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Conversions of Osmabenzyne and Isoosmabenzene

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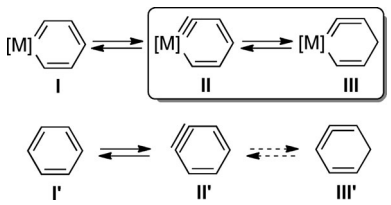
Abstract: We report herein the first example of the conversion of metallabenzyne **II** and isometallabenzene **III**. The osmium hydride vinylidene complex **1** reacts with $HC{\equiv}CCH(OEt)_2$ to give osmabenzyne **3** via isoosmabenzene **2**. Compound **3** exhibits high thermal stability in air. Nonetheless, nucleophilic attack at **3** provides isoosmabenzenes **4a** and **4b**, or opens the ring to produce **5a** and **5b**. We propose mechanisms to disclose the intrinsic connection between the six-membered metallacycles, and carry out DFT calculations to rationalize the regioselectivity of the nucleophilic addition reactions.

Keywords: isoosmabenzene · metallacycles · nucleophilic addition · osmabenzyne · osmium

Introduction

Metalla-aromatics[1] are derived from the replacement of a (hydro)carbon unit in aromatic hydrocarbons with a metal fragment. Considerable effort has been devoted to the study of metallabenzenes **I**, and these metal-containing analogues



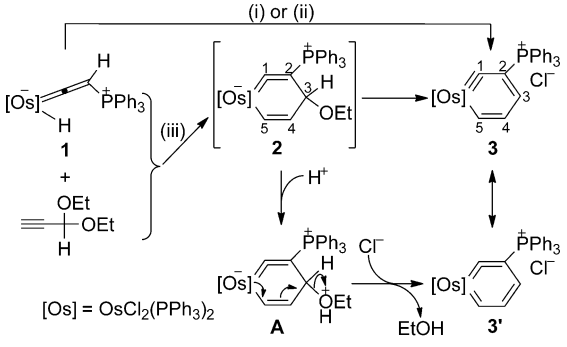
of benzene (**I′**) have been found to be isolable, stable, and aromatic.[2] Synthetic methods and the reactivity of metallabenzenes have now been established,[3–5] including some reactions that directly relate to classic benzene chemistry.[6–8]

The isolation of stable metallabenzynes **II**[9] and isometallabenzenes **III**[10] challenged the usual notions of highly strained rings. In comparison, benzyne (**II′**)[11,12] and isobenzene (**III′**)[13] are too reactive and short-lived to be isolated. Among the reactions of metallabenzynes,[9e–h] the interconversion of metallabenzyne and metallabenzene is particularly interesting[9g,14] because it resembles the mutual transformation of benzyne and benzene. On the other hand, isometallabenzenes remain rare,[10] thus restricting the in-depth studies of their chemistry. Herein, we show for the first time that isometallabenzene can transform into metallabenzyne, and metallabenzyne can undergo nucleophilic addition reactions to "restore" isometallabenzenes, or to go further and open the metallacycle.

Results and Discussion

Conversion of isoosmabenzene to osmabenzyne: Treatment of the osmium hydride vinylidene **1** with $HC{\equiv}CCH(OEt)_2$ in chloroform produced osmabenzyne **3** through a formal [3+3] cycloaddition reaction[10a] via the key intermediate isoosmabenzene **2** (Scheme 1). The reaction took 8 h to complete at room temperature (RT; Scheme 1, reaction conditions i), or 2 h if heated at reflux.

The structure of osmabenzyne **3** in the solid state has been verified by X-ray diffraction. As shown in Figure 1, the six-membered metallacycle in **3** is essentially planar. The maximum deviation from the least-squares plane through Os1 and C1–C5 is 0.028 Å for C5. The Os1-C1-C2 angle is



(i) $CHCl_3$, Et_4NCl, RT, 8 h, 85%
(ii) 1) $CHCl_3$, RT, 1 h; 2) HCl, RT, 15 min, 88%
(iii) $CHCl_3$, K_2CO_3, RT, 1 h

Scheme 1. Preparation of osmabenzyne **3** via isoosmabenzene **2**.

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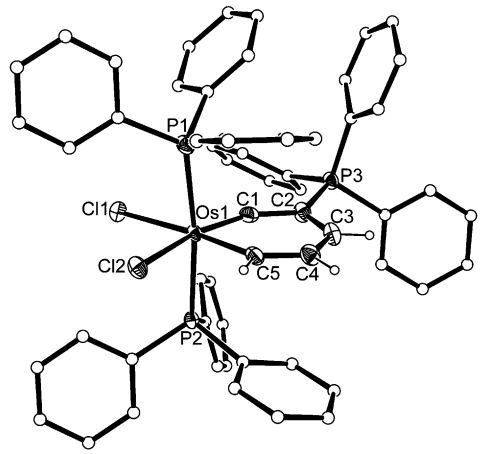


Figure 1. Molecular structure of the cation of osmabenzyne **3** (ellipsoids shown at the 50% probability level). The hydrogen atoms of PPh_3 are omitted for clarity. Selected bond lengths [Å] and angles [°]: Os1–C1: 1.775(6), Os1–C5: 2.011(7), C1–C2: 1.390(9), C2–C3: 1.403(9), C3–C4: 1.381(9), C4–C5: 1.389(9), C1-Os1-C5: 80.7(3), Os1-C1-C2: 148.6(5), C1-C2-C3: 113.1(6), C2-C3-C4: 123.5(6), C3-C4-C5: 123.7(6), C4-C5-Os1: 130.2(5).

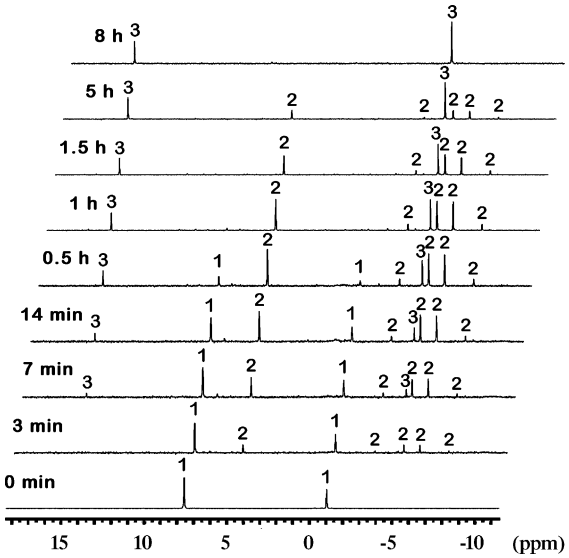


Figure 2. Time-evolved ^{31}P NMR spectra of the formation of isometallabenzene **2** and its conversion into metallabenzyne **3** at 293 K in $CDCl_3$.

148.6(5)°, the Os1≡C1 bond length is 1.775(6) Å and the Os1–C5 bond length is 2.011(7) Å. The C–C bond lengths in the metallacycle in **3** (1.381(9)–1.403(9) Å) suggest a delocalized nature. All of these structural features are comparable to the osmabenzynes produced by Jia's group.[9b–h]

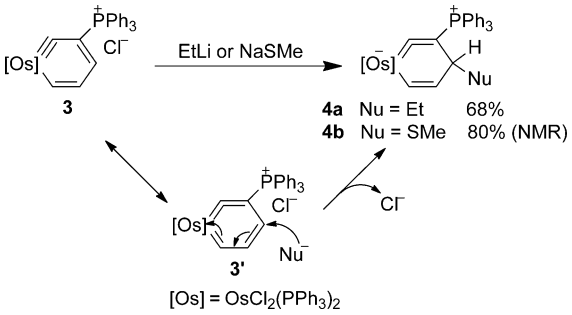
Osmabenzyne **3** and the intermediate isoosmabenzene **2** were characterized by NMR spectroscopy. The ring numbering system for osmabenzyne and isoosmabenzene is shown in Scheme 1. In the ^1H and ^{13}C NMR spectrum, compound **3** exhibits characteristic chemical shifts of an osmabenzyne. H5 has a characteristically low-field resonance at 13.9 ppm, and the metal-bound carbon atoms C1 and C5 show typical downfield signals at 287.9 and 246.7 ppm. The ^{31}P NMR spectrum of **3** consists of two singlets: 14.7 ppm for C*P*Ph_3 and −4.4 ppm for Os*P*Ph_3. The NMR spectra of **2** resemble those of previous isoosmabenzenes.[10] In the ^1H NMR spectrum, two vinyl protons resonate at 8.1 (H5) and 5.0 ppm (H4) with a coupling constant of 9.0 Hz, thus indicating a *cis* geometry. The H3 proton, attached to the saturated carbon atom C3, was found at 1.7 ppm. In the ^{31}P NMR spectrum of **2**, C*P*Ph_3 resonates at 4.4 ppm as a singlet, and two Os*P*Ph_3 signals appear as a characteristic AB quadruplet at −4.4 and −7.1 ppm ($^2J_{PP}$ = 350.3 Hz), due to the presence of a chiral center at C3.[10] The molecular formulae of **2** and **3** have been confirmed by high-resolution mass spectrometry (HRMS: *m/z* calcd for $C_{61}H_{53}OP_3ClOs$ (**2**): 1121.2613 $[M-Cl]^+$; found: 1121.2609; *m/z* calcd for $C_{59}H_{48}P_3Cl_2Os$ (**3**): 1111.1961 $[M]^+$; found: 1111.1956).

The formation of osmabenzyne **3** via isoosmabenzene **2** was monitored by in situ NMR spectroscopy at RT. As shown in Figure 2, isoosmabenzene **2** was formed preferentially in the beginning, and transformed gradually (at a slower rate than its formation) into osmabenzyne **3**. After 1 h, the starting material **1** had been consumed, and the reaction solution contained a mixture of **2** and **3**, with **2** as the main component. It took another 7 h for **2** to convert completely into **3**.

Based on these observations, we proposed a mechanism for the formation of **3** from **2** (Scheme 1). The mechanism for the formation of isoosmabenzene **2** is a formal [3+3] cycloaddition that has been discussed previously.[10a] Once **2** has been generated, its ethoxyl group on C3 extracts a proton (presumably from trace amounts of acids in chloroform or from the eliminated ethanol) to form an onium salt **A**, which undergoes ethanol elimination to generate **3′**, a resonance form of **3**.[9a,d,g]

Thus, we reasoned that the addition of an acid would accelerate the conversion from **2** to **3**. Indeed, after the reaction had been carried out at RT for 1 h, the addition of 1 equivalent of HCl caused a fast color change from green to deep blue. The transformation was complete within 15 min (Scheme 1, reaction conditions ii). In contrast, the addition of K_2CO_3 slowed down the conversion, and hence, facilitated the precipitation of **2** (Scheme 1, reaction conditions iii).

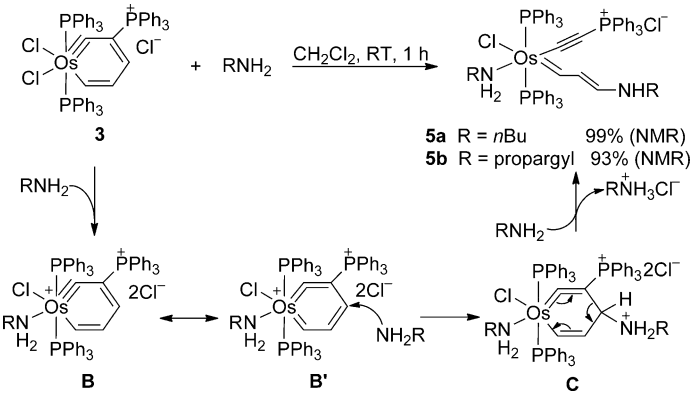
Conversion of osmabenzyne to isoosmabenzene: Osmabenzyne **3** is highly stable, even when heated in air at 120 °C for 5 h in the solid state or at 80 °C for 8 h in solution. This unusual stability is most likely attributable to the steric hindrance and electronic effects induced by the phosphonium group at C2. The same stabilizing effect in isoosmabenzenes has been studied by DFT calculations.[10a] According to theoretical studies, other π-accepting groups (silyl or boryl) at C2 or C4 also stabilize osmabenzynes.[9i] The inertness of **3** is likely for the same reasons. It remains intact in the presence of acids (HOAc, H_3PO_4, HBF_4, and HCl), bases (K_2CO_3 and NaOH), terminal alkynes, and nucleophiles (H_2O, MeOH, and $NaBH_4$).



Scheme 2. Nucleophilic addition of **3**: from metallabenzyne to isometallabenzene.

However, strong nucleophiles, such as ethyllithium (EtLi) or sodium methanethiolate (NaSMe), attack osmabenzyne **3** at C3 to generate isoosmabenzene **4a**[10a] or **4b** (Scheme 2). The addition of approximately 1 equivalent of EtLi to a solution of **3** in THF switched the color from deep blue to brownish red. A red solid was then isolated and identified as our reported isoosmabenzene **4a**.[10a] Excess EtLi decomposed **4a**. The nucleophilic attack by MeS^- gave isoosmabenzene **4b** as the main product, as shown by the presence of characteristic signals for an isoosmabenzene in the ^1H and ^{31}P NMR spectra generated in situ. Nevertheless, **4b** decomposed completely within 4 h at RT. Attempts to isolate **4b** were not successful. It would be interesting if treatment of osmabenzyne **3** with sodium ethoxide (NaOEt) could generate isoosmabenzene **2**, but upon NaOEt addition, **3** remained intact at RT and decomposed at higher temperatures.

Ring opening of osmabenzyne 3: Compared with the nucleophiles used above, amines react differently with osmabenzyne **3**. Primary amines (*n*-butylamine and 2-propargylamine) also attack at C3, but open the metallacycles rather than giving isoosmabenzenes (Scheme 3). Secondary and tertiary amines produced complicated mixtures. The structure of ring-opening product **5a** was inferred by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, and then confirmed by X-ray diffraction, with red crystals grown from the counteranion-exchanged complex **5a′** (BPh_4^- instead of Cl^-; Figure 3). The other product **5b** is less stable than **5a**, and can only be detected by in situ NMR spectroscopy.



Scheme 3. Nucleophilic addition and ring opening of **3**.

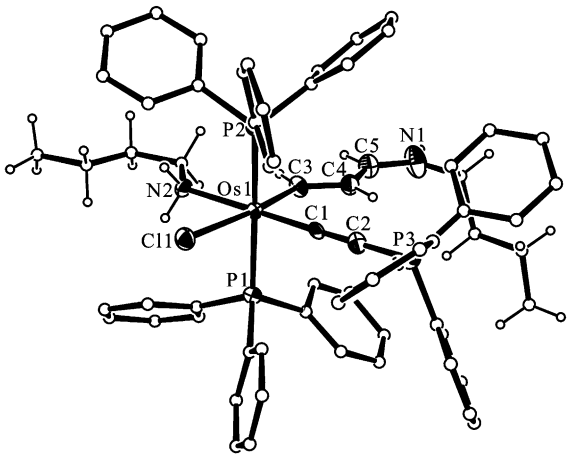
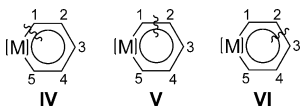


Figure 3. Molecular structure of the cation of **5a′** (ellipsoids shown at the 50% probability level). Some hydrogen atoms are omitted for clarity.

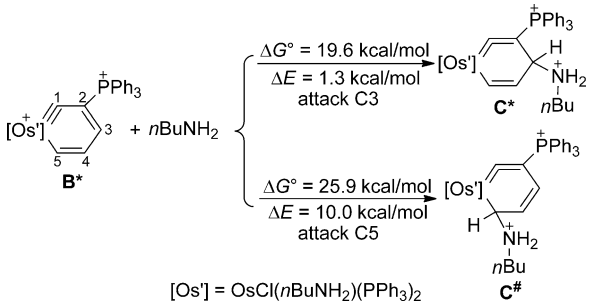
Possible mechanisms for the nucleophilic addition to osmabenzyne **3** are proposed in Schemes 2 and 3. The alternative resonance structure **3′** again bridges the transformation from **3** into **4a** (or **4b**). Carbon or sulfur nucleophiles attack **3′** at C3, producing isoosmabenzene **4a** or **4b** (Scheme 2). Amines take a similar path yet go further (Scheme 3). In the beginning, an amine replaces a chloride ligand to coordinate with the osmium center. The dicationic osmabenzyne **B** is more electrophilic than cationic osmabenzyne **3**. Hence, primary amines (weaker nucleophiles than EtLi and NaSMe) subsequently attack the C3 of **B′** (a resonance form of **B**) to give isoosmabenzene **C**. Besides a phosphonium on C2, **C** carries a quaternary ammonium on C3, which differs from **4a** or **4b**. The neighboring positively charged substituents in **C** weaken the C2–C3 bond, presumably due to decreased overall electron density and increased repulsive forces, thus driving the metallacycle to rearrange and open to give **5a** or **5b**.

Note that intermediate **A** (Scheme 1, structurally similar to **C**) tends to eliminate an ethanol molecule instead of opening the ring, because the cation in **A** carries only one positive charge, and ethanol is easier to lose than an amine. Meanwhile, although the ring opening of six-membered metalla-aromatics through M–C (**IV**, forming a carbene[9h] or cyclopentadienyl[4c,g] complex through carbene migratory insertion) and C1–C2 (**V**, forming a metallacyclopentadiene through ring contraction[4j,k]) bond cleavages has been reported, the transformation from osmabenzyne **3** to **5a** or **5b** represents the first C2–C3 bond cleavage (**VI**).

DFT calculations were carried out to rationalize the highly regioselective nucleophilic attack at C3 in osmaben-



zyne **3**.[15] Dicationic osmabenzyne **B*** is used as the model of the cation of **B** (R = *n*Bu). **C*** and **C**$^{\#}$ are models of cations of two possible intermediates (Scheme 4). The natural population analysis[16] on the full model of **B*** shows differ-



Scheme 4. Gibbs free energies ($\Delta G°$) and electronic energies (ΔE) of the reaction via two possible intermediates **C*** and **C**$^{\#}$.

ent charges on the metallacycle (from C1 to C5: 0.305, −0.610, −0.088, −0.317, and −0.188). This analysis indicates that the order of preferential sites for nucleophilic attack is C1 > C3 > C5, in line with previous studies.[9g,i] Because C1 in osmabenzyne **3** is surrounded by three bulky PPh_3 groups, the resulting steric hindrance would make nucleophilic attack at C1 difficult. Further examination of the contribution to the lowest unoccupied molecular orbital (LUMO, Figure 4) of **B*** from C1 (9.2%), C3 (23.3%), and C5

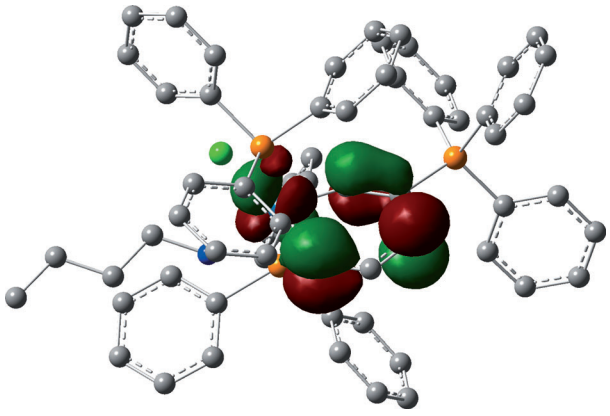


Figure 4. The spatial plot of the LUMO (isovalue = 0.04) of dicationic osmabenzyne **B***. All hydrogen atoms are omitted for clarity.

(19.7%) suggests that the nucleophilic attack at C3 is most favorable. Furthermore, the Gibbs free energy of **C*** is 6.3 kcal mol^{-1} lower than that of **C**$^{\#}$ (Scheme 4). Thus, steric hindrance and electronic effects contribute synergistically to the regioselectivity for nucleophilic attack at C3.

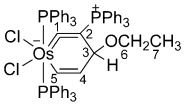
Conclusion

We have applied the formal [3+3] cycloaddition reaction to the preparation of metallabenzynes. The product is unique among metallabenzynes because it is formed via an isometallabenzene precursor, and can undergo regioselective nucleophilic additions to furnish isometallabenzenes. Hence, we have achieved the first formal interconversion of metallabenzyne and isometallabenzene.

Experimental Section

General comments: All manipulations were carried out under an inert atmosphere (Ar or N_2) by means of standard Schlenk techniques. Solvents were distilled from sodium/benzophenone (hexane and diethyl ether) or calcium hydride (dichloromethane, chloroform, and 1,2-dichloroethane) under N_2 prior to use. Methanol was used as received. NMR spectroscopic experiments were carried out on a Bruker 500 MHz spectrometer (^{1}H: 500.2; ^{13}C: 125.8; ^{31}P: 202.5 MHz). High-resolution mass spectra (HRMS) were recorded on a Bruker En Apex Ultra 7.0T FTMS mass spectrometer. Elemental analyses were performed on a Vario EL III elemental analyzer.

Compound 2: HC≡CCH(OEt)$_2$ (31 μL, 0.21 mmol) and K_2CO_3 (97 mg, 0.70 mmol) were added to a solution of [OsH{=C=CH(PPh$_3$)}Cl$_2$(PPh$_3$)$_2$] (**1**; 150 mg, 0.14 mmol) in $CHCl_3$ (15 mL). The mixture was stirred at room temperature (RT) for 1 h to give a green solution. After removing excess K_2CO_3 by filtration, the filtrate was evaporated under vacuum. The residue was washed with hexane (3 × 10 mL) and dried under vacuum to give a 3:1 mixture (estimated by ^{1}H NMR spectroscopy) of **2** and **3** as a light-green solid (129 mg, 60% for **2**). Diagnostic peaks for **2** are as follows: ^{1}H NMR (500 MHz, $CDCl_3$): δ = 8.1 (d, $^3J_{HH}$ = 9.0 Hz, 1H; H5), 5.0 (d, $^3J_{HH}$ = 9.0 Hz, 1H; H4), 3.0 (m, 1H; H6), 2.3 (m, 1H; H6), 1.7 (m, 1H; H3), 0.5 ppm (t, $^3J_{HH}$ = 7.0 Hz, 3H; H7); ^{31}P NMR (202 MHz, $CDCl_3$): δ = 4.4 (s; C*P*Ph$_3$), −4.4 (d, $^2J_{PP}$ = 350.3 Hz; Os*P*Ph$_3$), −7.1 ppm (d, $^2J_{PP}$ = 350.3 Hz; Os*P*Ph$_3$); HRMS (ESI): *m/z* calcd for $C_{61}H_{53}OP_3ClOs$: 1121.2613 $[M-Cl]^+$; found: 1121.2609.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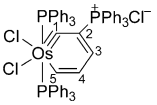
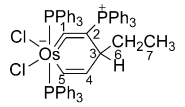
Compound 3:

Method A: HC≡CCH(OEt)$_2$ (52 μL, 0.35 mmol) was added to a mixture of [OsH{=C=CH(PPh$_3$)}Cl$_2$(PPh$_3$)$_2$] (**1**; 320 mg, 0.30 mmol) and Et_4NCl (60 mg, 0.36 mmol) in $CHCl_3$ (15 mL). The mixture was stirred at RT for 8 h or under reflux for 2 h to give a blue-green solution. The solvent was removed under vacuum. The residue was washed with $CHCl_3$ (10 mL), Et_2O (2 × 10 mL), and dried under vacuum to give **3** as a blue solid (290 mg, 85%).


3

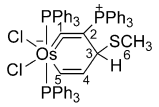
Method B: HC≡CCH(OEt)$_2$ (54 μL, 0.37 mmol) was added to a solution of [OsH{=C=CH(PPh$_3$)}Cl$_2$(PPh$_3$)$_2$] (**1**; 330 mg, 0.31 mmol) in $CHCl_3$ (15 mL). The mixture was stirred at RT for 1 h to give a green solution. The addition of concentrated HCl (14 μL, 0.45 mmol) changed the color from green to deep blue. After stirring for a further 15 min, the solvent was removed under vacuum. The residue was washed with $CHCl_3$ (10 mL), Et_2O (2 × 10 mL), and dried under vacuum to give **3** as a blue solid (310 mg, 88%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ = 13.9 (d, $^3J_{HH}$ = 7.5 Hz, 1H; H5), 7.9–6.9 (m, 46H; PPh$_3$ and H3), 6.6 ppm (t, $^3J_{HH}$ = 7.5 Hz, 1H; H4); ^{31}P NMR (202 MHz, CD_2Cl_2): δ = 14.7 (s; C*P*Ph$_3$), −4.4 ppm (s; Os*P*Ph$_3$); ^{13}C NMR plus HSQC (126 MHz, CD_2Cl_2): δ = 287.9 (m; C1), 246.7 (br; C5), 159.0 (d, $^2J_{PC}$ = 8.8 Hz; C3), 135.0–127.2 (m; PPh$_3$), 125.0 (d, $^3J_{PC}$ = 7.8 Hz; C4), 94.7 ppm (d, $^1J_{PC}$ = 110.7 Hz; C2); HRMS (ESI): *m/z* calcd for $C_{59}H_{48}P_3Cl_2Os$: 1111.1961 $[M]^+$; found: 1111.1956; elemental analysis calcd (%) for $C_{59}H_{48}P_3Cl_3Os$: C 61.81, H 4.22; found: C 61.41, H 4.46.

Compound 4a: A solution of **3** (120 mg, 0.10 mmol) in THF (7 mL) was cooled to −10 °C. EtLi (0.5 M in benzene and cyclohexane, 240 μL, 0.12 mmol) was added slowly, and the mixture was allowed to warm to RT and stirred for another 30 min, giving a brownish-red solution. The sol-


4a

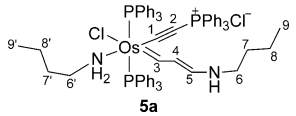
vent was removed under vacuum. The residue was washed with Et_2O (3× 10 mL), and dried under vacuum to give **4a** as a red solid (81 mg, 68%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=8.0 (d, $^3J_{HH}$=9.5 Hz, 1H; H5), 7.8–6.8 (m, 45H; PPh_3), 4.9 (m, 1H; H4), 3.8 (m, 1H; H3), 0.7 (m, 1H; H6), 0.4 (m, 1H; H6), 0.3 ppm (m, 3H; H7); ^{31}P NMR (202 MHz, $CDCl_3$): δ=2.2 (s; C*P*Ph_3), −3.0 (d, $^2J_{PP}$=362.5 Hz; Os*P*Ph_3), −6.9 ppm (d, $^2J_{PP}$= 362.5 Hz; Os*P*Ph_3); HRMS (ESI): *m/z* calcd for $C_{61}H_{53}P_3ClOs$: 1105.2663 $[M-Cl]^+$; found: 1105.2665.

Compound 4b: In an NMR tube, compound **3** (13 mg, 0.01 mmol) and NaSMe (6.4 mg, 0.09 mmol) were mixed in CD_2Cl_2 (0.4 mL). A brown-red solution was obtained after 30 min at RT. The NMR spectra were then collected (NMR yield: 80%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ=7.8 (t, $^3J_{PH}$=7.5 Hz, 1H; H5), 4.7 (br, 1H; H4), 4.6 (m, 1H; H3), 1.5 ppm (s, 3H; H6); ^{31}P NMR (202 MHz, CD_2Cl_2): δ=4.6 (s; C*P*Ph_3), −5.2 (d, $^2J_{PP}$=364.5 Hz; Os*P*Ph_3), −7.6 ppm (d, $^2J_{PP}$=364.5 Hz; Os*P*Ph_3).



4b

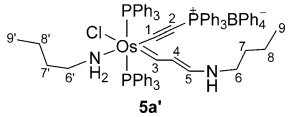
Compound 5a: nBuNH$_2$ (98 μL, 1.1 mmol) was added to a solution of **3** (240 mg, 0.21 mmol) in CH_2Cl_2 (13 mL). The reaction mixture was stirred



5a

at RT for 1 h to give a red solution (NMR yield: 99%). The solution was concentrated to approximately 2 mL, and passed through a syringe filter into a mixed hexane/Et_2O solution (40 mL, 3:1 v/v). The precipitate was collected, washed with Et_2O (3×10 mL) and dried under vacuum to give **5a** as a red solid (216 mg, 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=13.5 (d, $^3J_{HH}$=13.0 Hz, 1H; H3), 9.5 (br, 1H; OsCHCHCHN*H*), 7.9–6.8 (m, 45H; PPh_3), 5.8 (t, $^3J_{HH}$=13.0 Hz, 1H; H4), 3.5 (m, 1H; H5), 2.4 (br, 2H; H6), 2.2 (m, 2H; N$H_2$$CH_2CH_2CH_2CH_3$), 1.9 (m, 2H; H6′), 1.0–0.3 ppm (m, 14H; H7, H8, H9, H7′, H8′ and H9′); ^{31}P NMR (202 MHz, $CDCl_3$): δ=5.7 (s; C*P*Ph_3), −26.8 ppm (s; Os*P*Ph_3); ^{13}C NMR plus HSQC (126 MHz, $CDCl_3$): δ=235.1 (m; C3), 186.3 (s; C1), 160.6 (br; C4 and C5), 135.0–127.2 (m; PPh_3), 123.4 (d, $^1J_{PC}$=92.0 Hz; C2), 43.8 (s; C6), 43.0 (s; C6′), 34.6 (s; C7), 30.1 (s; C7′), 20.1 (s; C8), 19.5 (s; C8′), 13.6 (s; C9), 13.5 ppm (s; C9′); elemental analysis calcd (%) for $C_{67}H_{69}N_2P_3Cl_2Os$: C 64.05, H 5.54, N 2.23; found: C 64.04, H 5.61, N 1.86.

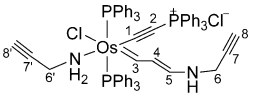
Compound 5a′: nBuNH$_2$ (100 μL, 1.1 mmol) was added to a solution of



5a'

3 (250 mg, 0.22 mmol) in CH_2Cl_2 (13 mL). The mixture was stirred at RT for 1 h to give a red solution. The solution was concentrated, and the residue was washed with Et_2O and then redissolved in CH_3OH (2 mL). $NaBPh_4$ (90 mg, 0.26 mmol) was added to the solution. A red precipitate appeared after stirring for 5 min. The precipitate was filtered, washed with CH_3OH (2×2 mL) and Et_2O (2×10 mL), and then dried under vacuum to give **5a′** as a red solid (309 mg, 92%). ^{1}H NMR (500 MHz, $CDCl_3$): δ=13.6 (d, $^3J_{HH}$=12.5 Hz, 1H; H3), 7.8–6.8 (m, 45H; PPh_3), 5.8 (m, 2H; H4 and H5), 4.3 (m, 1H; OsCHCHCHN*H*), 2.3 (m, 2H; H6), 2.0 (m, 2H; N$H_2$$CH_2CH_2CH_2CH_3$), 1.8 (m, 2H; H6′), 0.8–0.3 ppm (m, 14H; H7, H8, H9, H7′, H8′ and H9′); ^{31}P NMR (202 MHz, $CDCl_3$): δ= 4.9 (s; C*P*Ph_3), −26.6 ppm (s; Os*P*Ph_3); ^{13}C NMR plus HSQC (126 MHz, $CDCl_3$): δ=240.0 (m; C3), 185.0 (s; C1), 164.1 (m; BPh_4), 159.2 (br; 2C, C4 and C5), 122.6 (d, $^1J_{PC}$=91.8 Hz; C2), 136.2–121.8 (m; PPh_3), 43.5 (s; C6), 43.1 (s; C6′), 34.6 (s; C7), 29.7 (s; C7′), 19.7 (s; C8), 19.5 (s; C8′), 13.7 (s; C9), 13.5 ppm (s; C9′); elemental analysis calcd (%) for $C_{91}H_{89}BN_2P_3ClOs$: C 70.97, H 5.82, N 1.82; found: C 71.06, H 5.64, N 1.76.

Compound 5b: In an NMR tube, compound **3** (14 mg, 0.01 mmol) and 2-propargylamine (4 μL, 0.06 mmol) were mixed in CD_2Cl_2 (0.4 mL). A red solution was produced after 1 h at RT. Then, the NMR spectra were collected (NMR yield: 93%). ^{1}H NMR (500 MHz, CD_2Cl_2): δ=13.7 (d, $^3J_{HH}$= 14.0 Hz, 1H; H3), 10.0 (br, 1H; OsCHCHCHN*H*), 6.7 (m, 1H; H5), 6.1 (t, $^3J_{HH}$=14.0 Hz, 1H; H4), 3.2 (br, 2H; N$H_2$$CH_2CCH$), 2.5 (br, 2H; H6), 2.3 (br, 2H; H6′), 1.9 (s, 1H; H8), 1.8 ppm (s, 1H; H8′); ^{31}P NMR (202 MHz, CD_2Cl_2): δ=5.8 (s; C*P*Ph_3, −22.2 ppm (s; Os*P*Ph_3).



5b

X-ray crystallography: All single crystals were mounted on glass fibers and transferred into a cold stream of nitrogen. Diffraction data for **3** were obtained on an Oxford Gemini-S Ultra charge coupled device (CCD) diffractometer at 123(2) K, with graphite-monochromated $Mo_{K\alpha}$ radiation (λ=0.71073 Å). Diffraction data for **5a′** were collected on a Bruker CCD diffractometer at 173(2) K, with monochromated $Mo_{K\alpha}$ radiation (λ=0.71073 Å). Semiempirical or multiscan absorption corrections (SADABS) were applied.[17] Structures were solved by direct methods or the Patterson function, completed by subsequent difference Fourier map calculations, and refined by full matrix least-squares on F^2 with the SHELXTL program package.[18] Nonhydrogen atoms were refined anisotropically unless otherwise stated. Hydrogen atoms were placed at idealized positions and assumed the riding model. Details of crystal data, data collection, and refinements are summarized in Table 1.

For complex **3**, crystals suitable for X-ray diffraction were grown from a solution in $ClCH_2CH_2Cl$ layered with hexane. One chlorine atom of a

Table 1. Crystal data and structure refinement for **3** and **5a′**.

	3·2 $C_2H_4Cl_2$·2 H_2O	**5a′**·0.5 $C_2H_4Cl_2$·0.5 H_2O
formula	$C_{59}H_{48}Cl_3OsP_3$·2 $C_2H_4Cl_2$·2 H_2O	$C_{91}H_{89}BClN_2OsP_3$·0.5 $C_2H_4Cl_2$·0.5 H_2O
M_r	1380.37	1598.50
crystal system	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a [Å]	11.3929(3)	12.052(2)
b [Å]	14.1341(4)	16.299(3)
c [Å]	19.6739(5)	23.550(4)
α [°]	104.123(2)	109.731(3)
β [°]	94.344(2)	94.807(4)
γ [°]	92.607(2)	104.913(3)
V [Å^3]	3056.76(14)	4133.0(12)
Z	2	2
ρ_{calcd} [gcm^{-3}]	1.500	1.284
μ [mm^{-1}]	2.513	1.711
F (000)	1388	1644
θ range [°]	2.84 to 25.00	1.36 to 25.00
reflns collected	25077	21194
independent reflns	10747	14337
observed reflns [$I \geq 2\sigma(I)$]	9504	12068
data/restrains/params	10747/12/713	14337/30/937
GOF on F^2	1.000	1.006
R_1/wR_2 [$I \geq 2\sigma(I)$]	0.0493/0.1104	0.0629/0.1615
R_1/wR_2 (all data)	0.0589/0.1143	0.0748/0.1672
largest peak/hole [e Å^{-3}]	1.881/−1.292	1.604/−1.236

$ClCH_2CH_2Cl$ solvent molecule was disordered and refined with partial occupancy factors. Two water solvent molecules were refined with isotropic thermal parameters.

For complex **5a′**, crystals suitable for X-ray diffraction were grown from a solution in $ClCH_2CH_2Cl$ layered with hexane. The solvent water molecule and carbon atoms of the solvent $ClCH_2CH_2Cl$ were refined with isotropic thermal parameters.

CCDC-857968 (**3**) and CCDC-857969 (**5a′**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Computational details: All of the structures were optimized at the B3LYP level of density functional theory.[19] Frequency calculations were also performed to confirm the characteristics of the calculated structures as minima or transition states. In B3LYP calculations, the effective core potentials (ECPs) of Hay and Wadt with a double-ζ valence basis set (LanL2DZ) were used to describe Os, P, and Cl atoms, and the standard 6–31G(d) basis set was used for C, N, and H.[20] Polarization functions were added for Os ($\zeta(f)=0.886$), Cl ($\zeta(d)=0.514$), and P ($\zeta(d)=0.34$).[21] To study the solvation effects, all structures were optimized by the IEF-PCM model (radii = UAKS) with dichloromethane as the solvent.[22] All calculations were performed with the Gaussian 03 software package.[23]

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[1] a) J. R. Bleeke, *Acc. Chem. Res.* **2007**, *40*, 1035; b) G. Jia, *Coord. Chem. Rev.* **2007**, *251*, 2167; c) G. Jia, *Acc. Chem. Res.* **2004**, *37*, 479.

[2] a) C. W. Landorf, M. M. Haley, *Angew. Chem.* **2006**, *118*, 4018; *Angew. Chem. Int. Ed.* **2006**, *45*, 3914; b) L. J. Wright, *Dalton Trans.* **2006**, 1821; c) G. He, H. Xia, G. Jia, *Chin. Sci. Bull.* **2004**, *49*, 1543; d) J. R. Bleeke, *Chem. Rev.* **2001**, *101*, 1205.

[3] For recent examples of osmabenzenes, see: a) L. Gong, Z. Chen, Y. Lin, X. He, T. B. Wen, X. Xu, H. Xia, *Chem. Eur. J.* **2009**, *15*, 6258; b) L. Gong, Y. Lin, T. B. Wen, H. Zhang, B. Zeng, H. Xia, *Organometallics* **2008**, *27*, 2584; c) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2006**, *25*, 1771; d) H. Xia, G. He, H. Zhang, T. B. Wen, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2004**, *126*, 6862.

[4] For recent examples of iridabenzenes, see: a) A. F. Dalebrook, L. J. Wright, *Organometallics* **2009**, *28*, 5536; b) M. Paneque, M. L. Poveda, N. Rendón, E. Álvarez, E. Carmona, *Eur. J. Inorg. Chem.* **2007**, 2711; c) H. P. Wu, D. H. Ess, S. Lanza, T. J. R. Weakley, K. N. Houk, K. K. Baldridge, M. M. Haley, *Organometallics* **2007**, *26*, 3957; d) G. R. Clark, G. L. Lu, W. R. Roper, L. J. Wright, *Organometallics* **2007**, *26*, 2167; e) E. Álvarez, M. Paneque, M. L. Poveda, N. Rendón, *Angew. Chem.* **2006**, *118*, 488; *Angew. Chem. Int. Ed.* **2006**, *45*, 474; f) K. Ilg, M. Paneque, M. L. Poveda, N. Rendón, L. L. Santos, E. Camona, K. Mereiter, *Organometallics* **2006**, *25*, 2230; g) H. P. Wu, T. J. R. Weakley, M. M. Haley, *Chem. Eur. J.* **2005**, *11*, 1191; h) C. S. Chin, H. Lee, M. S. Eum, *Organometallics* **2005**, *24*, 4849; i) C. S. Chin, H. Lee, *Chem. Eur. J.* **2004**, *10*, 4518; j) J. R. Bleeke, R. Behm, *J. Am. Chem. Soc.* **1997**, *119*, 8503; k) J. R. Bleeke, R. Behm, Y. F. Xie, M. Y. Chiang, K. D. Robinson, A. M. Beatty, *Organometallics* **1997**, *16*, 606.

[5] For recent examples of other metallabenzenes, see: rhenabenzene: a) K. C. Poon, L. Liu, T. Guo, J. Li, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2010**, *122*, 2819; *Angew. Chem. Int. Ed.* **2010**, *49*, 2759; platinabenzenes: b) V. Jacob, C. W. Landorf, L. N. Zakharov, T. J. R. Weakley, M. M. Haley, *Organometallics* **2009**, *28*, 5183; c) C. W. Landorf, V. Jacob, T. J. R. Weakley, M. M. Haley, *Organometallics* **2004**, *23*, 1174; d) V. Jacob, T. J. R. Weakley, M. M. Haley, *Angew. Chem.* **2002**, *114*, 3620; *Angew. Chem. Int. Ed.* **2002**, *41*, 3470; ruthebenzene: e) H. Zhang, H. Xia, G. He, T. B. Wen, L. Gong, G. Jia, *Angew. Chem.* **2006**, *118*, 2986; *Angew. Chem. Int. Ed.* **2006**, *45*, 2920; f) J. Yang, W. M. Jones, J. K. Dixon, N. T. Allison, *J. Am. Chem. Soc.* **1995**, *117*, 9776.

[6] For electrophilic aromatic substitution reactions of metallabenzenes, see: a) G. R. Clark, P. M. Johns, W. R. Roper, L. J. Wright, *Organometallics* **2008**, *27*, 451; b) C. E. F. Rickard, W. R. Roper, S. D. Woodgate, L. J. Wright, *Angew. Chem.* **2000**, *112*, 766; *Angew. Chem. Int. Ed.* **2000**, *39*, 750.

[7] For nucleophilic aromatic substitution reactions of metallabenzenes, see: a) R. Lin, H. Zhang, S. Li, J. Wang, H. Xia, *Chem. Eur. J.* **2011**, *17*, 4223; b) G. R. Clark, L. A. Ferguson, A. E. McIntosh, T. Söhnel, L. J. Wright, *J. Am. Chem. Soc.* **2010**, *132*, 13443; c) T. Wang, S. Li, H. Zhang, R. Lin, F. Han, Y. Lin, T. B. Wen, H. Xia, *Angew. Chem.* **2009**, *121*, 6575; *Angew. Chem. Int. Ed.* **2009**, *48*, 6453.

[8] For nucleophilic addition reactions of metallabenzenes, see: a) H. Zhang, R. Lin, G. Hong, T. Wang, T. B. Wen, H. Xia, *Chem. Eur. J.* **2010**, *16*, 6999; 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; c) M. Paneque, C. M. Posadas, M. L. Poveda, N. Rendón, V. Salazar, E. Oñate, K. Mereiter, *J. Am. Chem. Soc.* **2003**, *125*, 9898.

[9] For preparation of metallabenzynes, see: a) J. Chen, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2011**, *123*, 10863; *Angew. Chem. Int. Ed.* **2011**, *50*, 10675; b) G. He, J. Zhu, W. Y. Hung, T. B. Wen, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2007**, *119*, 9223; *Angew. Chem. Int. Ed.* **2007**, *46*, 9065; c) T. B. Wen, W. Y. Hung, H. H. Y. Sung, I. D. Williams, G. Jia, *J. Am. Chem. Soc.* **2005**, *127*, 2856; d) T. B. Wen, Z. Y. Zhou, G. Jia, *Angew. Chem.* **2001**, *113*, 2005; *Angew. Chem. Int. Ed.* **2001**, *40*, 1951; for electrophilic substitution reactions of metallabenzynes, see: e) 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; f) 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; for nucleophilic addition reactions of metallabenzynes, see: g) W. Y. Hung, J. Zhu, T. B. Wen, K. P. Yu, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *J. Am. Chem. Soc.* **2006**, *128*, 13742; for the conversion of metallabenzynes into carbene complexes, see: h) J. Chen, C. Shi, H. H. Y. Sung, I. D. Williams, Z. Lin, G. Jia, *Angew. Chem.* **2011**, *123*, 7433; *Angew. Chem. Int. Ed.* **2011**, *50*, 7295; for theoretical studies, see: i) S. M. Ng, X. Huang, T. B. Wen, G. Jia, Z. Lin, *Organometallics* **2003**, *22*, 3898; for highlights, see: j) W. R. Roper, *Angew. Chem.* **2001**, *113*, 2506; *Angew. Chem. Int. Ed.* **2001**, *40*, 2440.

[10] a) Q. Zhao, L. Gong, C. Xu, J. Zhu, X. He, H. Xia, *Angew. Chem.* **2011**, *123*, 1390; *Angew. Chem. Int. Ed.* **2011**, *50*, 1354; b) P. Barrio, M. A. Esteruelas, E. Oñate, *J. Am. Chem. Soc.* **2004**, *126*, 1946.

[11] For recent reviews of benzynes, see: a) K. J. Cahill, A. Ajaz, R. P. Johnson, *Aust. J. Chem.* **2010**, *63*, 1007; b) H. H. Wenk, M. Winkler, W. Sander, *Angew. Chem.* **2003**, *115*, 518; *Angew. Chem. Int. Ed.* **2003**, *42*, 502; c) W. Sander, *Acc. Chem. Res.* **1999**, *32*, 669.

[12] For examples of benzynes, see: a) W. Sander, M. Exner, M. Winkler, A. Balster, A. Hjerpe, E. Kraka, D. Cremer, *J. Am. Chem. Soc.* **2002**, *124*, 13072; b) H. H. Wenk, A. Balster, W. Sander, D. A. Hrovat, W. T. Borden, *Angew. Chem.* **2001**, *113*, 2356; *Angew. Chem. Int. Ed.* **2001**, *40*, 2295; c) R. Marquardt, A. Balster, W. Sander, E. Kraka, D. Cremer, J. G. Radziszewski, *Angew. Chem.* **1998**, *110*, 1001; *Angew. Chem. Int. Ed.* **1998**, *37*, 955; d) A. Z. Bradley, R. P. Johnson, *J. Am. Chem. Soc.* **1997**, *119*, 9917.

[13] For examples of isobenzenes, see: a) A. Ajaz, A. Z. Bradley, R. C. Burrell, W. H. H. Li, K. J. Daoust, L. B. Bovee, K. J. DiRico, R. P. Johnson, *J. Org. Chem.* **2011**, *76*, 9320; b) I. D. Mackie, R. P. Johnson, *J. Org. Chem.* **2009**, *74*, 499; c) K. J. Daoust, S. M. Hernandez, K. M. Konrad, I. D. Mackie, J. Winstanley, Jr., R. P. Johnson, *J. Org. Chem.* **2006**, *71*, 5708; d) B. Engels, J. C. Schöneboom, A. F. Münster, S. Groetsch, M. Christl, *J. Am. Chem. Soc.* **2002**, *124*, 287; e) M. Prall, A. Krüger, P. R. Schreiner, H. Hopf, *Chem. Eur. J.* **2001**, *7*,

4386; f) R. C. Burrell, K. J. Daoust, A. Z. Bradley, K. J. DiRico, R. P. Johnson, *J. Am. Chem. Soc.* **1996**, *118*, 4218.
[14] B. Liu, H. Xie, H. Wang, L. Wu, Q. Zhao, J. Chen, T. B. Wen, Z. Cao, H. Xia, *Angew. Chem.* **2009**, *121*, 5569; *Angew. Chem. Int. Ed.* **2009**, *48*, 5461.
[15] See the Supporting Information for details.
[16] A. E. Reed, L. A. Curtiss, F. Weinhold, *Chem. Rev.* **1988**, *88*, 899.
[17] G. M. Sheldrick, *SADABS, Program for Semiempirical Absorption Correction*, University of Göttingen, Göttingen, **1997**.
[18] G. M. Sheldrick, *SHELXTL, Siemens Analytical X-ray Systems*, Madison, Wisconsin.
[19] a) A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648; b) B. Miehlich, A. Savin, H. Stoll, H. Preuss, *Chem. Phys. Lett.* **1989**, *157*, 200; c) C. Lee, W. Yang, R. G. Parr, *Phys. Rev. B* **1988**, *37*, 785.
[20] P. J. Hay, W. R. Wadt, *J. Chem. Phys.* **1985**, *82*, 299.
[21] *Gaussian Basis Sets for Molecular Calculations* (Ed.: S. Huzinaga), Elsevier Science, Amsterdam, **1984**.
[22] a) M. T. Cancès, B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *107*, 3032; b) M. Cossi, V. Barone, B. Mennucci, J. Tomasi, *Chem. Phys. Lett.* **1998**, *286*, 253; c) B. Mennucci, J. Tomasi, *J. Chem. Phys.* **1997**, *106*, 5151; d) M. Cossi, G. Scalmani, N. Rega, V. Barone, *J. Chem. Phys.* **2002**, *117*, 43.
[23] Gaussian 03, Revision E.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez, J. A. Pople, Gaussian, Inc., Wallingford CT, **2004**.

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