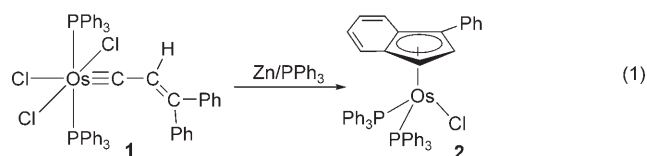


A Metallanaphthalene Complex from Zinc Reduction of a Vinylcarbyne Complex**

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Transition metal containing metallaaromatics are a fascinating class of compounds because they can show properties of both organometallic compounds and aromatic organic compounds.^[1] The most common metallaaromatics are metallabenzene, stable examples of which have been found for osmium,^[2] iridium,^[3] platinum,^[4] and ruthenium.^[5] Other interesting metallaaromatics and related compounds isolated in recent years include metallanaphthalene,^[6] metallapyrylium,^[7] metallathiabenzene,^[8] metallapyridine,^[9] metallabenzynes,^[10] isometallabenzene,^[11] and metallabenzvalene.^[12] Here we report the synthesis and characterization of the first metallanaphthalene.

Compared to metallabenzene, the chemistry of metallabenzynes is less developed, partly due to the lack of convenient methods to construct the metallabenzynes ring. In a search for new routes to metallabenzynes, we tried to reduce the carbyne complex $[\text{OsCl}_3(\equiv\text{CCH}=\text{CPh}_2)(\text{PPh}_3)_2]$ (**1**) with zinc.^[13] We envisaged that Zn might first reduce the carbyne complex to the 16e species $[\text{OsCl}(\equiv\text{CCH}=\text{CPh}_2)(\text{PPh}_3)_2]$, which could undergo C–H oxidative addition to give an osmanaphthalene. Treatment of **1** with zinc powder in THF heated at reflux for 1.5 h produced the indenyl complex $[\{\eta^5\text{-C}_9\text{H}_6(\text{Ph})\}\text{OsCl}(\text{PPh}_3)_2]$ (**2**), along with other unidentified species. Complex **2** can be isolated in 39% yield from the reaction. The reaction is cleaner in the presence of PPh_3 . In this case, complex **2** can be isolated as a red solid in 71% yield [Eq. (1)].



The structure of **2** was determined by single-crystal X-ray diffraction^[14] (Figure 1), which clearly revealed that the complex contains an indenyl, a chlorido, and two PPh_3

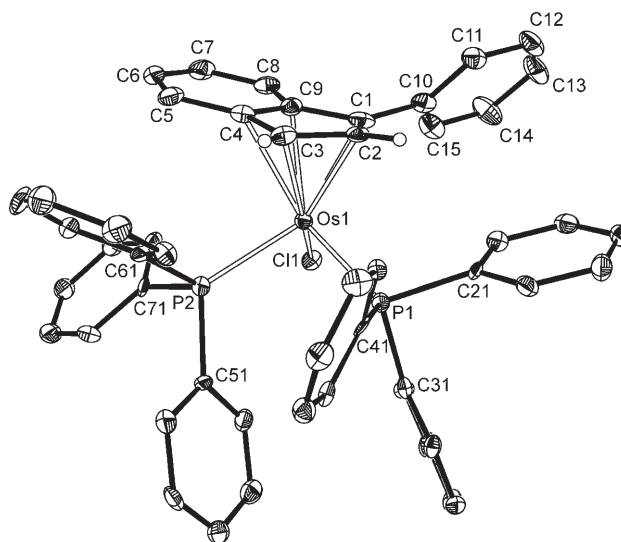
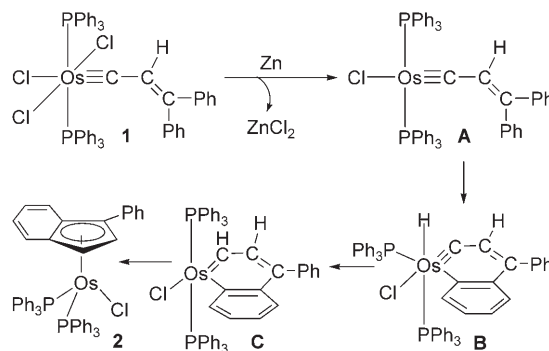


Figure 1. Molecular structure of $[\{\eta^5\text{-C}_9\text{H}_6(\text{Ph})\}\text{OsCl}(\text{PPh}_3)_2]$ (**2**).

ligands. The Os–C bond lengths (2.174(5)–2.359(5) Å) are comparable with those of the reported indenyl complex $[\text{Os}(\eta^5\text{-C}_9\text{H}_7)(\text{NCCH}_3)(\text{P}(\text{tPr})_3)_2]\text{OTf}$ (2.184(3)–2.417(3) Å).^[15]

The solid-state structure of **2** is supported by the solution NMR spectroscopic data. In particular, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum (in CD_2Cl_2) displayed two doublets at $\delta = -7.4$ and 0.3 ppm with a coupling constant of 17.1 Hz. Observation of two ^{31}P signals for **2** is expected, because the Os center is chiral. The ^1H spectrum (in CD_2Cl_2) showed signals of the η^5 -indenyl ring at $\delta = 3.63$ and 5.41 ppm. The $^{13}\text{C}\{^1\text{H}\}$ spectrum (in CD_2Cl_2) displayed the signals of the η^5 -indenyl ring at $\delta = 79.6, 84.2, 108.5, 108.6,$ and 110.6 ppm.

A plausible mechanism for the formation of **2** is shown in Scheme 1. Reduction of **1** with Zn may initially give 16e



Scheme 1. Proposed mechanism for the formation of **2**.

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carbyne complex **A**, which could undergo cyclometalation to give hydrido osmanaphthalene intermediate **B**. Migratory insertion of the carbyne into the Os–H bond of **B** gives osmanaphthalene **C**, which rearranges to the final product **2**. This is reasonable since formation of Cp complexes from metallabenzenes is known.^[3e,h]

Although the reaction intermediates shown in Scheme 1 were not identified, DFT calculations provide support for the proposed mechanism. Figure 2 shows the potential-energy profiles for the transformation of $[\text{OsCl}(\equiv\text{CCH}=\text{CHPh})(\text{PH}_3)_2]$ (**A'**, a model complex of **A**) to $[(\eta^5\text{-C}_9\text{H}_7)\text{OsCl}(\text{PH}_3)_2]$ (**2'**, a model complex of **2**).

The DFT calculations indicate that the pathway leading to formation of indenyl complex **2'** is both kinetically and thermodynamically feasible. The important step for the reaction is isomerization of **A'** to **A''**, a square-pyramidal complex with two *cis* PH_3 ligands. Once **A''** is formed, it undergoes C–H activation to give hydrido osmanaphthalene complex **B'** with almost no barrier. Complex **2'** is formed from **C'**, an osmanaphthalene intermediate generated by migratory insertion of **B'**, with a significant barrier.

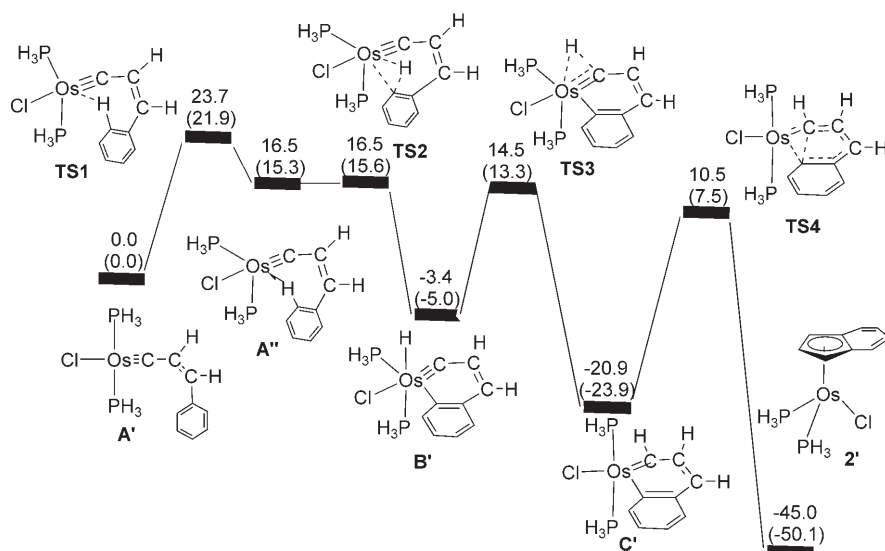
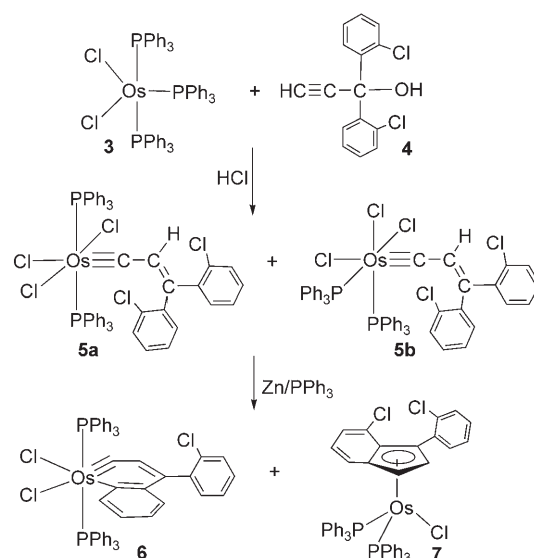


Figure 2. Energy profile for the formation of **2'** from **A'**. The calculated relative free energies and reaction energies (in parentheses) are given in kcal mol^{-1} .

The DFT results show that formation of osmanaphthalene complex **B** via C–H activation of **A** is energetically feasible. The problem is that it readily undergoes migratory insertion of the hydride ligand to finally give indenyl complex **2**. On the basis of the DFT results, we deduce that if the hydride ligand is replaced by a chloride ligand, the migratory insertion reaction should be discouraged and an osmanaphthalene complex could be isolated.

This theoretical prediction was confirmed by reaction of $[\text{OsCl}_3(\equiv\text{CCH}=\text{C}(\text{2-ClC}_6\text{H}_4)_2)(\text{PPh}_3)_2]$ (**5**) with Zn. The previously unknown complex **5** was obtained as a mixture of meridional and facial isomers in an approximate ratio of 4:3 from a one-pot reaction of $[\text{OsCl}_2(\text{PPh}_3)_3]$ (**3**) with $\text{HC}\equiv\text{CC}(\text{OH})(\text{2-ClC}_6\text{H}_4)_2$ (**4**) in the presence of HCl in CH_2Cl_2 (Scheme 2).



Scheme 2. Preparation of **6** and **7**.

Treatment of **5** with zinc powder in the presence of PPh_3 in THF produced the green osmanaphthalene complex **6** and the red indenyl complex **7**, owing to competitive oxidative addition of C–Cl and C–H bonds, respectively. Complexes **6** and **7** can be separated by chromatography. The structure of **7** can be assigned easily, as it has NMR data similar to those of **2**, which has been structurally characterized by single-crystal X-ray diffraction.

The most notable product formed in the reaction is compound **6**. As confirmed by single-crystal X-ray diffraction analysis, it contains an essentially planar metallanaphthalene unit (Figure 3). The maximum deviation from the least-squares plane of the metallacycle (Os1 , $\text{C1}–\text{C5}$) is $0.034(3) \text{ \AA}$ for C5 , and that for the whole metallanaphthalene system (Os1 , $\text{C1}–\text{C9}$) is $-0.081(2) \text{ \AA}$ for Os1 .

The Os–C1 bond length ($1.732(4) \text{ \AA}$) is within the range of those observed for typical $\text{Os}\equiv\text{C}$ bonds ($1.69–1.79 \text{ \AA}$)^[16,17] and is significantly smaller than those found for typical vinylidene complexes $\text{Os}=\text{C}=\text{CRR}'$ ($1.78–1.90 \text{ \AA}$).^[16,18] The Os–C5 bond length ($2.127(3) \text{ \AA}$) is within the range of those observed for typical Os–C(aryl) bonds ($1.98–2.28 \text{ \AA}$)^[16,19] and at the high end of typical Os=C(carbene) bonds ($1.78–2.14 \text{ \AA}$).^[16,20] Despite the large difference in the Os–C bond lengths, no simple C–C bond-distance alternation was observed for the metallacycle, as would be implied from the canonical form drawn in Scheme 2. The Os–C and C–C bond lengths within the six-membered ring, together with its planar nature, indicate that the metallacycle has a more delocalized nature. The $\text{Os1}–\text{C1}–\text{C2}$ angle of $155.0(3)^\circ$ is similar to those observed for osmabenzynes and is significantly smaller than

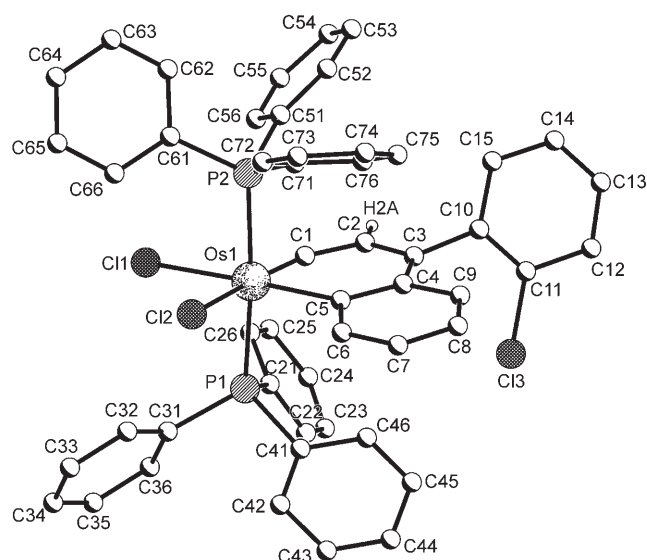


Figure 3. Molecular structure of **6**. Selected bond lengths [Å] and angles [°]: Os1–P1 2.4193(9), Os1–P2 2.4088(9), Os1–Cl1 2.4568(9), Os1–Cl2 2.4766(9), Os1–C1 1.732(4), Os1–C5 2.127(3), C1–C2 1.375(5), C2–C3 1.368(5), C3–C4 1.457(5), C4–C5 1.432(5), C5–C6 1.396(5), C6–C7 1.378(5), C7–C8 1.374(5), C8–C9 1.363(5), C9–C4 1.425(5), P1–Os1–P2 175.35(3), C1–Os1–C5 79.84(15), Os1–C1–C2 155.0(3), C1–C2–C3 112.6(3), C2–C3–C4 123.4(3), C3–C4–C5 124.0(3), C4–C5–Os1 125.0(3), C4–C5–C6 114.5(3), C5–C6–C7 123.9(4), C6–C7–C8 121.3(4), C7–C8–C9 117.9(4), C8–C9–C4 122.1(4), C9–C4–C5 120.1(4).

that expected for a carbyne or vinylidene complex owing to the constraint of the six-membered ring. Consistent with the solid-state structure, the $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of **6** displayed signals for $\text{Os}\equiv\text{C}$ and $\text{Os}-\text{C}5$ at $\delta=277.9$ and 164.4 ppm, respectively. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum showed two signals for the two PPh_3 ligands, that is, the two P atoms in **6** are magnetically inequivalent due to slow rotation of the *ortho*-chlorophenyl group.

Since the structure of **6** is closely related to that of 1,2-naphthalene, it can be regarded as a metallanaphthalene. 1,2-Naphthalenes^[21] generated in situ have often been used in organic synthesis.^[21a] However, they have low thermal stability and have only been detected in argon matrix at low temperature.^[21b,c]

In summary, we have synthesized the first well-characterized example of a metallanaphthalene **6** by Zn reduction of $[\text{OsCl}_3\{\text{C}\equiv\text{CCH}=\text{C}(2\text{-ClC}_6\text{H}_4)_2\}(\text{PPh}_3)_2]$. In addition, we also found that indenyl complexes can be formed from hydrido metallanaphthalenes, and this suggests that metallabenzynes could be important intermediates in organometallic reactions. Preparation of other metallanaphthalenes is now underway.

Experimental Section

6 and 7: A mixture of **5** (0.380 g, 0.35 mmol), zinc powder (0.480 g, 7.34 mmol), and triphenylphosphine (91.7 mg, 0.35 mmol) in THF (30 mL) was refluxed for 25 min. The solvent was removed completely under vacuum and the residue was extracted with benzene (13 mL) and filtered. The extract was concentrated to about 5 mL. Diethyl ether (15 mL) was added slowly to give an orange precipitate, which was removed by filtration, and the solvent of the brown filtrate was removed under vacuum and the residue dissolved in CH_2Cl_2

(1 mL). Addition of hexane (15 mL) to the solution gave a brownish green precipitate, which was collected by filtration, washed with hexane (2×2 mL) and diethyl ether (2×1 mL), and dried under vacuum to give 0.165 g of crude product containing predominantly **6** and a small amount of **7**. To separate **6** and **7**, the brownish green solid was dissolved in benzene (3 mL) and loaded onto a silica gel column. The column was eluted with benzene and CH_2Cl_2 sequentially to give red **7** and green **6**, respectively, which were dried under vacuum. Yield: **6**, 88 mg, 25%; **7**, 15 mg, 4.3%. Selected spectroscopic data of **6**: $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, C_6D_6): $\delta=-0.6$ (d, $J(\text{PP})=474.0$ Hz), -3.3 ppm (d, $J(\text{PP})=474.0$ Hz). ^1H NMR (300.13 MHz, C_6D_6): $\delta=3.77$ (s, 1H; $\text{Os}\equiv\text{CCH}=\text{C}$), 5.99 (t, $J(\text{HH})=7.5$ Hz, 1H; Ph), 6.13 (d, $J(\text{HH})=6.6$ Hz, 1H; Ph), 6.22 (t, $J(\text{HH})=7.4$ Hz, 1H; Ph), 8.86 (d, $J(\text{HH})=8.3$ Hz, 1H; Ph), 6.46–7.75 ppm (m, 34H; other aromatic protons); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, C_6D_6): $\delta=277.9$ (t, $J(\text{PC})=11.7$ Hz; $\text{Os}\equiv\text{C}$), 175.4 (s; $\text{Os}\equiv\text{CCH}=\text{C}$), 164.4 (t, $J(\text{PC})=6.7$ Hz; $\text{Os}-\text{C}$), 119.1 (s, $\text{Os}\equiv\text{CCH}=\text{C}$), 121.3–142.8 ppm (m, other aromatic carbon atoms); elemental analysis (%) calcd for $\text{C}_{51}\text{H}_{39}\text{Cl}_3\text{P}_2\text{Os}$: C 60.63, H 3.89; found: C 60.75, H 4.06; TOF LD + MS: m/z 973.2 $[\text{M}-\text{Cl}]^+$, 939.2 $[\text{M}-2\text{Cl}]^+$, 826.2 $[\text{M}-2\text{Cl}-\text{PhCl}]^+$. Selected spectroscopic data of **7**: $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CD_2Cl_2): $\delta=-6.9$ (d, $J(\text{PP})=16.9$ Hz), -0.5 ppm (d, $J(\text{PP})=16.9$ Hz); ^1H NMR (300.13 MHz, C_6D_6): $\delta=3.38$ (brs, 1H; $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$), 5.18 (d, $J(\text{HH})=5.3$ Hz, 1H; $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$), 5.32 (d, $J(\text{HH})=8.3$ Hz, 1H; $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$), 5.91 (t, $J(\text{HH})=7.8$ Hz, 1H; $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$), 6.25–7.40 (m, 34H; Ph, PPh_3 , $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$), 9.51 ppm (dd, $J(\text{HH})=7.8$, 1.5 Hz, 1H; $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$); $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CD_2Cl_2): $\delta=125.4$ – 140.4 (m; Ph, PPh_3 , $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$), 120.8 (s; $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$), 90.8 ppm (s, $\eta^5\text{-C}_9\text{H}_5\text{Cl}(2\text{-ClPh})$); elemental analysis (%) calcd for $\text{C}_{51}\text{H}_{39}\text{Cl}_3\text{P}_2\text{Os}$: C 60.63, H 3.89; found: C 61.00, H 4.16.

2 and 5: See the Supporting Information for details.

The DFT computational details are the same as those described in ref. [22].

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- [17] Recent examples: a) $[\text{Os}(\equiv\text{CCH}=\text{CPh})\text{H}(\text{OAc})(\text{P}i\text{Pr}_3)_2]\text{BF}_4$ (1.740(4) Å): T. Balaño, R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2007**, *26*, 2037; b) $[\text{Os}(\equiv\text{CCH}=\text{CPh})\text{H}(\text{OPh})(\text{MeCN})(\text{P}i\text{Pr}_3)_2]\text{BF}_4$ (1.740(5) Å): T. Balaño, R. Castarlenas, M. A. Esteruelas, E. Oñate, *J. Am. Chem. Soc.* **2007**, *129*, 8850; c) $[\text{Os}(\equiv\text{CC}_6\text{H}_4\text{CHMe}_2)_2\text{H}_2\{\text{N}(\text{SiMe}_2\text{CH}_2\text{PrBu}_2)_2\}]$ (1.746(3) Å): J. H. Lee, M. Pink, K. G. Caulton, *Organometallics* **2006**, *25*, 802; d) $[\text{OsH}(\equiv\text{CCH}=\text{CPh}_2)(\text{H}_2\text{O})_2(\text{P}i\text{Pr}_3)_2](\text{BF}_4)_2$ (1.733(6) Å): T. Balaño, R. Castarlenas, M. A. Esteruelas, F. J. Modrego, E. Oñate, *J. Am. Chem. Soc.* **2005**, *127*, 11184.
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- [19] For example: a) $[\text{Os}(\text{C}_6\text{H}_4\text{CPh}=\text{NH})\text{Cl}(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (2.038(2) Å): M. L. Buil, M. A. Esteruelas, E. Goni, M. Oliván, E. Oñate, *Organometallics* **2006**, *25*, 3076; b) $[\text{OsH}(\eta^5\text{-C}_5\text{H}_5)\text{-}[\text{C}_6\text{H}_4\text{C}(\text{O})\text{CH}_3](\text{P}i\text{Pr}_3)]\text{BF}_4$ (2.016(5) Å): M. A. Esteruelas, Y. A. Hernández, A. M. López, M. Oliván, E. Oñate, *Organometallics* **2005**, *24*, 5989; c) $[\text{CpOsH}(\text{C}_6\text{H}_4\text{CPh}=\text{NH})(\text{P}i\text{Pr}_3)]\text{OTf}$ (2.137(19) Å): M. A. Esteruelas, E. Gutierrez-Pueba, A. M. López, E. Oñate, J. I. Tolosa, *Organometallics* **2000**, *19*, 275.
- [20] Recent examples: a) $[\text{Os}(\equiv\text{CHPh})(\text{MeCN})_4(i\text{Pr})](\text{OTf})_2$ (1.926(6) Å): R. Castarlenas, M. A. Esteruelas, E. Oñate, *Organometallics* **2007**, *26*, 2129; b) $[\text{HP}i\text{Pr}_3][\text{OsCl}_2(\equiv\text{C}(\text{Ph})\text{CH}_2\text{Ph})(\text{CO})(\text{P}i\text{Pr}_3)_2]$ (1.929(3) Å), $[\text{OsCl}(\equiv\text{C}(\text{Ph})\text{CH}_2\text{Ph})(\text{CO})(\text{P}i\text{Pr}_3)_2]\text{BF}_4$ (1.888(3) Å): M. A. Esteruelas, López, E. Oñate, *Organometallics* **2007**, *26*, 3260.
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- [22] J. Zhu, G. Jia, Z. Lin, *Organometallics* **2007**, *26*, 1986.