H NMR (400.0 MHz, CD_2Cl_2): $\delta = 11.97$ (d, J(PH) = 16 Hz, 1 H, C1H), 7.99 (s, 1 H, C5H), 7.79 (br, 1 H, C3H), 7.84–6.41 ppm (m, 55 H, PPh_3 and NPh); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): $\delta = 14.02$ (s, CPPh$_3$), −6.21 (s, OsPPh$_3$), −144.48 ppm (septet, PF_6); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): $\delta = 240.1$ (t, J(PC) = 5.7 Hz, C1), 191.4 (t, J(PC) = 11.4 Hz, C7), 181.8 (d, J(PC) = 23.6 Hz, C3), 169.9 (br, C5), 157.5 (td, J(PC) = 16.8, 9.1 Hz, C4), 152.9 (s, C6), 150.0–121.5 (m, Ph), 120.5 ppm (d, J(PC) = 87.9 Hz, C2); elemental analysis calcd (%) for $C_{73}H_{58}F_6N_2OOsP_4S$: C 60.91, H 4.06, N 1.95; found: C 60.93, H 4.27, N 1.84.

Synthesis of complex 3: A similar reaction procedure to that of complex **2** was applied to synthesize **3** by using complex **1a** (300 mg, 0.21 mmol), silver oxide (146 mg, 0.63 mmol), Et_3N (146 μL, 1.05 mmol), and isopropyl isothiocyanate (112 μL, 1.05 mmol), which after purification by column chromatography (neutral alumina, acetone/dichloromethane, 1:20) gave product **3** as a green solid (183 mg, 62%). ^{1}H NMR (400.0 MHz, CD_2Cl_2): δ=11.82 (dd, *J*(PH)=17, 2 Hz, 1 H, C1H), 7.86 (s, 1 H, C5H), 7.66 (br, 1 H, C3H), 7.82–6.29 (m, 51 H, PPh_3 and NPh and C3H), 3.97 (m, 1 H, C8H), 0.71 ppm (d, *J*(HH)=6 Hz, 6 H, C9H); ^{31}P{^{1}H} NMR (161.9 MHz, CD_2Cl_2): δ=13.94 (s, C*P*Ph_3), −4.52 (s, Os*P*Ph_3), −144.40 ppm (septet, *P*F_6); ^{13}C{^{1}H} NMR (100.6 MHz, CD_2Cl_2, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): δ=236.6 (t, *J*(PC)=5.7 Hz, C1), 192.2 (t, *J*(PC)=11.4 Hz, C7), 178.9 (d, *J*(PC)=23.6 Hz, C3), 170.1 (br, C5), 157.8 (dt, *J*(PC)=26.0, 9.2 Hz, C4), 150.4 (s, C6), 147.6–126.6 (m, Ph), 120.9 (d, *J*(PC)=88.3 Hz, C2), 54.5 (s, C8), 22.9 ppm (s, C9); elemental analysis calcd (%) for $C_{70}H_{60}F_6N_2OOsP_4S$: C 59.82, H 4.30, N 1.99; found: C 59.86, H 4.44, N 1.53.

Synthesis of complex 4: Et_3N (257 μL, 1.85 mmol) was added to a mixture of complex **1b** (500 mg, 0.37 mmol) and silver oxide (257 mg, 1.11 mmol) in CH_2Cl_2 (10 mL) followed by phenyl isothiocyanate (221 μL, 1.85 mmol), and the mixture was heated at reflux for about 2 h to give a green suspension. The mixture was filtered through a Celite pad to remove the silver salt, and the filtrate was reduced to approximately 2 mL under vacuum. The residue was purified by column chromatography (neutral alumina, acetone/dichloromethane, 1:20) to give the mixture of isomers **4a** and **b** (1.00:0.55) as a green solid (352 mg, 70%). NMR spectral data for isomer **4a**: ^{1}H NMR (600.1 MHz, CD_2Cl_2): δ=11.08 (d, *J*(PH)=18 Hz, 1 H, C1H), 7.11 (br, 1 H, C3H), 7.01 (br, 1 H, C5H), 6.83 (br, 1 H, N1H), 7.82–6.89 ppm (m, 52 H, PPh_3 and Ph and C3*H*/C5H); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2): δ=12.86 (s, C*P*Ph_3), 1.06 (s, Os*P*Ph_3), −144.47 ppm (septet, *P*F_6); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): δ=230.6 (br, C1), 191.1 (t, *J*(PC)=10.7 Hz, C7), 178.4 (s, C5), 173.1 (d, apparent t, *J*(PC)=23.6 Hz, C3), 172.7 (s, C6), 165.9 (dt, apparent br, C4), 141.4–123.2 (m, Ph), 120.5 ppm (d, *J*(PC)=88.2 Hz, C2); NMR spectral data for isomer **4b**: ^{1}H NMR (600.1 MHz, CD_2Cl_2): δ=10.93 (d, *J*(PH)=19 Hz, 1 H, C01H), 7.01 (br, 1 H, C05H), 7.00 (br, 1 H, C03H), 7.82–6.89 ppm (m, 52 H, PPh_3 and Ph and C03*H*/C05H), 6.82 ppm (br, 1 H, N1H);^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2): δ=12.43 (s, C*P*Ph_3), 1.23 (s, Os*P*Ph_3), −144.47 ppm (septet, *P*F_6); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): δ=229.7 (br, C01), 190.9 (t, *J*(PC)=11.5 Hz, C07), 178.4 (br, C05), 172.7 (br, C06), 171.0 (d, *J*(PC)=23.5 Hz, C03), 166.9 (dt, apparent br, C04), 141.4–123.2 (m, Ph), 120.6 ppm (d, *J*(PC)=87.9 Hz, C02); HRMS (ESI): *m*/*z* calcd for $C_{67}H_{54}N_2OOsP_3S^+$: 1219.2779 $[M-PF_6]^+$; found: 1219.2746; elemental analysis calcd (%) for $C_{67}H_{54}F_6N_2OOsP_4S$: C 59.03, H 3.99, N 2.05; found: C 58.68, H 4.25, N 1.73.

Synthesis of complex 5: A similar reaction procedure to that of complex **4** was applied to synthesize **5** by using complex **1b** (475 mg, 0.35 mmol), silver oxide (243 mg, 1.05 mmol), Et_3N (243 μL, 1.75 mmol), and isopropyl isothiocyanate (187 μL, 1.75 mmol), which after purification by column chromatography (neutral alumina, acetone/dichloromethane, 1:20) gave product **5a** and **b** (1.00:0.18) as a green solid (270 mg, 58%). NMR spectral data for isomer **5a**: ^{1}H NMR (600.1 MHz, CD_2Cl_2): δ=10.63 (d, *J*(PH)=19 Hz, 1 H, C1H), 6.79 (br, 2 H, C5*H* and C3H), 7.87–6.87 ppm (m, 45 H, PPh_3), 6.69 (br, 1 H, N1H), 3.98 (m, 1 H, C8H), 1.00 ppm (d, *J*(HH)=6 Hz, 6 H, C9H); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2): δ=12.13 (s, C*P*Ph_3), 2.42 (s, Os*P*Ph_3), −144.47 ppm (septet, *P*F_6); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): δ=226.1 (br, C1), 191.5 (t, *J*(PC)=10.8 Hz, C7), 177.7 (br, C5), 173.4 (br, C6), 168.7 (dt, apparent t, *J*(PC)=11.7 Hz, C4), 168.0 (d, *J*(PC)=23.0 Hz, C3), 134.7–119.4 (m, Ph), 120.7 (d, *J*(PC)=88.7 Hz, C2), 47.5 (s, C8), 21.7 ppm (s, C9); NMR spectral datea for isomer **5b**: ^{1}H NMR (600.1 MHz, CD_2Cl_2): δ=10.80 (d, *J*(PH)=19 Hz, 1 H, C01H), 7.00 (br, 1 H, C05H), 6.93 (br, 1 H, C03H), 7.87–6.87 ppm (m, 45 H, P*Ph*), 6.37 (d, *J*(HH)=7.68 Hz, 1 H, N01H), 3.65 (m, 1 H, C08H), 0.85 ppm (d, *J*(HH)=6.8 Hz, 6 H, C9H); ^{31}P{^{1}H} NMR (242.9 MHz, CD_2Cl_2): δ=12.30 (s, C*P*Ph_3), 1.20 (s, Os*P*Ph_3), −144.47 ppm (septet, *P*F_6); ^{13}C{^{1}H} NMR (150.9 MHz, CD_2Cl_2, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): δ=228.4 (br, C01), 191.5 (t, *J*(PC)=10.8 Hz, C07), 179.0 (br, C05), 174.7 (br, C06), 170.5 (d, *J*(PC)=23.0 Hz, C03), 168.5 (dt, apparent t, *J*(PC)=12.7 Hz, C04), 134.7–119.4 (m, Ph), 118.6 (d, *J*(PC)=81.7 Hz, C02), 47.6 (s, C08), 22.7 ppm (s, C09); HRMS (ESI): *m*/*z* calcd for $C_{64}H_{56}N_2OOsP_3S^+$: 1185.2936 $[M-PF_6]^+$; found: 1185.2903; elemental analysis calcd (%) for $C_{64}H_{56}F_6N_2OOsP_4S$: C 57.83, H 4.25, N 2.11; found: C 57.87, H 4.09, N 1.69.

Synthesis of complex 6: $HBF_4{\cdot}Et_2O$ (41 μL, 0.30 mmol) was added to a solution of complex **2** (145 mg, 0.10 mmol) in CH_2Cl_2 (5 mL), and the mixture was stirred at room temperature for 10 min to give a green solution. The volume was reduced to about 2 mL under vacuum. Addition of ether (10 mL) to the solution produced a green solid, which was collected by filtration, washed with diethyl ether (3×5 mL), and dried under vacuum to give product **6** (129 mg, 87%). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ=13.01 (d, *J*(PH)=13 Hz, 1 H, C1H), 8.14 (br, 1 H, C3H), 7.82 (br, 1 H, C5H), 7.83–6.56 ppm (m, 45 H, PPh_3, 10 H, NPh), 0.87 ppm (br, 1 H, N*H*); ^{31}P{^{1}H} NMR (202.5 MHz, $CDCl_3$): δ=14.32 (s, C*P*Ph_3), −7.71 ppm (s, Os*P*Ph_3); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): δ=267.9 (br, C1), 197.7 (d, *J*(PC)=20.5 Hz, C3), 187.4 (t, *J*(PC)=11.1 Hz, C7), 166.8 (s, C6), 163.6 (s, C5), 158.6 (td, *J*(PC)=24.5, 8.0 Hz, C4), 139.3–125.7 (m, Ph), 118.6 ppm (d, *J*(PC)=89.4 Hz, C2); elemental analysis calcd (%) for $C_{73}H_{59}B_2F_8N_2OOsP_3S$: C 59.68, H 4.05, N 1.91; found: C 60.00, H 4.47, N 1.48.

Synthesis of complex 7: A similar reaction procedure to that of complex **6** was applied to synthesize **7** by using complex **3** (150 mg, 0.11 mmol) and $HBF_4{\cdot}Et_2O$ (45 μL, 0.33 mmol) to give product **7** (129 mg, 84%). ^{1}H NMR (600.1 MHz, $CDCl_3$): δ=12.88 (dd, *J*(PH)=13, 2 Hz, 1 H, C1H), 8.17 (m, 1 H, C3H), 7.82 (br, 1 H, C5H), 7.81–6.17 (m, 45 H, PPh_3, 5 H, NPh), 4.19 (m, 1 H, C8H), 1.26 (br, 1 H, N*H*), 0.91 ppm (d, *J*(HH)=6.5 Hz, 6 H, C9H); ^{31}P{^{1}H} NMR (242.9 MHz, $CDCl_3$): δ=14.76 (s, C*P*Ph_3), −6.70 ppm (s, Os*P*Ph_3); ^{13}C{^{1}H} NMR (150.9 MHz, $CDCl_3$, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): δ=265.5 (br, C1), 196.9 (d, *J*(PC)=21.3 Hz, C3), 188.1 (t, *J*(PC)=10.0 Hz, C7), 164.6 (s, C5), 164.0 (s, C6), 157.5 (td, *J*(PC)=25.5, 7.8 Hz, C4), 138.7–126.1 (m, Ph), 118.1 (d, *J*(PC)=89.3 Hz, C2), 50.8 (s, C8), 20.9 ppm (s, C9); elemental analysis calcd (%) for $C_{70}H_{61}B_2F_8N_2OOsP_3S$: C 58.59, H 4.28, N 1.95; found: C 58.18, H 4.55, N 1.48.

Synthesis of complex 8: $HBF_4{\cdot}Et_2O$ (90 μL, 0.66 mmol) was added to a mixture of isomers **4a** and **b** (300 mg, 0.22 mmol) in CH_2Cl_2 (10 mL), and the mixture was stirred at room temperature for 15 min to give a green solution. The volume was reduced to about 2 mL under vacuum. Addition of ether (10 mL) to the solution produced a yellow-green solid, which was collected by filtration, washed with diethyl ether (3×5 mL), and dried under vacuum to give product **8** as a yellow-green solid (254 mg, 83%). ^{1}H NMR (500.2 MHz, $CDCl_3$): δ=12.75 (dd, *J*(PH)=14, 2 Hz, 1 H, C1H), 10.07 (br, 1 H, PhN*H*), 9.32 (br, 1 H, N*H*), 7.66 (br, 1 H, C3H), 7.03 (br, 1 H, C5H), 7.85–6.86 ppm (m, 52 H, PPh_3 and Ph and C3 and C5); ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): δ=14.58 (s, C*P*Ph_3), −0.54 ppm (s, Os*P*Ph_3); ^{13}C{^{1}H} NMR (125.8 MHz, $CDCl_3$, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): δ=260.2 (br, C1), 193.3 (d, *J*(PC)=20.8 Hz, C3), 188.0 (t, *J*(PC)=10.7 Hz, C7), 163.7 (s, C6), 160.4 (s, C5), 159.4 (td, *J*(PC)=24.7, 9.3 Hz, C4), 135.4–125.3 (m, Ph), 118.4 ppm (d, *J*(PC)=88.8 Hz, C2); elemental analysis calcd (%) for

$C_{67}H_{55}B_2F_8N_2OOsP_3S$: C 57.77, H 3.98, N 2.01; found: C 57.82, H 4.17, N 1.69.

Synthesis of complex 9: A similar reaction procedure to that of complex **8** was applied to synthesize **9** by using complex **5** (200 mg, 0.15 mmol) and $HBF_4{\cdot}Et_2O$ (62 μL, 0.45 mmol) to give product **9** (164 mg, 80%). ^{1}H NMR (500.2 MHz, CD_2Cl_2): $\delta = 12.86$ (dd, *J*(PH) = 14, 2 Hz, 1 H, C1H), 8.33 (d, *J*(HH) = 7 Hz, 1 H, N1H), 7.63 (br, 1 H, C3H), 6.81 (d, *J*(HH) = 7 Hz, 1 H, C5H), 7.88–6.86 (m, 47 H, PPh_3 and C3 and C5), 4.04 (m, 1 H, C8H), 1.79 (br, 1 H, N2H), 1.04 ppm (d, *J*(HH) = 6 Hz, 6 H, C9H); ^{31}P{^{1}H} NMR (202.5 MHz, CD_2Cl_2): $\delta = 14.61$ (s, C*P*Ph_3), -0.97 ppm (s, Os*P*Ph_3); ^{13}C{^{1}H} NMR (125.8 MHz, CD_2Cl_2, plus ^{13}C-DEPT-135, ^{1}H–^{13}C HSQC and ^{1}H–^{13}C HMBC): $\delta = 259.7$ (br, C1), 192.4 (d, *J*(PC) = 20.4 Hz, C3), 188.8 (t, *J*(PC) = 10.0 Hz, C7), 162.8 (s, C6), 160.7 (s, C5), 158.7 (td, apparent d, *J*(PC) = 25.2 Hz, C4), 135.5–129.1 (m, Ph), 119.0 (d, *J*(PC) = 86.6 Hz, C2), 49.5 (s, C8), 21.3 ppm (s, C9); elemental analysis calcd (%) for $C_{64}H_{57}B_2F_8N_2OOsP_3S$: C 56.56, H 4.23, N 2.06; found: C 56.65, H 4.41, N 1.62.

X-ray crystallographic analysis

Crystals that were suitable for X-ray diffraction were grown from a CH_2Cl_2 solution layered with ethyl ether for complexes **1b**, **2**, **8**, and **9**, and from the CH_2Cl_2 solution layered with toluene for complex **7**. Single-crystal X-ray diffraction data were collected on an Oxford Gemini S Ultra CCD Area Detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) for complexes **1b** and **9**. Complex **2** was collected on a multiwire proportional Area Detector with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å); complexes **7** and **8** were collected on an XtaLAB Synergy, Dualflex, HyPix Area Detector with mirror-monochromated $Cu_{K\alpha}$ radiation ($\lambda = 1.54184$ Å). All of the data were corrected for absorption effects by using the multiscan technique. By using Olex2,[32] the structures of complexes **1b**, **7**, and **8** were solved with the olex2.solve[33] structure solution program by using Charge Flipping; the structure of complex **2** was solved with the XS[34] structure solution program by using the Patterson Method; the structure of complex **9** was solved with the XT[35] structure solution program by using Intrinsic Phasing; all the structures were refined with the ShelXL[36] refinement package by using least-squares minimization. All of the non-hydrogen atoms were refined anisotropically, unless otherwise stated. The hydrogen atoms were placed at their idealized positions and refined by using a riding model, unless otherwise stated. The diffuse electron densities resulting from the residual solvent molecules in complex **7** were removed from the data set by using the SQUEEZE routine of PLATON. The solvent CH_2Cl_2, H_2O, and phenyl groups on PPh_3 were disordered and refined by using restraints. CCDC 1878325 (**1b**), 1878322 (**2**), 1878382 (**7**), 1878383 (**8**), and 1878392 (**9**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: [4+2] cyclization · 1,3-thizaine · heteroatoms · metallacycles · osmium

[1] For selected reviews, see: a) L. J. Wright, *Dalton Trans.* **2006**, 1821–1827; b) C. W. Landorf, M. M. Haley, *Angew. Chem. Int. Ed.* **2006**, *45*, 3914–3936; *Angew. Chem.* **2006**, *118*, 4018–4040; c) B. J. Frogley, L. J. Wright, *Coord. Chem. Rev.* **2014**, *270–271*, 151–166; d) X.-Y. Cao, Q. Zhao, Z. Lin, H. Xia, *Acc. Chem. Res.* **2014**, *47*, 341–354; e) B. J. Frogley, L. J. Wright, *Chem. Eur. J.* **2018**, *24*, 2025–2038.

[2] For selected reviews, see: a) G. Jia, *Coord. Chem. Rev.* **2007**, *251*, 2167–2187; b) G. Jia, *Organometallics* **2013**, *32*, 6852–6866; c) J. Chen, G. Jia, *Coord. Chem. Rev.* **2013**, *257*, 2491–2521.

[3] a) J. Wei, Y. Zhang, Y. Chi, L. Liu, W.-X. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2016**, *138*, 60–63; b) J. Chen, K.-H. Lee, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem. Int. Ed.* **2016**, *55*, 7194–7198; *Angew. Chem.* **2016**, *128*, 7310–7314.

[4] For selected reviews, see: a) S. Roy, U. Rosenthal, E. D. Jemmis, *Acc. Chem. Res.* **2014**, *47*, 2917–2930; b) X. Yan, C. Xi, *Acc. Chem. Res.* **2015**, *48*, 935–946; c) W. Ma, C. Yu, T. Chen, L. Xu, W.-X. Zhang, Z. Xi, *Chem. Soc. Rev.* **2017**, *46*, 1160–1192; d) M. Cui, R. Lin, G. Jia, *Chem. Asian J.* **2018**, *13*, 895–912; e) H. Wang, X. Zhou, H. Xia, *Chin. J. Chem.* **2018**, *36*, 93–105; f) J. Wei, W.-X. Zhang, Z. Xi, *Chem. Sci.* **2018**, *9*, 560–568.

[5] Examples of non metal-bridged polycyclic metallacycles, see: a) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, *J. Am. Chem. Soc.* **2003**, *125*, 9898–9899; b) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, L. L. Santos, E. Álvarez, V. Salazar, K. Mereiter, E. Oñate, *Organometallics* **2007**, *26*, 3403–3415; c) M. Talavera, J. Bravo, J. Castro, S. García-Fontán, J. M. Hermida-Ramón, S. Bolaño, *Dalton Trans.* **2014**, *43*, 17366–17374; d) Á. Vivancos, Y. A. Hernández, M. Paneque, M. L. Poveda, V. Salazar, E. Álvarez, *Organometallics* **2015**, *34*, 177–188; e) Á. Vivancos, F. Vattier, J. López-Serrano, M. Paneque, M. L. Poveda, E. Álvarez, *J. Am. Chem. Soc.* **2015**, *137*, 4074–4077; f) W. Ruan, T.-F. Leung, C. Shi, K. H. Lee, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Chem. Sci.* **2018**, *9*, 5994–5998; g) M.-X. Zhang, Z. Xu, T. Lu, J. Yin, S. H. Liu, *Chem. Eur. J.* **2018**, *24*, 14891–14895.

[6] Examples of metal-bridged polycyclic metallacycles, see: a) J. M. O'Connor, L. Pu, R. Chadha, *Angew. Chem. Int. Ed. Engl.* **1990**, *29*, 543–545; *Angew. Chem.* **1990**, *102*, 586–588; b) J. M. O'Connor, L. Pu, R. K. Chadha, *J. Am. Chem. Soc.* **1990**, *112*, 9627–9628; c) J. M. O'Connor, L. Pu, A. L. Rheingold, *J. Am. Chem. Soc.* **1990**, *112*, 9663–9665; d) J. Chen, R. J. Angelici, *Organometallics* **1992**, *11*, 992–996; e) J. M. O'Connor, K. Hiibner, R. Merwin, P. K. Gantzel, B. S. Fong, M. Adams, A. L. Rheingold, *J. Am. Chem. Soc.* **1997**, *119*, 3631–3632; f) J. C. Jeffery, M. Green, J. M. Lynam, *Chem. Commun.* **2002**, 3056–3057; g) M. Paneque, M. L. Poveda, N. Rendón, K. Mereiter, *J. Am. Chem. Soc.* **2004**, *126*, 1610–1611; h) G. R. Clark, G.-L. Lu, W. R. Roper, L. J. Wright, *Organometallics* **2007**, *26*, 2167–2177; i) M. Paneque, M. L. Poveda, N. Rendón, K. Mereiter, *Organometallics* **2009**, *28*, 172–180; j) A. F. Dalebrook, L. J. Wright, *Organometallics* **2009**, *28*, 5536–5540; k) T. Wang, H. Zhang, F. Han, R. Lin, Z. Lin, H. Xia, *Angew. Chem. Int. Ed.* **2012**, *51*, 9838–9841; *Angew. Chem.* **2012**, *124*, 9976–9979; l) M. Luo, L. Long, H. Zhang, Y. Yang, Y. Hua, G. Liu, Z. Lin, H. Xia, *J. Am. Chem. Soc.* **2017**, *139*, 1822–1825; m) Y. Zhang, J. Wei, Y. Chi, X. Zhang, W.-X. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2017**, *139*, 5039–5042; n) J. Li, H. Kang, K. Zhuo, Q. Zhuo, H. Zhang, Y.-M. Lin, H. Xia, *Chin. J. Chem.* **2018**, *36*, 1156–1160.

[7] C. Zhu, S. Li, M. Luo, X. Zhou, Y. Niu, M. Lin, J. Zhu, Z. Cao, X. Lu, T. Wen, Z. Xie, P. v. R. Schleyer, H. Xia, *Nat. Chem.* **2013**, *5*, 698–703.

[8] C. Zhu, M. Luo, Q. Zhu, J. Zhu, P. v. R. Schleyer, J. I.-C. Wu, X. Lu, H. Xia, *Nat. Commun.* **2014**, *5*, 3265–3271.

[9] C. Zhu, C. Yang, Y. Wang, G. Lin, Y. Yang, X. Wang, J. Zhu, X. Chen, X. Lu, G. Liu, H. Xia, *Sci. Adv.* **2016**, *2*, e1601031.

[10] a) C. Zhu, H. Xia, *Acc. Chem. Res.* **2018**, *51*, 1691–1700; b) Q. Zhuo, H. Zhang, Y. Hua, H. Kang, X. Zhou, X. Lin, Z. Chen, J. Lin, K. Zhuo, H. Xia, *Sci. Adv.* **2018**, *4*, eaat0336; c) X. Zhou, Y. Li, Y. Shao, Y. Hua, H. Zhang, Y.-

M. Lin, H. Xia, *Organometallics* **2018**, *37*, 1788 – 1794; d) Z. Lu, Q. Lin, Y. Cai, S. Chen, J. Chen, W. Wu, X. He, H. Xia, *ACS Macro Lett.* **2018**, *7*, 1034 – 1038; e) Y. Hua, Q. Lan, J. Fei, C. Tang, J. Lin, H. Zha, S. Chen, Y. Lu, J. Chen, X. He, H. Xia, *Chem. Eur. J.* **2018**, *24*, 14531 – 14538.

[11] R. Li, Z. Lu, Y. Cai, F. Jiang, C. Tang, Z. Chen, J. Zheng, J. Pi, R. Zhang, J. Liu, Z.-B. Chen, Y. Yang, J. Shi, W. Hong, H. Xia, *J. Am. Chem. Soc.* **2017**, *139*, 14344 – 14347.

[12] Z. Lu, Y. Cai, Y. Wei, Q. Lin, J. Chen, X. He, S. Li, W. Wu, H. Xia, *Polym. Chem.* **2018**, *9*, 2092 – 2100.

[13] a) C. Zhu, Y. Yang, M. Luo, C. Yang, J. Wu, L. Chen, G. Liu, T. Wen, J. Zhu, H. Xia, *Angew. Chem. Int. Ed.* **2015**, *54*, 6181 – 6185; *Angew. Chem.* **2015**, *127*, 6279 – 6283; b) C. Yang, G. Lin, C. Zhu, X. Pang, Y. Zhang, X. Wang, X. Li, B. Wang, H. Xia, G. Liu, *J. Mater. Chem. B* **2018**, *6*, 2528 – 2535; c) Q. Lin, S. Li, J. Lin, M. Chen, Z. Lu, C. Tang, Z. Chen, X. He, J. Chen, H. Xia, *Chem. Eur. J.* **2018**, *24*, 8375 – 8381.

[14] a) K. J. Weller, I. Filippov, P. M. Briggs, D. E. Wigley, *Organometallics* **1998**, *17*, 322 – 329; b) B. Liu, H. Wang, H. Xie, B. Zeng, J. Chen, J. Tao, T. B. Wen, Z. Cao, H. Xia, *Angew. Chem. Int. Ed.* **2009**, *48*, 5430 – 5434; *Angew. Chem.* **2009**, *121*, 5538 – 5542.

[15] a) J. Chen, L. M. Daniels, R. J. Angelici, *J. Am. Chem. Soc.* **1990**, *112*, 199 – 204; b) W. D. Jones, L. Dong, *J. Am. Chem. Soc.* **1991**, *113*, 559 – 564; c) W. D. Jones, R. M. Chin, *J. Am. Chem. Soc.* **1992**, *114*, 9851 – 9858; d) J. R. Bleeke, P. V. Hinkle, N. P. Rath, *Organometallics* **2001**, *20*, 1939 – 1951; e) J. G. Planas, D. Prim, F. Rose-Munch, E. Rose, R. Thouvenot, J. Vaissermann, *Organometallics* **2002**, *21*, 4385 – 4389; f) J. R. Bleeke, P. V. Hinkle, M. Shokeen, N. P. Rath, *Organometallics* **2004**, *23*, 4139 – 4149.

[16] a) Q. Zhuo, Z. Chen, Y. Yang, X. Zhou, F. Han, J. Zhu, H. Zhang, H. Xia, *Dalton Trans.* **2016**, *45*, 913 – 917; b) Q. Zhuo, X. Zhou, H. Kang, Z. Chen, Y. Yang, F. Han, H. Zhang, H. Xia, *Organometallics* **2016**, *35*, 1497 – 1504.

[17] a) H. Yamazaki, K. Aoki, *J. Organomet. Chem.* **1976**, *122*, C54 – C58; b) R. Birk, U. Grössmann, H.-U. Hund, H. Berke, *J. Organomet. Chem.* **1988**, *345*, 321 – 329; c) U. Grössmann, H.-U. Hund, H. W. Bosch, H. Schmalle, H. Berke, *J. Organomet. Chem.* **1991**, *408*, 203 – 218; d) M. I. Bruce, B. C. Hall, B. W. Skelton, E. R. T. Tiekink, A. H. White, N. N. Zaitseva, *Aust. J. Chem.* **2000**, *53*, 99 – 107; e) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2006**, *25*, 1771 – 1777; f) G. R. Clark, T. R. O'Neale, W. R. Roper, D. M. Tonei, L. J. Wright, *Organometallics* **2009**, *28*, 567 – 572; g) G. R. Clark, P. M. Johns, W. R. Roper, T. Söhnel, L. J. Wright, *Organometallics* **2011**, *30*, 129 – 138; h) B. J. Frogley, L. J. Wright, *Angew. Chem. Int. Ed.* **2017**, *56*, 143 – 147; *Angew. Chem.* **2017**, *129*, 149 – 153; i) B. J. Frogley, A. F. Dalebrook, L. J. Wright, *Organometallics* **2016**, *35*, 400 – 409; j) B. J. Frogley, L. C. Perera, L. J. Wright, *Chem. Eur. J.* **2018**, *24*, 4304 – 4309.

[18] T. Wang, S. Li, H. Zhang, R. Lin, F. Han, Y. Lin, T. B. Wen, H. Xia, *Angew. Chem. Int. Ed.* **2009**, *48*, 6453 – 6456; *Angew. Chem.* **2009**, *121*, 6575 – 6578.

[19] T. Wang, H. Zhang, F. Han, L. Long, Z. Lin, H. Xia, *Angew. Chem. Int. Ed.* **2013**, *52*, 9251 – 9255; *Angew. Chem.* **2013**, *125*, 9421 – 9425.

[20] F. Han, T. Wang, J. Li, H. Zhang, H. Xia, *Chem. Eur. J.* **2014**, *20*, 4363 – 4372.

[21] T. Wang, F. Han, H. Huang, J. Li, H. Zhang, J. Zhu, Z. Lin, H. Xia, *Sci. Rep.* **2015**, *5*, 9584 – 9590.

[22] a) G. R. Clark, T. J. Collins, K. Marsden, W. R. Roper, *J. Organomet. Chem.* **1983**, *259*, 215 – 232; b) R. Flügel, O. Gevert, H. Werner, *Chem. Ber.* **1996**, *129*, 405 – 410; c) C. E. F. Rickard, W. R. Roper, S. D. Woodgate, L. J. Wright, *J. Organomet. Chem.* **2001**, *623*, 109 – 115.

[23] J. Chen, Z.-A. Huang, Y. Hua, H. Zhang, H. Xia, *Organometallics* **2015**, *34*, 340 – 347.

[24] For the preparation and characterization of complex **1 b**, please see the Experimental Section and the Supporting Information.

[25] a) O. Seidelmann, L. Beyer, R. Richter, T. Herr, *Inorg. Chim. Acta* **1998**, *271*, 40 – 48; b) A. L. Grieb, J. S. Merola, *J. Organomet. Chem.* **2012**, *713*, 163 – 168; c) C. O'Connor, D. C. Lawlor, C. Robinson, H. Müller-Bunz, A. D. Phillips, *Organometallics* **2018**, *37*, 1860 – 1875; d) S. K. Bera, S. Panda, S. D. Baksi, G. K. Lahiri, *Dalton Trans.* **2018**, *47*, 15897 – 15906.

[26] K. M. Doxsee, J. B. Farahi, H. Hope, *J. Am. Chem. Soc.* **1991**, *113*, 8889 – 8898.

[27] J. Chen, Z.-A. Huang, Z. Lu, H. Zhang, H. Xia, *Chem. Eur. J.* **2016**, *22*, 5363 – 5375.

[28] G. P. Elliott, W. R. Roper, J. M. Waters, *J. Chem. Soc. Chem. Commun.* **1982**, 811 – 813.

[29] H. Quiniou, O. Guilloton, Advances in Heterocyclic Chemistry, *Vol. 50* (Eds.: A. R. Katritzky), Academic Press, **1990**, pp. 85 – 156.

[30] a) M. Yokoyama, M. Nakamura, H. Ohteki, T. Imamoto, K.-ichi. Yamaguchi, *J. Org. Chem.* **1982**, *47*, 1090 – 1094; b) J. P. Pradere, J. C. Roze, H. Quiniou, R. Danion-Bougot, D. Danion, L. Toupet, *Can. J. Chem.* **1986**, *64*, 597 – 602; c) M. Bakasse, G. Duguay, R. Quiniou, L. Toupet, *Tetrahedron* **1988**, *44*, 139 – 146; d) A. Boussoufi, P. Hudhomme, P. Hitchcock, G. Duguay, *Tetrahedron: Asymmetry* **1991**, *2*, 157 – 164; e) K. T. Potts, T. Rochanapruk, A. Padwa, S. J. Coats, L. Hadjiarapoglou, *J. Org. Chem.* **1995**, *60*, 3795 – 3805; f) M. Y. Bugera, K. V. Tarasenko, V. P. Kukhar, G.-V. Röschenthaler, I. I. Gerus, *Synthesis* **2013**, *45*, 3157 – 3163.

[31] T. Wang, H. Zhang, F. Han, L. Long, Z. Lin, H. Xia, *Chem. Eur. J.* **2013**, *19*, 10982 – 10991.

[32] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339 – 341.

[33] L. J. Bourhis, O. V. Dolomanov, R. J. Gildea, J. A. K. Howard, H. Puschmann, *Acta Crystallogr. Sect. A* **2015**, *71*, 59 – 75.

[34] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2008**, *64*, 112 – 122.

[35] G. M. Sheldrick, *Acta Crystallogr. Sect. A* **2015**, *71*, 3 – 8.

[36] G. M. Sheldrick, *Acta Crystallogr. Sect. C* **2015**, *71*, 3 – 8.

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