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Carbolong Chemistry

Synthesis and Characterization of Photothermal Osmium Carbolong Complexes

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Abstract: Metallacycles with chelating polydentate conjugated-carbon chain ligands are called carbolong complexes, which are expected to have interesting properties. In this work, the preparation of 12-carbon carbolong complexes in which all of the coordinated atoms in the equatorial plane are carbon atoms was studied. With the help of the well-established mechanism, a new approach to prepare coplanar carbolong complexes bearing different organic functional groups was developed by adding different terminal alkynes in sequence. In the presence of HBF_4, these coplanar carbolong complexes were converted to η^3-allyl osmapentalene derivatives, which can be produced directly from the reaction of cyclopropaosmapentalene **1** with terminal alkynes in the presence of $AgBF_4$ under anhydrous conditions. This study offers a new route for the preparation of functional osmium carbolong complexes with excellent photothermal properties, which can be used to prepare photothermal materials.

Introduction

Metallacycles constructed with conjugated-carbon ring(s) and isolobal metal fragment(s) are interesting organometallic complexes. Reported metallacycles include metallabenzenes,[1,2] metallabenzynes,[3,4] metallaannulenes,[5] and other metallacycles.[6,7] Most of them are Hückel metallaaromatics.[8] Recently, we have prepared a series of Craig-type Möbius metallaaromatics,[9,10] in which metal centers are chelated by a conjugated-carbon chain. This conjugated-carbon chain was called a "carbolong ligand", and its metal chelate complex a "carbolong complex".[11] Carbolong complexes were expected to show interesting properties owing to their highly conjugated structures. For example, we have reported that the first 12-carbon osmium carbolong complexes **2** and **3** show broad absorptions covering the region from UV/Vis to near-infrared (NIR) and exhibit excellent photothermal properties.[12]

These 12-carbon carbolong complexes were used for NIR photothermal ablation of tumor cells in vivo.[12,13] In addition, they were also chemically linked with methoxypolyethylene glycols to improve their water solubility and biocompatibility.[14] However, the strategy to prepare derivatives bearing organic functional groups is still limited. Herein, we report the preparation of new 12-carbon osmium carbolong complexes under different reaction conditions and improved synthetic methods. These 12-carbon osmium carbolong complexes, in which all of the coordinated atoms in the equatorial plane are carbon atoms, are a new type of photothermal molecular material.

Results and Discussion

Wet or anhydrous synthesis

In our previous study, complex **2** was isolated in 47% yield from the reaction of cyclopropaosmapentalene **1** with an excess of phenylacetylene and water in the presence of $AgBF_4$ at room temperature (Scheme 1).[12] Under anhydrous conditions, the reaction of complex **1** with an excess of phenylacetylene produced unexpected purple complex **4** (Scheme 1).

The structure of complex **4** was confirmed by single-crystal X-ray diffraction analysis. As shown in Figure 1, all of the coordination sites in the equatorial plane of **4** are occupied by carbon atoms, and the axial positions are occupied by two phosphorus atoms. Compared to complex **2**, the metallacyclic unit in **4** is no longer planar. The torsion angle of C8–C9 and C10–C11 of 96.33° shows that the interaction of the π-allyl moiety (C10–C12) with the remaining π-carbolong ligand (C1–C10) is significantly reduced. Nevertheless, the osmapentalene substructure (comprising Os1 and C1–C7) is almost planar. The Os1–C1 (2.084 Å), Os1–C4 (2.098 Å), and Os1–C7 (2.074 Å) bond lengths are within the range of those for reported osmapentalenes (1.926–2.175 Å)[9i–n 12] and indicative of delocalized

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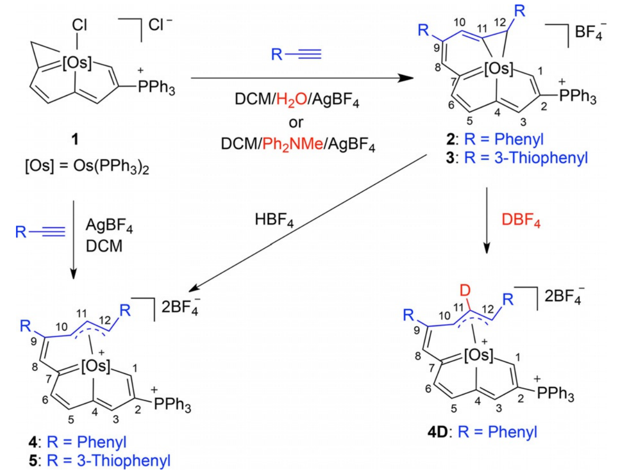


Scheme 1. Reaction of complex **1** with terminal alkynes in the presence of $AgBF_4$ under different conditions.

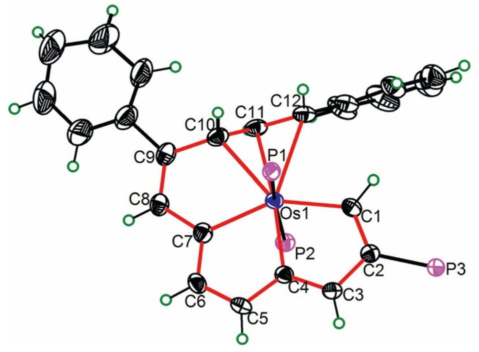


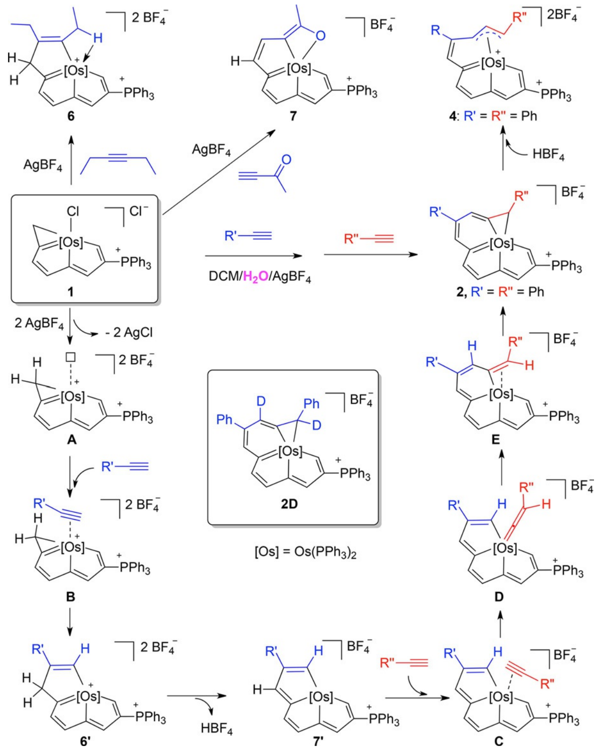
Figure 1. X-ray molecular structure of the cation of complex **4** with 50% probability ellipsoids. The phenyl groups of PPh_3 moieties were omitted for clarity. Selected bond lengths [Å] and angles [°]: Os–C1 2.084(4), Os1–C4 2.098(4), Os1–C7 2.074(4), Os1–C10 2.267(5), Os1–C11 2.317(6) Os1–C12 2.537(4), C1–C2 1.383(6), C2–C3 1.414(5), C3–C4 1.375(5), C4–C5 1.409(5), C5–C6 1.368(6), C6–C7 1.410(6), C7–C8 1.444(6), C8–C9 1.347(6), C9–C10 1.485(6), C10–C11 1.417(6), C11–C12 1.396(6); Os1-C1-C2 118.9(3), C1-C2-C3 114.0(4), C2-C3-C4 113.8(3), C3-C4-Os1 118.8(3), C4-Os1-C1 74.5(1), Os1-C4-C5 117.6(3), C4-C5-C6 114.6(3), C5-C6-C7 114.3(3), C6-C7-Os1 118.7(3), C7-Os1-C4 74.8(2), C7-Os1-C10 72.5(2), C7-Os1-C11 97.7(2), C7-C8-C9 115.4(4), C8-C9-C10 114.1(4), C9-C10-C11 122.4(4), C10-C11-Os1 70.1(2), C11-Os1-C12 36.0(1), C11-C12-Os1 70.1(3), C10-C11-C12 122.2(4), Os1-C11-C12 82.2(3), P1-Os1-P2 170.4(4).

metal–carbon bonds of the osmapentalene substructure (Os1 and C1–C7). The Os1–C10 (2.267 Å), Os1–C11 (2.317 Å), and Os1–C12 (2.537 Å) bond lengths are similar to those for reported Os–C(η^3-allyl) bonds.[15] Structurally, complex **4** still has a 12-atom carbon chain (C1–C12) as a multidentate ligand coordinated to a transition metal center (Os).

The structure of **4** was further confirmed by NMR spectroscopy, HRMS, and elemental analysis. In the ^{1}H NMR spectrum, the resonance of H1 is located at 12.54 ppm (d, $J_{P\text{-}H}=17.0$ Hz), which is similar to the corresponding signals for reported osmapentalenes (11.94–14.01 ppm).[9n, 12] The signals of other protons on the fused rings are observed in the aromatic region (7.82–8.94 ppm). In the $^{31}P\{^1H\}$ NMR spectrum, the $CPPh_3$ signal appears at 11.93 ppm as an apparent triplet ($J_{P\text{-}P}=4.3$ Hz), and the two $OsPPh_3$ signals appear at −13.70 (dd, $J_{P\text{-}P}=223.8$, 3.8 Hz) and −16.20 (dd, $J_{P\text{-}P}=226.8$, 4.0 Hz) ppm. The $^{13}C\{^1H\}$ NMR spectrum of complex **4** shows signals in the downfield region at 233.9 (t, $J_{P\text{-}C}=7.1$ Hz, C7), 210.5 (t, $J_{P\text{-}C}=9.2$ Hz, C1), and 192.8 ppm (dt, $J_{P\text{-}C}=21.6$ Hz, $J_{P\text{-}C}=6.1$ Hz, C4) for metal-bonded carbon atoms and signals in the upfield region at 101.5 ppm for C10, 88.7 ppm for C12, and 87.5 ppm for C11, as expected for η^3-allyl organometallics.

The reaction of complex **1** with an excess of 3-ethynylthiophene also gave complex **5** in the presence of $AgBF_4$ under anhydrous conditions (Scheme 1). Complex **5** has NMR data similar to those of complex **4**, which suggest that they have similar structures.

As shown in Scheme 2, the proposed mechanism for the formation of complex **2** from the reaction of complex **1** and alkyne in the presence of $AgBF_4$ was supported by the isolation of complex **6**[16] (to support the presence of intermediate **6′**) by using an internal alkyl alkyne and by the isolation of complex **7**[9f] (to support the presence of intermediate **7′**) by using an alkynone.



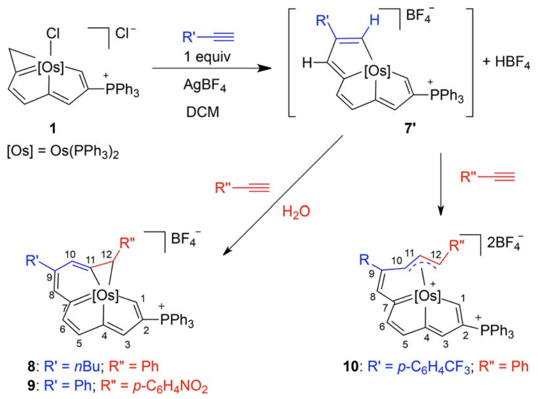
Scheme 2. Reaction of complex **1** with alkynes in the presence of $AgBF_4$ and the proposed reaction mechanism.

When wet PhC≡CD was used, the deuterium-labeled complex **2D** could be isolated, and its formula was confirmed by ^{2}D NMR and HRMS data (Figures S1–S3, Supporting Information), and this supports the rearrangement of intermediate **C** to **2** via intermediates **D** and **E** (Scheme 2). Further study showed that complex **4** was produced by protonation of complex **2** by HBF_4 generated in situ (see Figure S4 for the in situ NMR reaction of complex **2** with HBF_4). This result was further confirmed by the isolation of deuterium-labeled complex **4D** (Scheme 1, see ^{2}D NMR and HRMS data in Figures S5 and S6 of the Supporting Information) from the reaction of complex **2** and DBF_4.

In the reaction of complex **1** and alkyne in the presence of $AgBF_4$, the generation of HBF_4 (intermediate **6′** would release HBF_4 to give intermediate **7′**)[16] is further supported by the pH value (pH ≤ 1, tested by pH paper, Figure S7 of the Supporting Information) of the reaction mixture. Hence, we added *N*-methyldiphenylamine as an acid (HBF_4) scavenger to the reaction of complex **1** and alkyne in the presence of $AgBF_4$ under anhydrous conditions. As a result, the reaction produced complex **2** as the final product (Scheme 1, see in situ NMR reaction of Figure S8 in the Supporting Information). Interestingly, complex **2** was also produced as the final product in the presence of water (Figure S8), likely due to the extraction of acid (HBF_4) generated in situ by water and the subsequent removal of acid (HBF_4) from the organic reactant phase (CH_2Cl_2).

New approach to prepare 12-carbon osmium carbolong complexes

Inspired by the fact that intermediate **7′** can react with another alkyne to give complex **2** (Scheme 2), we envisioned that osmium carbolong complexes bearing organic functional groups could be prepared by using functional terminal alkynes. Thus, the intermediate was generated in situ from the reaction of complex **1** with 1 equiv alkyne in the presence of $AgBF_4$, and then the second alkyne was added subsequently to give complexes **8** and **9** in the presence of water (Scheme 3).



Scheme 3. New approach to prepare 12-carbon osmium carbolong complexes.

Complexes **8** and **9** were characterized by multinuclear NMR, elemental analysis, and HRMS. The molecular structure of complex **9** was also confirmed by single-crystal X-ray diffraction analysis. As shown in Figure 2, the metallacyclic unit in **9** is almost planar, as reflected by the small mean deviation from the least-squares plane (0.024 Å). The most interesting feature is the presence of a nitro group on the phenyl group attached at C12 of the metallacycle, supporting the incorporation of an organic functional group. The nitro group of metallaaromatics has been used to prepare amino-containing metallaaromatics.[2a]

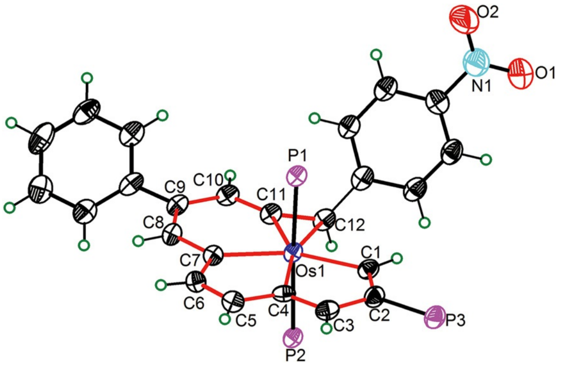


Figure 2. X-ray molecular structure of the cation of complex **9** with 50% probability ellipsoids. The phenyl groups of PPh_3 moieties are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os–C1 2.087(5), Os1–C4 2.116(4), Os1–C7 2.092(4), Os1–C11 2.033(4), Os1–C12 2.252(4), C1–C2 1.375(6), C2–C3 1.436(7), C3–C4 1.364(7), C4–C5 1.404(7), C5–C6 1.356(7), C6–C7 1.423(7), C7–C8 1.436(6), C8–C9 1.388(6), C9–C10 1.433(6), C10–C11 1.348(6), C11–C12 1.413(6); Os1-C1-C2 117.6(3), C1-C2-C3 115.3(4), C2-C3-C4 113.7(4), C3-C4-Os1 117.9(3), C4-Os1-C1 75.5(2), Os1-C4-C5 116.0(3), C4-C5-C6 115.5(4), C5-C6-C7 116.6(4), C6-C7-Os1 115.6(3), C7-Os1-C4 76.3(2), C7-Os1-C11 80.7(2), C7-C8-C9 126.2(4), C8-C9-C10 120.9(4), C9-C10-C11 121.7(4), C10-C11-Os1 139.5(4), C11-Os1-C12 38.1(2), C11-C12-Os1 62.5(2), C10-C11-C12 141.0(4), Os1-C11-C12 79.4(3), P1-Os1-P2 167.9(4).

The molecular structure of complex **9** was further confirmed by multinuclear NMR spectroscopy. In the ^{1}H NMR spectrum (Figure S30 of the Supporting Information), the signals of H1, H3 H8, H10, H5, H6, and H12 are located at 13.18, 8.68, 7.84, 7.82, 7.66, 7.57, and 6.63 ppm, respectively, similar to those of complex **2**. In the ^{31}P{^{1}H} NMR spectrum (Figure S31 of the Supporting Information), the $CPPh_3$ signal appears at 10.1 ppm, and the two $OsPPh_3$ signals appear at −9.8 and −18.1 ppm. In the ^{13}C{^{1}H} NMR spectrum (Figure S32 of the Supporting Information), the signals of C1, C4, C7, C11, and C12 are located at 207.2 (td, $J_{P\text{-}C} = 12.5$ Hz, $J_{P\text{-}C} = 5.0$ Hz), 199.9 (dt, $J_{P\text{-}C} = 25.2$ Hz, $J_{P\text{-}C} = 6.2$ Hz), 230.6 (t, $J_{P\text{-}C} = 7.6$ Hz), 215.8 (t, $J_{P\text{-}C} = 5.1$ Hz), and 15.0 ppm (s), respectively. The molecular formula of complex **9** was also confirmed by HRMS (*m*/*z* = 1328.3538, Figure S36 of the Supporting Information). Complex **8** has NMR data similar to those of complex **9**, which suggest that they have similar structures.

In the absence of water, the reaction of complex **1** with $AgBF_4$ and 1 equiv of HC≡C(*p*-$C_6H_4CF_3$) followed by the second alkyne (HC≡CPh) directly produced complex **10**. The molecular structure of complex **10** was also confirmed by single-crystal X-ray diffraction analysis. As shown in Figure 3, the structure of complex **10** is similar to that of complex **4**, except that it contains a CF_3 group on the phenyl group attached at C9. The molecular structure of complex **10** was further confirmed by multinuclear NMR spectroscopy, elemental analysis, and HRMS (Figures S37–S43 of the Supporting Information). In particular, the CF_3 and BF_4^- signals in the ^{19}F NMR spectrum (Figure S39 of the Supporting Information) are located at −63.1 and −152.1 ppm, respectively.

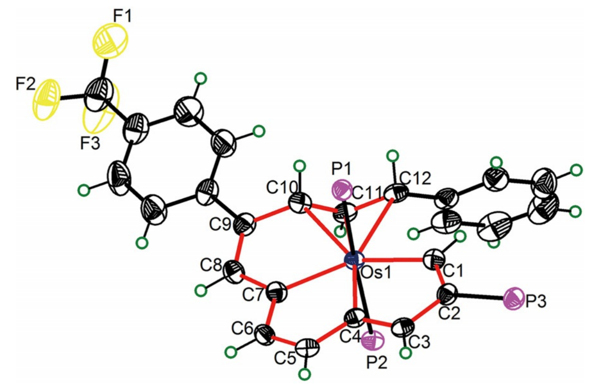


Figure 3. X-ray molecular structure of the cation of complex **12** with 50 % probability ellipsoids. The phenyl groups of PPh_3 moieties are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os–C1 2.086(5), Os1–C4 2.091(5), Os1–C7 2.067(5), Os1–C10 2.253(5), Os1–C11 2.312(5), Os1–C12 2.515(4), C1–C2 1.384(7), C2–C3 1.427(6), C3–C4 1.371(7), C4–C5 1.414(6), C5–C6 1.369(7), C6–C7 1.413(6), C7–C8 1.438(7), C8–C9 1.354(6), C9–C10 1.487(7), C10–C11 1.422(6); C11–C12 1.395(7), Os1-C1-C2 118.3(3), C1-C2-C3 113.9(4), C2-C3-C4 113.4(4), C3-C4-Os1 119.5(4), C4-Os1-C1 74.5(2), Os1-C4-C5 118.2(3), C4-C5-C6 114.1(4), C5-C6-C7 113.8(4), C6-C7-Os1 119.2(3), C7-Os1-C4 74.5(2), C7-Os1-C11 97.0(2), C7-C8-C9 115.3(4), C8-C9-C10 113.5(4), C9-C10-C11 122.1(4), C10-C11-Os1 69.6(3), C11-Os1-C12 33.2(1), C11-C12-Os1 65.4(3), C10-C11-C12 118.1(4), Os1-C11-C12 81.4(3), P1-Os1-P2 171.8(4).

UV/Vis/NIR spectra and photothermal properties

Complexes **8** and **9** exhibit broad absorptions in the UV/Vis/NIR region, which are similar to those of complexes **2** and **3**.[12] The absorption maximum of **9** in the low-energy absorption region is 814 nm (Figure 4 a, $\lg\varepsilon=3.67$, where ε is the molar absorption coefficient in $\text{M}^{-1}\text{cm}^{-1}$). The absorption maximum of **8** in the low-energy absorption region is blueshifted to 760 nm ($\lg\varepsilon=3.61$). The analogous complexes with two alkyl substituents on the metallacycle show blueshifted absorptions at about 740 nm.[12] These results indicate that alkyl groups attached to the metallacycle lead to blueshifts and aryl groups attached to the metallacycle to redshifts of the UV/Vis/NIR absorption. Thus, the absorptions of these osmium carbolong complexes cover a broad range in the UV/Vis/NIR region. In contrast, the maximum absorption wavelength of the purple complexes **4**, **5**, and **10** only reached about 550 nm (Figure 4 a and Figure S44 in the Supporting Information), which is much shorter than those of complexes **2**, **3**, **8**, and **9**. These results suggest that the conjugated systems of complexes **4**, **5**, and **10** are smaller than those of complexes **2**, **3**, **8**, and **9**. The result is understandable, since the structures of complexes **4** and **10** are twisted (Figure 1 and 3), and this decreases their conjugated length.

Similar to complex **2**,[13] complexes **8** and **9** showed very high photothermal conversion efficiency. For example, the temperature of a 0.1 $\text{mg}\,\text{mL}^{-1}$ solution of complex **9** in water/ethanol (95/5 v/v) significantly increased from 30 to 66 °C within 5 min (Figure 4 b) under NIR radiation (808 nm, 1 $\text{W}\,\text{cm}^{-2}$). In contrast, no temperature changes were observed for complex **4** (Figure S45 in the Supporting Information), since it did not absorb any light with wavelength longer than 700 nm. Apparently, metal carbolong complexes that contain a 12-carbon coplanar metallacycle (e.g., complexes **2**, **3**, **8**, and **9**) have excellent NIR photothermal properties owing to their highly conjugated ligand systems.

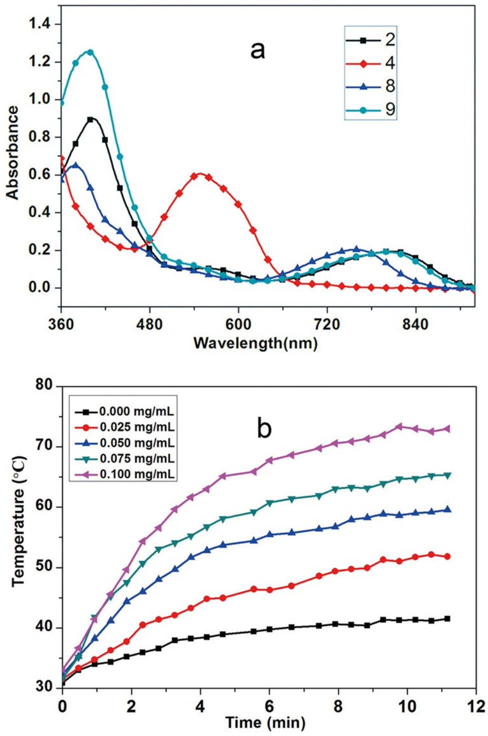


Figure 4. a) UV/Vis/NIR absorption spectra of **2**, **4**, **8**, and **9** (5.0×10^{-5} M) in CH_2Cl_2. b) Temperature curves of water/ethanol (95/5 v/v) with different concentrations of **9** (0.025, 0.050, 0.075, and 0.100 $\text{mg}\,\text{mL}^{-1}$) irradiated by an 808 nm laser at a power density of 1.0 $\text{W}\,\text{cm}^{-2}$.

Conclusions

A new method was developed to prepare osmium carbolong complexes that contain a 12-carbon metallacyclic framework and functional groups. The resulting coplanar osmium carbolong complexes showed excellent NIR photothermal efficiency. Surprisingly, when the reaction was carried out under anhydrous conditions, it produced a purple carbolong complex with a coordinated terminal η^3-allyl group formed by protonation of the coplanar carbolong complex by HBF_4 generated in situ. This study enriches the family of functional carbolong complexes, which can be easily developed as photothermal materials by chemical modification.

Experimental Section

General information

All reactions were carried out under a nitrogen atmosphere by using standard Schlenk techniques unless otherwise stated. Complex **1** was prepared by following the procedure in the literature.[9j] Other commercial reagents were used without further purification. NMR spectroscopy was performed with a Bruker AVIII-400 (^{1}H 400.1 MHz, ^{13}C 100.6 MHz, ^{31}P 162.0 MHz) spectrometer or a Bruker AVIII-500 (^{1}H 500.2 MHz, ^{13}C 125.8 MHz, ^{31}P 202.5 MHz) spectrometer at room temperature. ^1H and ^{13}C NMR chemical shifts δ are relative to tetramethylsilane, and ^{31}P NMR chemical shifts are relative to 85 % H_3PO_4. HRMS was performed with a Bruker En Apex Ultra 7.0T FT-MS spectrometer. Elemental analysis was performed with a Vario EL III elemental analyzer. The UV/Vis/NIR spectra of complexes **2**, **4**, **5**, and **8**–**10** (5.0×10^{-5} M) in dichloromethane at room temperature were recorded with a Shimadzu UV2550 UV/Vis spectrophotometer.

Synthesis

Complex 2D: PhC≡CD (55 μL, 0.49 mmol) was injected into a mixture of complex **1** (200 mg, 0.16 mmol), $AgBF_4$ (96 mg, 0.49 mmol), and water (0.1 mL) in dichloromethane (5 mL). The reaction mixture was stirred at 30 °C for 1 h to give a yellowish green suspension. The precipitate was removed by filtration and the filtrate was concentrated under vacuum to about 2 mL. The residue was loaded on a silica gel (200–300 mesh) column and eluted with dichloromethane/acetone (v/v = 10/1). The green band was collected and the solvent was removed under vacuum. The residue was washed with diethyl ether (10 mL × 3) to give complex **2D** as a green solid, which was dried under vacuum. Yield: 97 mg, 47 %. ^2D NMR (92.1 MHz, CH_2Cl_2): $\delta = 7.89$ (s, D8), 6.73 ppm (s, D12); HRMS (ESI): *m/z* calcd for $[C_{78}H_{60}D_2OsP_3]^+$: 1285.37992; found: 1285.37823.

Complex 4: Phenylacetylene (273 μL, 2.46 mmol) was injected into a mixture of complex **1** (1000 mg, 0.82 mmol) and $AgBF_4$ (479 mg, 2.46 mmol) in anhydrous dichloromethane (10 mL). The reaction mixture was stirred at 30 °C for 24 h to give a purple suspension. The precipitate was removed by filtration and the filtrate was reduced under vacuum to about 2 mL. The residue was loaded on a silica gel (200–300 mesh) column and eluted with dichloromethane/acetone (v/v = 10/1). The purple band was collected and the solvent was removed under vacuum. The residue was washed with diethyl ether (10 mL × 3) to give complex **4** as a purple solid, which was dried under vacuum. Yield: 768 mg, 56 %. ^1H NMR plus ^1H–^{13}C HSQC (400.1 MHz, CD_2Cl_2): $\delta = 12.54$ (d, $J_{\mathrm{P-H}} = 17.1$ Hz, 1 H, H1), 8.94 (s, 1 H, H3), 8.76 (d, $J_{\mathrm{P-H}} = 4.0$, 1 H, H5), 8.66 (s, 1 H, H8), 7.22 (m, 1 H, H6), 5.90 (m, 3 H, 1H for H10 and 2H for Ph), 4.75 (dd, $J_{\mathrm{P-H}} = 3.8$, $J_{\mathrm{H-H}} = 12.2$ 1 H, H12), 4.52 (t, $J_{\mathrm{P-H}} = 11.0$, $J_{\mathrm{H-H}} = 9.4$, 1 H, H11), 5.86–7.84 ppm (m, 53 H, Ph); $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): $\delta = 11.93$ (t, $J_{\mathrm{P-P}} = 4.3$ Hz, $CPPh_3$), -13.70 (dd, $J_{\mathrm{P-P}} = 223.8$ Hz, $J_{\mathrm{P-P}} = 3.8$ Hz, $OsPPh_3$), -16.20 ppm (dd, $J_{\mathrm{P-P}} = 226.8$ Hz, $J_{\mathrm{P-P}} = 4.0$ Hz, $OsPPh_3$); $^{13}C\{^1H\}$ NMR plus DEPT-135, ^1H-^{13}C HMBC, and ^1H–^{13}C HSQC (100.6 MHz, CD_2Cl_2): $\delta = 233.9$ (t, $J_{\mathrm{P-C}} = 8.0$ Hz, C7), 210.5 (t, $J_{\mathrm{P-C}} = 9.9$ Hz, C1), 192.8 (dt, $J_{\mathrm{P-C}} = 21.6$ Hz, $J_{\mathrm{P-C}} = 6.1$ Hz, C4), 168.1 (s, C5), 164.2 (s, C9), 156.7 (s, C6), 156.5 (d, $J_{\mathrm{P-C}} = 21.1$ Hz, C3), 134.9 (s, C8), 138.9 (dt, $J_{\mathrm{P-C}} = 69.8$ Hz, $J_{\mathrm{P-C}} = 3.7$ Hz, C2), 118.8–156.6 (m, other aromatic C atoms), 101.5 (s, C10), 88.7 (s, C12), 87.5 ppm (s, C11); elemental analysis calcd (%) for $C_{78}H_{63}B_2F_8OsP_3$: C 64.30, H 4.36; found: C 64.02, H 4.712; HRMS (ESI): *m/z* calcd for $[C_{78}H_{63}OsP_3]^{2+}$: 642.18732; found: 642.18869.

Complex 5: 3-Ethynylthiophene (242 μL, 2.46 mmol) was injected into a mixture of complex **1** (1000 mg, 0.82 mmol) and $AgBF_4$ (479 mg, 2.46 mmol) in anhydrous dichloromethane (10 mL). The reaction mixture was stirred at 30 °C for 24 h to give a purple suspension. The precipitate was removed by filtration and the filtrate was concentrated under vacuum to about 2 mL. The residue was loaded on a silica gel (200–300 mesh) column and eluted with dichloromethane/acetone (v/v = 10/1). The purple band was collected and the solvent was removed under vacuum. The residue was washed with diethyl ether (10 mL × 3) to give complex **5** as a purple solid of, which was dried under vacuum. Yield: 768 mg, 52 %. ^1H NMR plus ^1H–^{13}C HSQC (400.1 MHz, CD_2Cl_2): $\delta = 12.25$ (br, 1 H, H1), 8.95 (s, 1 H, H3), 8.76 (s, 1 H, H5), 8.55 (s, 1 H, H8), 7.30 (m, 1 H, H6), 5.72 (m, 1 H, H10), 4.82 (br, 1 H, H12), 4.52 (m, 1 H, H11), 5.96–7.93 ppm (m, 51 H, other aromatic protons). $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): $\delta = 12.08$ (br, $CPPh_3$), -14.56 (d, $J_{\mathrm{P-P}} = 227.8$ Hz, $OsPPh_3$), -16.40 ppm (d, $J_{\mathrm{P-P}} = 227.8$ Hz, $OsPPh_3$). $^{13}C\{^1H\}$ NMR plus DEPT-135, ^1H–^{13}C HMBC, and ^1H–^{13}C HSQC (100.6 MHz, CD_2Cl_2): $\delta = 235.4$ (t, $J_{\mathrm{P-C}} = 8.0$ Hz, C7), 213.2 (br, C1), 192.7 (d, $J_{\mathrm{P-C}} = 21.2$ Hz, C4), 167.8 (s, C5), 159.1 (s, C9), 156.5 (s, C6), 156.1 (d, $J_{\mathrm{P-C}} = 21.1$ Hz, C3), 154.9 (s, C8), 138.2 (d, $J_{\mathrm{P-C}} = 69.9$ Hz, C2), 127.0–156.1 (m, other aromatic C atoms), 102.1 (s, C10), 86.1 (s, C12), 85.1 ppm (s, C11); elemental analysis calcd (%) for $C_{74}H_{59}B_2F_8OsP_3S_2$: C 60.50, H 4.05, found: C 60.31, H 4.440; HRMS (ESI): *m/z* calcd for $[C_{74}H5_9OsP_3S_2]^{2+}$: 648.14374; found: 648.14348.

Complex 8: 1-Hexyne (116 μL, 0.82 mmol) was injected into a mixture of complex **1** (1000 mg, 0.82 mmol) and $AgBF_4$ (479 mg, 2.46 mmol) in dichloromethane (10 mL) and water (0.2 mL). The reaction mixture was stirred at 30 °C for 1 h to give a copper-brown suspension. Then, a solution of phenylacetylene (91 μL, 0.82 mmol) in dichloromethane (1 mL) was injected and further stirred at 30 °C for 24 h to give a brown suspension. The precipitate was removed by filtration and the filtrate was reduced under vacuum to about 2 mL. The residue was loaded on a silica gel (200–300 mesh) column and eluted with dichloromethane/acetone (v/v = 40/1). The brown band was collected and the solvent was concentrated under vacuum. The residue was washed with diethyl ether (10 mL × 3) to give complex **8** as a brown solid, which was dried under vacuum. Yield: 488 mg, 44 %. ^1H NMR plus ^1H–^{13}C HSQC (400.1 MHz, CD_2Cl_2): $\delta = 13.09$ (d, $J_{\mathrm{P-H}} = 21.2$ Hz, 1 H, H1), 8.63 (s, 1 H, H3), 7.57 (s, 1 H, H5), 7.46 (s, 1 H, H10), 7.34 (s, 1 H, H6), 7.20(s, 1 H, H8), 6.54 (s, 1 H, H12), 3.06 (t, $J_{\mathrm{H-H}} = 8.2$ Hz, 2 H, H13), 2.20 (m, 2 H, H14), 1.78 (m, 2 H, H15), 1.21 (t, $J_{\mathrm{H-H}} = 7.3$ Hz, 3 H, H16), 5.76–7.90 ppm (m, 50 H, other aromatic protons); $^{31}P\{^1H\}$ NMR (162.0 MHz, CD_2Cl_2): $\delta = 8.91$ (t, $J_{\mathrm{P-P}} = 6.5$ Hz, $CPPh_3$), -8.57 (dd, $J_{\mathrm{P-P}} = 254.3$ Hz, $J_{\mathrm{P-P}} = 6.0$ Hz, $OsPPh_3$), -19.73 ppm (dd, $J_{\mathrm{P-P}} = 254.3$ Hz, $J_{\mathrm{P-P}} = 7.4$ Hz, $OsPPh_3$); $^{13}C\{^1H\}$ NMR plus DEPT-135, ^1H–^{13}C HMBC, and ^1H–^{13}C HSQC (100.6 MHz, CDCl3): $\delta = 234.5$ (t, $J_{\mathrm{P-C}} = 8.4$ Hz, C7), 218.1 (t, $J_{\mathrm{P-C}} = 4.4$ Hz, C11), 207.9 (td, $J_{\mathrm{P-C}} = 12.1$ Hz, $J_{\mathrm{P-C}} = 5.6$ Hz, C1), 199.9 (dt, $J_{\mathrm{P-C}} = 25.7$ Hz, $J_{\mathrm{P-C}} = 5.6$ Hz, C4), 165.5 (s, C9), 162.2 (s, C6), 159.5 (s, C5), 136.5 (d, $J_{\mathrm{P-C}} = 25.4$ Hz, C3), 132.8 (dt, $J_{\mathrm{P-C}} = 79.3$ Hz, $J_{\mathrm{P-C}} = 5.1$ Hz, C2), 129.3 (s, C8), 117.0 (s, C10), 39.8 (s, C13), 32.7 (s, C14), 24.0 (s, C15), 14.6 (s, C12), 14.4 (s, C16), 121.1–148.7 ppm (m, other aromatic C atoms); elemental analysis calcd (%) for $C_{76}H_{66}BF_4OsP_3$: C 67.65, H 4.93; found: C 67.52, H 4.734; HRMS (ESI): *m/z* calcd for $[C_{76}H_{66}OsP_3]^+$: 1263.39867; found: 1263.40197.

Complex 9: Phenylacetylene (91 μL, 0.82 mmol) was injected into a mixture of complex **1** (1000 mg, 0.82 mmol) and $AgBF_4$ (479 mg, 2.46 mmol) in dichloromethane (10 mL) and water (0.2 mL). The reaction mixture was stirred at 30 °C for 0.5 h to give an ochre-brown suspension. Then, a solution of 4-nitrophenylacetylene (241 mg, 1.64 mmol) in dichloromethane (1 mL) was injected. The reaction mixture was stirred at 30 °C for a further 4 h to give a brown suspension. The precipitate was removed by filtration and the filtrate was concentrated under vacuum to about 2 mL. The residue was loaded on a silica gel (200–300 mesh) column and eluted with dichloromethane/acetone (v/v = 20/1). The yellow-brown band was collected and the solvent was removed under vacuum. The residue was washed with diethyl ether (10 mL × 3) to give complex **9** as a yellowish brown solid, which was dried under vacuum. Yield: 637 mg, 45 %. ^1H NMR plus ^1H–^{13}C HSQC (400.1 MHz, $CDCl_3$): $\delta = 13.18$ (d, $J_{\mathrm{P-H}} = 21.0$ Hz, 1 H, H1), 8.68 (s, 1 H, H3), 7.84 (s, 1 H, H8), 7.82 (s, 1 H, H10), 7.66 (s, 1 H, H5), 7.57 (s, 1 H, H6), 6.63 (s, 1 H, H12), 5.75–8.02 ppm (m, 54 H, other aromatic protons); ^{31}P{^{1}H} NMR (162.0 MHz, CDCl$_3$): $\delta = 10.1$ (t, $J_{\text{P-P}} = 6.5$ Hz, CPPh$_3$), -9.8 (dd, $J_{\text{P-P}} = 252.5$ Hz, $J_{\text{P-P}} = 5.8$ Hz, OsPPh$_3$), -18.1 ppm (dd, $J_{\text{P-P}} = 252.5$ Hz, $J_{\text{P-P}} = 5.8$ Hz, OsPPh$_3$); ^{13}C{^{1}H} NMR plus DEPT-135, ^{1}H–^{13}C HMBC, and ^{1}H–^{13}C HSQC (100.6 MHz, CDCl$_3$): $\delta = 230.6$ (t, $J_{\text{P-C}} = 7.6$ Hz, C7), 215.8 (t, $J_{\text{P-C}} = 5.1$ Hz, C11), 207.2 (td, $J_{\text{P-C}} = 12.5$ Hz, $J_{\text{P-C}} = 5.0$ Hz, C1), 199.9 (dt, $J_{\text{P-C}} = 25.2$, $J_{\text{P-C}} = 6.2$, C4), 163.6 (s, C6), 160.1(s, C5), 159.2 (s, C9), 159.0 (s, C13), 137.0 (d, $J_{\text{P-C}} = 24.9$ Hz, C3), 134.0 (dt, $J_{\text{P-C}} = 79.8$ Hz, $J_{\text{P-C}} = 5.1$ Hz, C2), 129.0 (s, C8), 114.8 (s, C10), 15.0 (s, C12), 124.2.8–142.2 ppm (m, other aromatic C atoms); elemental analysis calcd (%) for $C_{78}H_{61}BF_4NO_2OsP_3$: C 66.24, H 4.35, N 0.99; found: C 65.93, H 4.632, N 1.025; HRMS (ESI): m/z calcd for $[C_{78}H_{61}NO_2OsP_3]^+$: 1328.35245; found: 1328.35375.

Complex 10: 4-Ethynyltrifluorotoluene (134 µL, 0.82 mmol) was injected into a mixture of complex **1** (1000 mg, 0.82 mmol) and AgBF$_4$ (479 mg, 2.46 mmol) in anhydrous dichloromethane (10 mL). The reaction mixture was stirred at 30 °C for 1 h to give a copper-brown suspension. Then, phenylacetylene (90 µL, 0.82 mmol) was injected. The reaction mixture was stirred at 30 °C for a further 24 h. The precipitate was removed by filtration and the filtrate was reduced under vacuum to about 2 mL. The residue was loaded on silica gel (200–300 mesh) column and eluted with dichloromethane/acetone (v/v = 10/1). The purple band was collected and the solvent was removed under vacuum. The residue was washed with diethyl ether (10 mL × 3) to give a purple solid of complex **10**, which was dried under vacuum. Yield: 662 mg, 53 %. ^{1}H NMR plus ^{1}H–^{13}C HSQC (400.1 MHz, CD$_2$Cl$_2$): $\delta = 12.69$ (d, $J_{\text{P-H}} = 16.8$ Hz, 1 H, H1), 9.04 (s, 1 H, H3), 8.84 (d, 1 H, H5), 8.77 (s, 1 H, H8), 7.30 (m, 1 H, H6), 5.86–8.82 (m, 54 H, other aromatic protons), 5.86 (m, 1 H, H10), 4.82 (d, $J_{\text{H-H}} = 9.3$, 1 H, H12), 4.47 ppm (m, 1 H, H11). ^{31}P{^{1}H} NMR (162.0 MHz, CD$_2$Cl$_2$): $\delta = 12.06$ (s, CPPh$_3$), -13.20 (d, $J_{\text{P-P}} = 225.0$ Hz, $J_{\text{P-P}} = 5.4$ Hz, OsPPh$_3$), -17.00 ppm (dd, $J_{\text{P-P}} = 225.0$ Hz, $J_{\text{P-P}} = 5.4$ Hz, OsPPh$_3$); ^{19}F NMR (376.4 MHz, CD$_2$Cl$_2$): $\delta = -63.1$ (s, CF$_3$), -152.1 ppm (s, BF$_4^-$); ^{13}C{^{1}H} NMR plus DEPT-135, ^{1}H–^{13}C HMBC, and ^{1}H–^{13}C HSQC (100.6 MHz, CD$_2$Cl$_2$): $\delta = 231.7$ (t, $J_{\text{P-C}} = 7.6$ Hz C7), 210.2 (t, $J_{\text{P-C}} = 10.0$ Hz, C1), 192.4 (dt, $J_{\text{P-C}} = 21.2$, $J_{\text{P-C}} = 6.0$, C4), 167.2 (s C5), 159.6 (s, C9), 156.6 (s, C6), 156.3 (d, $J_{\text{P-C}} = 20.5$ Hz, C3), 156.2 (s, C8), 138.6 (dt, $J_{\text{P-C}} = 69.8$ Hz, $J_{\text{P-C}} = 3.5$ Hz, C2), 125.8–156.2 (m, other aromatic carbons), 100.3 (s, C10), 88.4 (s, C12), 86.4 ppm (s, C11); elemental analysis calcd (%) for $C_{79}H_{62}B_2F_{11}OsP_3$: C 62.22, H 4.10; found: C 62.54, H 4.582; HRMS (ESI): m/z calcd for $[C_{79}H_{62}F_3OsP_3]^{2+}$: 676.18101; found: 676.18190.

X-ray crystallographic analysis

Single crystals suitable for X-ray diffraction were grown from dichloromethane solutions of **4** and **9** layered with hexane, and from a 1,2-dichloroethane solution of **10** layered with hexane. Single-crystal XRD data were collected with a Rigaku R-Axis Spider IP CCD area detector with Mo$_{K\alpha}$ radiation ($\lambda = 0.71073$ Å). The data were corrected for absorption effects by the multiscan technique. By using Olex2,[17] the structures of **4**, **9**, and **10** were solved with the ShelXT[18] structure solution program by using intrinsic phasing and refined with the ShelXL[19] refinement package by 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 with a riding model unless otherwise stated. The solvent molecules CH$_2$Cl$_2$ and C$_2$H$_4$Cl$_2$ as well as phenyl groups on PPh$_3$ were disordered and refined with restraints.

CCDC 1822516 (**4**), 1822517 (**9**), and 1822518 (**10**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre.

Crystal data for **4**: $[C_{78}H_{63}OsP_3](BF_4)_2{\cdot}CH_2Cl_2$ ($M = 1541.94$ g mol^{-1}): triclinic, crystal dimensions 0.40 × 0.40 × 0.30 mm, space group $P\bar{1}$ (no. 2), $a = 13.0475(3)$, $b = 15.8684(6)$, $c = 19.3296(8)$ Å, $\alpha = 73.996(4)$, $\beta = 80.198(3)$, $\gamma = 83.024(3)^\circ$, $V = 3779.0(2)$ Å^3, $Z = 2$, $T = 293(2)$ K, $\mu(\text{Mo}_{K\alpha}) = 1.882$ mm^{-1}, $\rho_{\text{calcd}} = 1.355$ g cm^{-3}, 34 519 reflections measured ($5.998^\circ \leq 2\theta \leq 55^\circ$), 17 343 of which were unique ($R_{\text{int}} = 0.0463$, $R_{\text{sigma}} = 0.0671$) and were used in all calculations. The final R_1 was 0.0428 [$I > 2\sigma(I)$] and wR_2 was 0.1038 (all data). GOF = 1.041. Max./min. residual electron density: 1.95/−1.45 e Å^{-3}.

Crystal data for **9**: $[C_{78}H_{61}NO_2OsP_3]BF_4{\cdot}2\,CH_2Cl_2{\cdot}0.25\,H_2O$ ($M = 1588.05$ g mol^{-1}): monoclinic, crystal dimensions 0.20 × 0.20 × 0.10 mm, space group $C2/c$ (no. 15), $a = 42.8001(10)$, $b = 12.7642(3)$, $c = 25.0451(4)$ Å, $\alpha = 90$, $\beta = 91.844(2)$, $\gamma = 90^\circ$, $V = 13675.3(5)$ Å^3, $Z = 8$, $T = 293(2)$ K, $\mu(\text{Mo}_{K\alpha}) = 2.153$ mm^{-1}, $\rho_{\text{calcd}} = 1.543$ g cm^{-3}, 34 742 reflections measured ($5.732^\circ \leq 2\theta \leq 55^\circ$), 15 684 of which were unique ($R_{\text{int}} = 0.0369$, $R_{\text{sigma}} = 0.0525$) and were used in all calculations. The final R_1 was 0.0489 [$I > 2\sigma(I)$] and wR_2 was 0.1196 (all data). GOF = 1.061. Max./min. residual electron density: 2.47/ −1.61 e Å^{-3}.

Crystal data for **10**: $[C_{79}H_{62}F_3OsP_3]2\,BF_4{\cdot}3\,C_2H_4Cl_2$ ($M = 1821.87$ g mol^{-1}): triclinic, crystal dimensions 0.40 × 0.40 × 0.30 mm, space group $P\bar{1}$ (no. 2), $a = 13.1839(5)$, $b = 16.2148(4)$, $c = 21.5247(6)$ Å, $\alpha = 106.523(2)$, $\beta = 97.638(3)$, $\gamma = 93.199(2)^\circ$, $V = 4351.0(2)$ Å^3, $Z = 2$, $T = 173.4(6)$ K, $\mu(\text{Mo}_{K\alpha}) = 1.770$ mm^{-1}, $\rho_{\text{calcd}} = 1.391$ g cm^{-3}, 38541 reflections measured ($6.054^\circ \leq 2\Theta \leq 54.998^\circ$), 19 923 of which were unique ($R_{\text{int}} = 0.0362$, $R_{\text{sigma}} = 0.0599$) and were used in all calculations. The final R_1 was 0.0501 [$I > 2\sigma(I)$] and wR_2 was 0.1193 (all data). GOF = 1.026. Max./min. residual electron density: 2.32/−2.28.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: chelates · metallacycles · osmium · photothermal materials · reaction mechanisms

[1] For reviews see: a) B. J. Frogley, L. J. Wright, *Chem. Eur. J.* **2018**, *24*, 2025 – 2038; b) B. J. Frogley, L. J. Wright, *Coord. Chem. Rev.* **2014**, *270–271*, 151 – 166; c) X. Cao, Q. Zhao, Z. Lin, H. Xia, *Acc. Chem. Res.* **2014**, *47*, 341 – 354; d) C. Zhu, X. Cao, H. Xia, *Chin. J. Org. Chem.* **2013**, *33*, 657; e) A. F. Dalebrook, L. J. Wright, *Adv. Organomet. Chem.* **2012**, *60*, 93 – 177; f) M. Paneque, M. L. Poveda, N. Rendón, *Eur. J. Inorg. Chem.* **2011**, 19 – 33; g) J. R. Bleeke, *Acc. Chem. Res.* **2007**, *40*, 1035 – 1047; h) L. J. Wright, *Dalton Trans.* **2006**, 1821 – 1827; i) C. W. Landorf, M. M. Haley, *Angew. Chem. Int. Ed.* **2006**, *45*, 3914 – 3936; *Angew. Chem.* **2006**, *118*, 4018 – 4040; j) G. He, H. Xia, G. Jia, *Chin. Sci. Bull.* **2004**, *49*, 1543 – 1553; k) J. R. Bleeke, *Chem. Rev.* **2001**, *101*, 1205 – 1228; l) J. R. Bleeke, *Acc. Chem. Res.* **1991**, *24*, 271 – 277.

[2] See, for example: a) B. J. Frogley, L. C. Perera, L. J. Wright, *Chem. Eur. J.* **2018**, *24*, 4304 – 4309; b) Y. García-Rodeja, I. Fernández, *Chem. Eur. J.* **2017**, *23*, 6634 – 6642; c) B. J. Frogley, L. J. Wright, *Angew. Chem. Int. Ed.* **2017**, *56*, 143 – 147; *Angew. Chem.* **2017**, *129*, 149 – 153; d) F. Han, J. Li, H. Zhang, T. Wang, Z. Lin, H. Xia, *Chem. Eur. J.* **2015**, *21*, 565 – 567; e) R. Lin, K. H. Lee, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Organometallics* **2015**, *34*, 167 – 176; f) Á. Vivancos, Y. Hernández, A. M. Paneque, M. L.

Poveda, V. Salazar, E. Álvarez, *Organometallics* **2015**, *34*, 177 – 188; g) F. Han, T. Wang, J. Li, H. Zhang, H. Xia, *Chem. Eur. J.* **2014**, *20*, 4363 – 4372; h) R. Lin, K. Lee, K. C. Poon, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Chem. Eur. J.* **2014**, *20*, 14885 – 14899; i) Á. Vivancos, M. Paneque, M. L. Poveda, E. Álvarez, *Angew. Chem. Int. Ed.* **2013**, *52*, 10068 – 10071; *Angew. Chem.* **2013**, *125*, 10252 – 10255; j) T. Wang, H. Zhang, F. Han, L. Long, Z. Lin, H. Xia, *Chem. Eur. J.* **2013**, *19*, 10982 – 10991; k) 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; l) K. C. Poon, L. Liu, T. Guo, J. Li, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem. Int. Ed.* **2010**, *49*, 2759 – 2762; *Angew. Chem.* **2010**, *122*, 2819 – 2822; m) G. R. Clark, L. A. Ferguson, A. E. McIntosh, T. Sohnel, L. J. Wright, *J. Am. Chem. Soc.* **2010**, *132*, 13443 – 13452; n) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, *J. Am. Chem. Soc.* **2003**, *125*, 9898 – 9899; o) V. Jacob, T. J. R. Weakley, M. M. Haley, *Angew. Chem. Int. Ed.* **2002**, *41*, 3470 – 3473; *Angew. Chem.* **2002**, *114*, 3620 – 3623; p) R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *Chem. Eur. J.* **2000**, *6*, 437 – 441; q) R. D. Gilbertson, T. J. R. Weakley, M. M. Haley, *J. Am. Chem. Soc.* **1999**, *121*, 2597 – 2598; r) G. P. Elliott, W. R. Roper, J. M. Waters, *J. Chem. Soc. Chem. Commun.* **1982**, 811 – 813.

[3] For reviews, see: a) G. Jia, *Organometallics* **2013**, *32*, 6852 – 6866; b) J. Chen, G. He, G. Jia, *Chin. J. Org. Chem.* **2013**, *33*, 792 – 798; c) J. Chen, G. Jia, *Coord. Chem. Rev.* **2013**, *257*, 2491 – 2521; d) G. Jia, *Coord. Chem. Rev.* **2007**, *251*, 2167 – 2187; e) G. Jia, *Acc. Chem. Res.* **2004**, *37*, 479 – 486.

[4] See, for example: a) T. B. Wen, K. H. Lee, J. Chen, W. Y. Hung, W. Bai, H. Li, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Organometallics* **2016**, *35*, 1514 – 1525; b) Q. Zhuo, X. Zhou, H. Kang, Z. Chen, Y. Yang, F. Han, H. Zhang, H. Xia, *Organometallics* **2016**, *35*, 1497 – 1504; c) J. Chen, K. H. Lee, T. B. Wen, F. Gao, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Organometallics* **2015**, *34*, 890 – 896; d) J. Chen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Chem. Eur. J.* **2012**, *18*, 14128 – 14139; e) J. Chen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem. Int. Ed.* **2011**, *50*, 7295 – 7299; *Angew. Chem.* **2011**, *123*, 7433 – 7437; f) J. Chen, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem. Int. Ed.* **2011**, *50*, 10675 – 10678; *Angew. Chem.* **2011**, *123*, 10863 – 10866; g) W. Y. Hung, B. Liu, W. Shou, T. B. Wen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2011**, *133*, 18350 – 18360; h) B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao, J. Chen, T. B. Wen, Z. Cao, H. Xia, *Angew. Chem. Int. Ed.* **2009**, *48*, 5461 – 5464; *Angew. Chem.* **2009**, *121*, 5569 – 5572; i) G. He, J. Zhu, W. Y. Hung, T. B. Wen, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem. Int. Ed.* **2007**, *46*, 9065 – 9068; *Angew. Chem.* **2007**, *119*, 9223 – 9226; j) T. B. Wen, W. Y. Hung, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 2856 – 2857; k) T. B. Wen, S. M. Ng, W. Y. Hung, Z. Y. Zhou, M. F. Lo, L. Y. Shek, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2003**, *125*, 884 – 885; l) T. B. Wen, Z. Y. Zhou, G. Jia, *Angew. Chem. Int. Ed.* **2001**, *40*, 1951 – 1954; *Angew. Chem.* **2001**, *113*, 2005 – 2008.

[5] a) R. Grande-Aztatzi, J. M. Mercero, E. Matito, G. Frenking, J. M. Ugalde, *Phys. Chem. Chem. Phys.* **2017**, *19*, 9669 – 9675; b) K. An, T. Shen, J. Zhu, *Organometallics* **2017**, *36*, 3199 – 3204; c) 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; d) J. Wei, Y. Zhang, Y. Chi, L. Liu, W. X. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2016**, *138*, 60 – 63.

[6] See, for example: a) J. Wei, W. X. Zhang, Z. Xi, *Chem. Sci.* **2018**, *9*, 560 – 568; b) H. Wang, X. Zhou, H. Xia, *Chin. J. Chem.* **2018**, *36*, 93 – 105; c) W. Ma, C. Yu, Y. Chi, T. Chen, L. Wang, J. Yin, B. Wei, L. Xu, W. Zhang, Z. Xi, *Chem. Sci.* **2017**, *8*, 6852 – 6856; d) Y. Zhang, Y. Chi, J. Wei, Q. Yang, Z. Yang, H. Chen, R. Yang, W. X. Zhang, Z. Xi, *Organometallics* **2017**, *36*, 2982 – 2986; e) W. Ma, C. Yu, T. Chen, L. Xu, W. Zhang, Z. Xi, *Chem. Soc. Rev.* **2017**, *46*, 1160 – 1192; f) Y. Zhang, J. Wei, Y. Chi, X. Zhang, W. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2017**, *139*, 5039 – 5042; g) L. Liu, M. Zhu, H. T. Yu, W. Zhang, Z. Xi, *J. Am. Chem. Soc.* **2017**, *139*, 13688 – 13691; h) G. He, J. Chen, H. Xia, *Sci. Bull.* **2016**, *61*, 430 – 442; i) J. Wei, W. Zhang, Z. Xi, *Angew. Chem. Int. Ed.* **2015**, *54*, 5999 – 6002; *Angew. Chem.* **2015**, *127*, 6097 – 6100; j) J. Wei, Y. Zhang, W. Zhang, Z. Xi, *Angew. Chem. Int. Ed.* **2015**, *54*, 9986 – 9990; *Angew. Chem.* **2015**, *127*, 10124 – 10128.

[7] See, for example: a) M. Batuecas, R. Castro-Rodrigo, M. A. Esteruelas, C. García-Yebra, A. M. López, E. Oñate, *Angew. Chem. Int. Ed.* **2016**, *55*, 13749 – 13753; *Angew. Chem.* **2016**, *128*, 13953 – 13957; b) J. Alós, M. A. Esteruelas, M. Oliván, E. Oñate, P. Puylaert, *Organometallics* **2015**, *34*, 4908 – 4921; c) M. A. Esteruelas, C. Larramona, E. Oñate, *Organometallics* **2013**, *32*, 2567 – 2575; d) P. Barrio, M. A. Esteruelas, E. Oñate, *J. Am. Chem. Soc.* **2004**, *126*, 1946 – 1947.

[8] a) F. Feixas, E. Matito, J. Poater, M. Solà, *Chem. Soc. Rev.* **2015**, *44*, 6434 – 6451; b) I. Fernández, G. Frenking, G. Merino, *Chem. Soc. Rev.* **2015**, *44*, 6452 – 6463; c) I. Fernández, G. Frenking, *Chem. Eur. J.* **2007**, *13*, 5873 – 5884; d) L. Thorn, R. Hoffmann, *Nouv. J. Chim.* **1979**, *3*, 39 – 45.

[9] a) Q. Zhuo, J. Lin, Y. Hua, X. Zhou, Y. Shao, S. Chen, Z. Chen, J. Zhu, H. Zhang, H. Xia, *Nat. Commun.* **2017**, *8*, 1912; b) R. Li, Z. Lu, Y. Cai, F. Jiang, C. Tang, Z. Chen, J. Zheng, J. Pi, R. Zhang, J. Liu, Z. Chen, Y. Yang, J. Shi, W. Hong, H. Xia, *J. Am. Chem. Soc.* **2017**, *139*, 14344 – 14347; c) M. Luo, L. Long, H. Zhang, Y. Yang, Y. Hua, G. Liu, Zh. Lin, H. Xia, *J. Am. Chem. Soc.* **2017**, *139*, 1822 – 1825; d) X. Zhou, J. Wu, Y. Hao, C. Zhu, Q. Zhuo, H. Xia, J. Zhu, *Chem. Eur. J.* **2018**, *24*, 2389 – 2395; e) Z. Lu, C. Zhu, Y. Cai, J. Zhu, Y. Hua, Z. Chen, J. Chen, H. Xia, *Chem. Eur. J.* **2017**, *23*, 6426 – 6431; f) C. Zhu, J. Wu, S. Li, Y. Yang, J. Zhu, X. Lu, H. Xia, *Angew. Chem. Int. Ed.* **2017**, *56*, 9067 – 9071; *Angew. Chem.* **2017**, *129*, 9195 – 9199; g) Z. Lu, J. Chen, H. Xia, *Chin. J. Org. Chem.* **2017**, *37*, 1181 – 1188; h) Q. Zhu, C. Zhu, Z. Deng, G. He, J. Chen, J. Zhu, H. Xia, *Chin. J. Chem.* **2016**, *34*, 628 – 634; i) M. Luo, C. Zhu, L. Chen, H. Zhang, H. Xia, *Chem. Sci.* **2016**, *7*, 1815 – 1818; j) C. Zhu, X. Zhou, H. Xing, K. An, J. Zhu, H. Xia, *Angew. Chem. Int. Ed.* **2015**, *54*, 3102 – 3106; *Angew. Chem.* **2015**, *127*, 3145 – 3149; k) C. Zhu, Y. Yang, M. Luo, C. Yang, J. Wu, L. Chen, G. Liu, T. B. Wen, J. Zhu, H. Xia, *Angew. Chem. Int. Ed.* **2015**, *54*, 6181 – 6185; *Angew. Chem.* **2015**, *127*, 6279 – 6283; l) C. Zhu, Y. Yang, J. Wu, M. Luo, J. Fan, J. Zhu, H. Xia, *Angew. Chem. Int. Ed.* **2015**, *54*, 7189 – 7192; *Angew. Chem.* **2015**, *127*, 7295 – 7298; m) C. Zhu, Q. Zhu, J. Fan, J. Zhu, X. He, X. Y. Cao, H. Xia, *Angew. Chem. Int. Ed.* **2014**, *53*, 6232 – 6236; *Angew. Chem.* **2014**, *126*, 6346 – 6350; n) 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; o) C. Zhu, S. Li, M. Luo, X. Zhou, Y. Niu, M. Lin, J. Zhu, Z. Cao, X. Lu, T. B. Wen, Z. Xie, P. V. R. Schleyer, H. Xia, *Nat. Chem.* **2013**, *5*, 698 – 703.

[10] a) M. Mauksch, S. B. Tsogoeva, *Chem. Eur. J.* **2010**, *16*, 7843 – 7851; b) Q. Zheng, *Sci. China Chem.* **2014**, *57*, 1059 – 1060.

[11] a) X. Zhou, J. Wu, Y. Hao, C. Zhu, Q. Zhuo, H. Xia, J. Zhu, *Chem. Eur. J.* **2018**, *24*, 2296; b) S. K. Ritter, *C&EN.* **2016**, *94* (37), 9; c) *Chin. J. Chem.* **2018**, *36*, 78.

[12] 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.

[13] 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.

[14] X. He, X. He, S. Li, K. Zhuo, W. Qin, S. Dong, J. Chen, L. Ren, G. Liu, H. Xia, *Polym. Chem.* **2017**, *8*, 3674 – 3678.

[15] a) A. Arce, Y. D. Sanctis, E. Galarza, M. T. Garland, R. Baggio, *Acta Crystallogr. Sect. C* **2013**, *69*, 363 – 366; b) M. A. Esteruelas, A. M. Lopez, S. Mozo, E. Oñate, *Organometallics* **2012**, *31*, 440 – 444; c) P. Srinivasan, J. Tan, W. K. Leong, *J. Organomet. Chem.* **2006**, *691*, 1288 – 1294; d) Y. Chi, H. F. Hsu, S. M. Peng, G. H. Lee, *J. Chem. Soc. Chem. Commun.* **1991**, 1019 – 1023; e) M. H. Cheng, G. H. Lee, S. M. Peng, R. S. Liu, *Organometallics* **1991**, *10*, 3600 – 3606; f) W. Y. Yeh, J. R. Shapley, J. W. Ziller, M. R. Churchill, *Organometallics* **1987**, *6*, 1 – 7; g) R. D. Adams, J. P. Selegue, *Inorg. Chem.* **1980**, *19*, 1795 – 1801.

[16] J. Chen, Q. Lin, S. Li, Z. Lu, J. Lin, Z. Chen, H. Xia, *Organometallics* **2018**, *37*, 618 – 623.

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

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

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

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