A Metallanaphthalynyl 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 metallabenzenes, 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 metallanapthalene,[6] metallapyrylium,[7] metallathiabenzene,[8] metallapyridine,[9] metallabenzyne,[10] isometallabenzenes,[11] and metallabenzvalene.[12] Here we report the synthesis and characterization of the first metallanaphthalynyl.

Compared to metallenbenzenes, the chemistry of metallenbenzyynes is less developed, partly due to the lack of convenient methods to construct the metallenbenzyyne ring. In a search for new routes to metallenbenzyynes, we tried to reduce the carbyne complex \[\text{OsCl}_3(^{16}C_17CCH\equivCPh_2)(PPh_3)_2\] (1) with zinc.[13] We envisaged that Zn might first reduce the carbyne complex to the 16e species \[\text{OsCl}(^{16}C_17CCH\equivCPh_2)(PPh_3)_2\], which could undergo C–H oxidative addition to give an osmanaphthalynyl. Treatment of 1 with zinc powder in THF heated at reflux for 1.5 h produced the indenyl complex \[\{h^5-C_9H_6(Ph)\text{OsCl}(PPh_3)_2\}\] (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 PPh₃. 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 PPh₃ ligands. The Os–C bond lengths (2.174(5)–2.359(5) Å) are comparable with those of the reported indenyl complex \[\text{Os}(h^5-C_9H_7)(NCCH_3)(P_iPr_3)_2\] 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}P\{^1H\} NMR spectrum (in CD₂Cl₂) 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 CD₂Cl₂) showed signals of the \(h^5\)-indenyl ring at \(\delta = \) 3.63 and 5.41 ppm. The \(^{13}C\{^1H\} spectrum (in CD₂Cl₂) displayed the signals of the \(h^5\)-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...
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carbyne complex A, which could undergo cyclometalation to give hydrido osmanaphthylene 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 [OsCl(≡CCH=CHPh)(PPh3)] (A', a model complex of A) to [(η^2-C₅H₅)OsCl(PPh3)] (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 PPh3 ligands. Once A'' is formed, it undergoes C–H activation to give hydrido osmanaphthylene 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.

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 [OsCl(≡CCH=CH2)(PPh3)] (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 [OsCl3(PPh3)3] (3) with HCC(=CH2). The Os–C bond length (1.732(4) Å) is within the range of those observed for typical Os=C bonds (1.69–1.79 Å).\[16,17\] and is significantly smaller than those found for typical vinylidene complexes Os=C=C(R) (1.78–1.90 Å).\[18,19\] The Os–C bond length (2.127(3) Å) is within the range of those observed for typical Os–C(aryl) bonds (1.98–2.28 Å).\[18,19\] and at the high end of typical Os–C(carbene) bonds (1.78–2.14 Å).\[16,20\] 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 Os1-C1-C2 angle of 155.0(3)° is similar to those observed for osmabenzenes and is significantly smaller than

![Figure 2. Energy profile for the formation of 2' from A'. The calculated relative free energies and reaction energies (in parentheses) are given in kcalmol⁻¹.](image)

Treatment of 5 with zinc powder in the presence of PPh3 in THF produced the green osmanaphthylene 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 metallanaphthalyne unit (Figure 3). The maximum deviation from the least-squares plane of the metallacycle (Os1, C1–C5) is 0.034(3) Å for C5, and that for the whole metallanaphthalyne system (Os1, C1–C9) is −0.081(2) Å for Os1.
that expected for a carbyne or vinylidene complex owing to the constraint of the six-membered ring. Consistent with the solid-state structure, the $^{13}$C($^1$H) NMR spectrum of 6 displayed signals for Os(C and Os–C at $\delta = 277.9$ and 164.4 ppm, respectively. The $^{31}$P($^1$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 the 6 is closely related to that of 1,2-naphthylidyne, it can be regarded as a metallanaphthylidyne. 1,2-Naphthylidyne$^{[20]}$ generated in situ have often been used in organic synthesis.$^{[21]}$ However, they have low thermal stability and have only been detected in argon matrix at low temperature.$^{[21c,22]}$

In summary, we have synthesized the first well-characterized example of a metallanaphthylidyne 6 by Zn reduction of [OsCl$_2$][C=C(2-C$_6$H$_5$Cl)$_3$][PPh$_3$]$_2$. In addition, we also found that indenyl complexes can be formed from hydrido metallanaphthalenes, and this suggests that metallabenzenes could be important intermediates in organometallic reactions. Preparation of other intermediates in metallacycles 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$_2$Cl$_2$ (1 mL). Addition of hexane (15 mL) to the solution gave a brown 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$_2$Cl$_2$ sequentially to give red 6 and green 7, respectively, which were dried under vacuum. Yield: 6, 88 mg, 25%; 7, 15 mg, 4.3%. Selected spectroscopic data of $^{31}$P($^1$H) NMR (121.5 MHz, CD$_2$Cl$_2$): $\delta = -0.6$ (d, J(PP) = 474.0 Hz), $-3.3$ ppm (d, J(PP) = 474.0 Hz). $^{1}$H NMR (300.13 MHz, CD$_2$Cl$_2$): $\delta = 3.77$ (s, 1 H; Os=OCCPh), 5.99 (t, J(PP) = 7.5 Hz, 1 H; Ph), 6.13 (d, J(PP) = 6.6 Hz, 1 H; Ph), 6.22 (t, J(PP) = 7.4 Hz, 1 H; Ph), 8.86 (d, J(PP) = 8.3 Hz, 1 H; Ph), 6.46–7.75 ppm (m, 34 H; other aromatic protons).$^{[21d]}$ $^{13}$C($^1$H) NMR (75.5 MHz, CD$_2$Cl$_2$): $\delta = 277.9$ (t, J(PP) = 11.7 Hz; Os=C), 175.4 (s; Os=OCCPh), 164.4 (t, J(PP) = 6.7 Hz; Os=C), 119.1 (s; Os=OCCPh), 121.3–142.8 ppm (m, other aromatic carbon atoms); elemental analysis (%) calcd for C$_8$H$_7$Cl$_2$P$_2$Os: C 60.63, H 3.89; found: C 60.75, H 4.06; TOF LD $^{2}$ and See the Supporting Information for details.

**Keywords:** carbyne ligands· cyclization · indenyl ligands · metallacycles · osmium

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[14] See the Supporting Information for single-crystal X-ray diffraction data.


[16] Based on a search of the Cambridge Structural Database, CSD version 5.27 (August 2006).


[20] Recent examples: a) [Os=C=CPH(MeCN)i(Pr)][O(Tf)] (1.926(6) Å); R. Castarainas, M. A. Esteruelas, E. Oñate, Organometallics 2007, 26, 2129; b) [H3P(Pr)2][OsCl(C=CPH)C=CPH(PCy3)] (1.929(5) Å); [OsCl(C=CPH)C=CPH(PCy3)]BF4 (1.888(3) Å); M. A. Esteruelas, López, E. Oñate, Organometallics 2007, 26, 3260.
