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Strained Metallacycles

Synthesis of Five-Membered Osmacycloallenes and Conversion into Six-Membered Osmacycloallenes**

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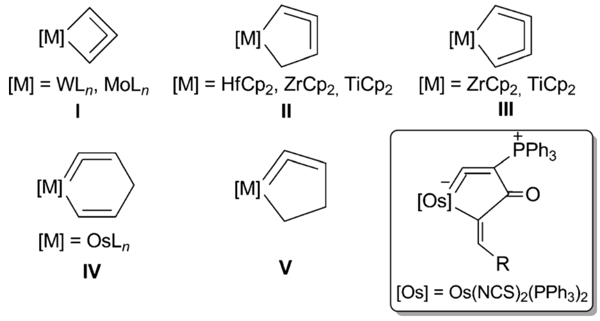
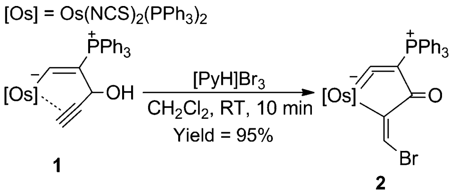
Allenes constitute a unique class of unsaturated organic compounds that contain two cumulative double bonds, a motif that has inspired considerable interest among experimental and theoretical chemists.[1] The linear geometry of allene-type structures makes the synthesis of cycloallenes particularly difficult, especially when the allenic structure is part of a small carbocycle. Only all-carbon cycloallenes containing more than seven carbon atoms have been characterized, even by low-temperature NMR spectroscopy.[2] The introduction of a transition metal atom or a main group hetero atom is an efficient strategy to address the ring strain inherent in small cycloallenes. The synthesis of small, strained metallacycloallenes has not been reported as frequently as the preparation of the related metallacycloallenes containing more than six atoms.[3] As shown in Scheme 1, the existence of four- (**I**, Scheme 1)[4] and five-membered metallacycloallenes (**II**)[5] has been confirmed. Examples of more strained metallacycles (for example, the five-membered metallacyclocumulene **III**) have been reported by Rosenthal's group.[6] However, other small-ring metallacycloallenes derived from formal replacement of the terminal sp^2-hybrized carbon atom in the allene moiety with an isolable transition metal have not been investigated thoroughly. The only two examples of such metallacycloallene moieties are six-membered rings, which have been defined as iso-osmabenzenes (**IV**).[7] Five-membered metallacycloallenes containing a metal–vinylidene moiety (**V**) have not been prepared to date. Herein, we describe the synthesis and full characterization of the first five-membered metallacycloallenes (**V**) and the conversion of these compounds to six-membered metallacycloallenes.



Scheme 1. Examples of all-carbon metallacycloallenes.

As shown in Equation (1), treatment of complex **1**[8] with three equivalents of pyridinium tribromide in dichloromethane led to the formation of complex **2**, which was isolated as a brown solid in 95% yield. Complex **2** was characterized by multinuclear NMR spectroscopy, single-crystal X-ray diffraction analysis, and high-resolution mass spectroscopy. The characteristic methylene signal appears at 5.2 ppm in the ^{1}H NMR spectrum. The $^{31}P\{^1H\}$ NMR spectrum shows two singlet peaks at −1.4 (Os*P*Ph$_3$) and 3.7 (C*P*Ph$_3$) ppm. The carbon signal of the exocyclic methylene appears at 102.7 ppm in the $^{13}C\{^1H\}$ NMR spectrum, whereas the four carbon signals from the five-membered metallacycle appear at $\delta = 294.6$ (Os*Csp*), 88.2 (*C*PPh$_3$), 197.4 (*C*O), and 150.4 ppm (Os*Csp*^{2}).



(1)

The structure of complex **2** has been further determined by single-crystal X-ray diffraction.[9] As shown in Figure 1, **2** contains an essentially planar five-membered metallacycloallenoid configuration with a C=C bond located outside the metallacycle. The co-planarity is reflected by the mean deviation (0.0194 Å) from the least-squares plane through the five atoms Os1, C1, C2, C3, and C4. The most interesting structural feature is the metal–vinylidene moiety in the five-membered ring. The Os1−C1 (1.800(3) Å) and C1−C2 (1.350(4) Å) bond lengths are similar to those observed in other osmium–vinylidene complexes.[7,10] Notably, the Os1-C1-C2 angle (137.8(2)°) deviates considerably from linearity but is much smaller than the corresponding angles found in the two reported six-membered metallacycloallenes (155.1(8)°[7a] and 158.5(3)°[7b]). For comparison, the angles for the cumulative double bonds in the five-membered metallacycloallenoids range from 153.6(3)° to 158.7(2)° in **II**[5] and from 145.8(5)° to 153.5(4)° in **III**.[6] Strained five- or six-membered metallacycloalkynes, such as metallacyclopen-

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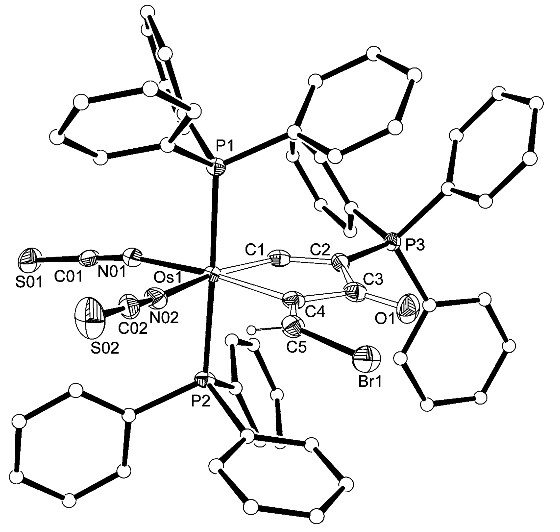
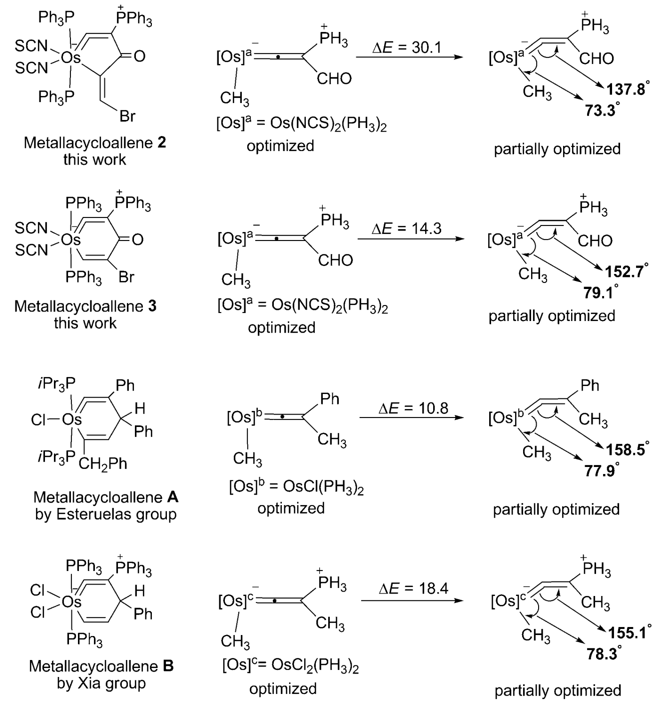


Figure 1. X-ray structure of complex **2** (ellipsoids set at 50% probability). The hydrogen atoms of PPh_3 are omitted for clarity. Selected bond distances [Å] and angles [°]: Os1–C1 1.800(3), Os1–C4 2.143(3), C1–C2 1.350(4), C2–C3 1.495(4), C3–O1 1.210(4), C3–C4 1.527(5), C4–C5 1.317(5), C5–Br1 1.893(3); C1-Os1-C4 73.26(13), Os1-C1-C2 137.8(2), C1-C2-C3 105.6(3), C2-C3-C4 109.3(3), C3-C4-Os1 113.9(2).

tynes,[11] metallapentalyne,[12] metallabenzynes,[13] and metallapyridyne,[14] display distorted angles at the carbyne carbon, which can be represented by resonance structures of metallacycloallenes.

In general, substitution of carbon atoms by metals decreases ring strain owing to the longer length of the metal–carbon bonds. Density functional theory (DFT) calculations further support the notion that introduction of osmium results in a significant relief of ring strain. The optimized structure of the model complex **2′**, in which the PPh_3 groups were replaced with PH_3, effectively reproduces the structural features of osmacycloallene **2** described above. The angle of the cumulative double bonds in the parent five-membered cycloallene $[(CH{=}C{=}C(PH_3){-}COC){=}CHBr]^+$ was calculated to be 112.0°. This value is much smaller than the angle in the model complex **2′** (132.2°). The strain energy of the parent five-membered cycloallene was estimated to be 54.1 kcal mol^{-1} on the basis of an isodesmic reaction.[15] This is in good agreement with the value predicted earlier by Johnson et al. for 1,2-cyclopentadiene (51.1 $kcal\,mol^{-1}$).[16] In sharp contrast, the computationally derived strain energy of the model complex **2′** is remarkably diminished and is expected to be 27.0 $kcal\,mol^{-1}$.[17]

Model DFT computations also provided estimates of the strain differences between the five- and six-membered metallacycloallenes owing to the non-linear distortion of the cumulative double-bond angles. As shown in Scheme 2, the reference species on the left-hand side of the equations are free of strain owing to their linear structures. For the right-hand reference species, the angles given in boldface are fixed in the partial optimizations. The fixed values were obtained from the X-ray structures of metallacycloallenes **2**, **3**, **A**,[7b] and **B**.[7a] The computed energy difference is 30.1 $kcal\,mol^{-1}$ for the first equation and decreases to 14.3 $kcal\,mol^{-1}$ for the

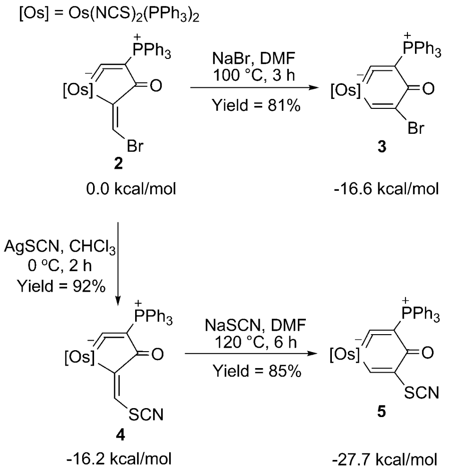


Scheme 2. The calculated strain energies of five- and the six-membered metallacycloallenes based on acyclic reference compounds.

second equation. This is understandable because the strain decreases as the angle of the cumulative double bonds increases. We also calculated the strain of iso-metallabenzenes **A** and **B** (Scheme 2), which are structurally similar to complex **3**. Furthermore, the sizable energy differences between the equations indicates a high energetic driving force for the formation of the more stable six-membered metallacycloallene over the less stable five-membered species. Consistent with these calculations, conversions from **2** into **3** and from **4** into **5** were observed experimentally (see below). Similar conversion of five-membered metallacycloallenes to seven-membered metallacycloallenes was described,[5a] and the general statement that the incorporation of heteroatoms could stabilize such compounds were also stated in the literatures.[3a,12b]

Prompted by the calculations, we tested the persistence and stability of complex **2**. Complex **2** exhibits remarkable thermal stability both in the solid state and in solution under an air atmosphere. When a solution of **2** in DMF was heated at 100 °C in the presence of purposely introduced NaBr, the reaction was complete within three hours and gave **3** as the dominant product (Scheme 3). A possible mechanism and the experimental detail for the formation of **2** and **3** is proposed in the Supporting Information, Scheme S1.

Complex **3** was isolated by column chromatography, and its structure has been determined by X-ray crystallography.[9] As shown in Figure 2, the X-ray diffraction study indicated that complex **3** can be regarded as an isomer of osmacycloallene **2**, albeit one that contains a planar six-membered metallacycle. The co-planarity is reflected by the small mean deviations (0.0209 Å) from the least-squares planes through the six atoms Os1, C1, C2, C3, C4, and C5. For the osmium–



Scheme 3. Conversion of five-membered metallacycloallenes to six-membered metallacycloallenes.

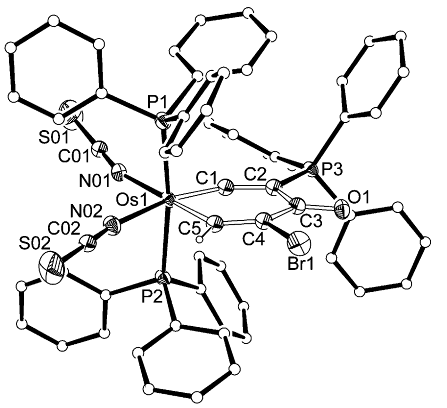


Figure 2. X-ray structure of complex **3** (ellipsoids set at 50% probability). The hydrogen atoms of PPh_3 are omitted for clarity. Selected bond distances [Å] and angles [°]: Os1–C1 1.781(6), Os1–C5 2.048(7), C1–C2 1.352(9), C2–C3 1.470(9), C3–O1 1.231(8), C3–C4 1.470(8), C4–C5 1.331(9), C4–Br1 1.924(6); C1-Os1-C5 79.1(3), Os1-C1-C2 152.7(5), C1-C2-C3 114.4(5), C2-C3-C4 115.5(5), C3-C4-C5 128.2(6), C4-C5-Os1 129.6(5).

vinylidene motif, the angle (Os1-C1-C2, 152.7(5)°) and the bond lengths (Os1−C1, 1.781(6) Å; C1−C2, 1.352(9) Å) are comparable to those of the structurally related iso-osmabenzene.[7] Complex **3** can be regarded as an iso-osmabenzenone.

The presence of a halogen atom in complex **2** offers a potential synthetic handle for diversification. As shown in Scheme 3, treatment of **2** with excess silver thiocyanate in $CHCl_3$ at 0 °C led to the formation of complex **4** in 92% yield. The structure of complex **4** has been determined by X-ray diffraction studies.[9] The structural features associated with the metallacycle of **4** are quite similar to those found in **2**. The metallacycle is essentially planar (the mean deviation from the least-squares plane through five atoms is 0.0116 Å). The characteristic bond lengths (Os1−C1 1.811(5) Å, C1−C2 1.358(7) Å) and the Os1-C1-C2 angle (137.9(5)°) are very close to those of **2**.

Similarly, the five-membered osmacycloallene **4** can also be converted into the six-membered osmacycloallene **5**. When a mixture of **4** and NaSCN (10 equiv) in DMF was stirred at 120 °C for approximately 6 h, the expected complex **5** was isolated in 85% yield (Scheme 3). Complex **5** was characterized by NMR spectroscopy and HRMS, and its structure was determined unambiguously by X-ray crystal structure analysis.[9] All the characterization data are in accord with the predicted six-membered osmacycloallene with a thiocyanate substituent at C4.

As observed from the calculated energy differences shown in Scheme 3, the six-membered osmacycloallenes **3** and **5** are much more stable than the five-membered osmacycloallenes **2** and **4**. Therefore, we can conclude that conversion of five-membered osmacycloallenes into six-membered osmacycloallenes is thermodynamically favorable. Experimentally, the conversion of **4** to **5** was more difficult and could only be achieved at 120 °C (Scheme 3). This may be attributed to the higher stability of **4** compared to its analogue **2**.

In summary, we have described the synthesis and characterization by X-ray crystallography of highly stable, unusual five-membered metallacycloallene systems. Computational analyses revealed that incorporation of transition-metal moieties relieved considerable ring strain and indicated a trend toward ring enlargement in the five-membered metallacycloallenes. Consistent with the calculation results, five-membered metallacycloallenes could be converted experimentally into six-membered metallacycloallenes. We have described herein the smallest metallacycloallenes containing a metal–vinylidene fragment that have never been reported to date. This result opens up new avenues of investigation into strained, small-ring cycloallene systems.

Experimental Section

2: A solution of pyridinium tribromide (460 mg, 1.44 mmol) in methanol (3 mL) was added dropwise to a solution of **1** (563 mg, 0.480 mmol) in CH_2Cl_2 (30 mL). The mixture was stirred at room temperature for approximately 10 min to give a brown solution. The solvent was removed under vacuum, and the residue was washed with methanol (3×5 mL) to give a brown solid. Yield: 570 mg, 95%. ^1H NMR (500.2 MHz, CD_2Cl_2): $\delta = 5.2$ (s, 1H, C^5H), 6.9–7.7 ppm (m, 45H, Ph). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): $\delta = 3.7$ (s, $C(PPh_3)$), −1.4 ppm (s, $OsPPh_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): $\delta = 294.6$ (br, C^1), 88.2 (d, $J(PC) = 119.5$ Hz, C^2), 197.4 (s, C^3), 150.4 (s, C^4), 102.7 (s, C^5), 147.2 and 143.5 (s, $Os(NCS)_2$), 121.1–135.0 ppm (m, ph). HRMS (ESI): m/z calcd. for $C_{61}H_{46}N_2S_2P_3BrOOsNa$: 1273.0955 $[M+Na]^+$; found: 1273.0946.

3: A mixture of **2** (360 mg, 0.288 mmol) and sodium bromide (298 mg, 2.90 mmol) in DMF (30 mL) was heated at 100 °C for approximately 3 h to give a brown solution. The solution was diluted with CH_2Cl_2 (50 mL) and washed with distilled water (5×50 mL). The organic phase was dried over anhydrous Na_2SO_4, and the solid suspension was removed by filtration. The filtrate was concentrated to approximately 2 mL under vacuum, and the product was purified by column chromatography over neutral alumina and eluted with acetone/dichloromethane (1:30, v/v) to give complex **3** as a yellow solid. Yield: 292 mg, 81%. ^1H NMR (500.2 MHz, CD_2Cl_2): $\delta = 9.5$ (s, 1H, C^5H), 7.0–7.6 ppm (m, 45H, Ph). $^{31}P\{^1H\}$ NMR (202.5 MHz, CD_2Cl_2): $\delta = 7.5$ (s, $C(PPh_3)$), −2.2 ppm (s, $OsPPh_3$). $^{13}C\{^1H\}$ NMR (125.8 MHz, CD_2Cl_2): $\delta = 290.8$ (br, C^1), 89.5 (d, $J(PC) = 118.1$ Hz, C^2), 179.7 (s, C^3), 114.4 (s, C^4), 178.2 (br, C^5), 145.8 and 142.9 (s, $Os(NCS)_2$), 121.9–135.4 ppm (m, ph). HRMS (ESI): m/z calcd. for $C_{61}H_{46}N_2S_2P_3BrOOsNa$: 1273.0955 $[M+Na]^+$; found: 1273.0922.

Details of the preparation and characterization of **4** and **5** can be found in the Supporting Information.

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