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Communication

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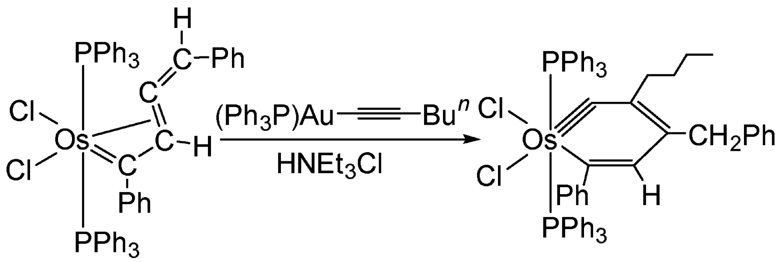

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COMMUNICATIONS

Syntheses of Metallabenzynes from an Allenylcarbene Complex

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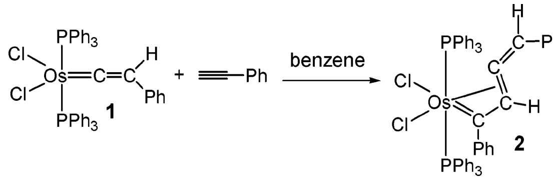
The chemistry of transition metal-containing metallabenzenes[1] has attracted considerable attention both experimentally[2] and theoretically.[3] In contrast, the chemistry of the related compounds, metallabenzynes, is much less developed,[4] partially due to the lack of convenient synthetic routes to construct metallabenzyne rings. The only reported route to construct a metallabenzyne ring is the reaction of $OsCl_2(PPh_3)_3$ with $HC\equiv CSiMe_3$ in wet benzene.[4a] However, extension of the chemistry involving $OsCl_2(PPh_3)_3$ as the starting material to prepare metallabenzynes apparently failed when other alkynes such as $HC\equiv CCMe_3$ and $HC\equiv CCH(OH)Ph_2$ were used.[5] To develop the chemistry of metallabenzynes, it is obviously highly desirable to find alternative and more general routes to prepare metallabenzynes. In this Communication, we disclose a more efficient route to prepare osmabenzynes starting from an allenylcarbene complex.

A metallacyclobutene complex formed from cycloaddition of $HC\equiv CSiMe_3$ with $OsCl_2({=}C{=}CH_2)(PPh_3)_2$ was proposed as one of the key intermediates in the formation of the osmabenzyne complex $Os({\equiv}CC(SiMe_3){=}C(CH_3)C(SiMe_3){=}CH)Cl_2(PPh_3)_2$.[4a] However, the intermediate could not be isolated. We have now isolated the related cycloaddition product from the reaction of the vinylidene complex $OsCl_2({=}C{=}CHPh)(PPh_3)_2$[6] with $HC\equiv CPh$. The X-ray as well as the NMR data suggest that the compound can be best described as an η^3-allenylcarbene complex.

The allenylcarbene complex $OsCl_2({=}CPh\text{-}\eta^2\text{-}CH{=}C{=}CHPh)(PPh_3)_2$ (**2**) was obtained as a green precipitate by treatment of the vinylidene complex $OsCl_2({=}C{=}CHPh)(PPh_3)_2$[6] with $HC\equiv CPh$ in benzene (eq 1). The complex could also be prepared from the one-pot reaction of $OsCl_2(PPh_3)_3$ with $HC\equiv CPh$ in benzene, where **2** is presumably formed from the cycloaddition reaction of $HC\equiv CPh$ with $OsCl_2({=}C{=}CHPh)(PPh_3)_2$ generated in situ. Grubbs et al. have recently reported the related ruthenium η^3-vinylcarbene complex $RuCl_2(\eta^3\text{-}PhC{=}CPhCHPh)(H_2IMes)$ from the reaction of $PhC\equiv CPh$ with $RuCl_2({=}CHPh)(PCy_3)(H_2IMes)$ [H_2IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene].[7]



(1)

Complex **2** has been characterized by elemental analysis, MS, and NMR spectroscopy.[8] The structure of **2** has also been confirmed by an X-ray diffraction study (Figure 1). The most interesting structural feature of **2** is that it contains a bent four-membered metallacycle. The Os−C(4) bond distance of 1.894(9) Å is characteristic of an osmium−carbon double bond and is almost identical to the values found in the osmium carbene complexes such as $OsCl_2({=}CHCH_2Ph)(CO)(P^iPr_3)_2$ (1.887(9) Å)[9a] and $OsCl_2({=}CHPh)(CO)(P^iPr_3)_2$ (1.89(2) Å.[9b] The bond distances of Os−C(2) (2.067(11) Å) and Os−C(3) (2.167(11) Å) are comparable to the values reported for typical Os−C single bonds[10] and are similar to the Os−C(allene) bond distances in $OsCl(C(Me{=}CHPh)(\eta^2\text{-}CH_2{=}C{=}CHPh)(PPh_3)_2$.[11] The C−C bond distances within the metallacycle (C(2)−C(3) = 1.441(15) Å, C(3)−C(4) = 1.437(15) Å) are comparable, indicating the presence of substantial π-electron delocalization. On the basis of the structural data, this complex can be described as an η^3-allenylcarbene complex with contributions from limiting structures such as **2**, **2A** (which most closely resembles the actual structure), and **2B**. The structural features associated with Os, C(2), C(3), and C(4), are similar to those of $RuCl_2(\eta^3\text{-}PhC{=}CPhCHPh)(H_2IMes)$, where the C−C bond distances within the metallacycle are observed at 1.437(6) and 1.409(6) Å.[7]

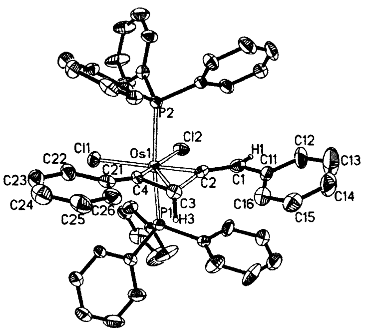
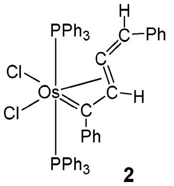
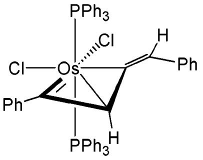


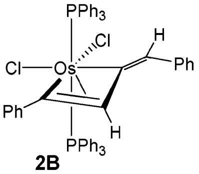
Figure 1. Structure of **2**. Selected bond distances (Å) and angles (°): Os(1)−C(2), 2.067(11); Os(1)−C(3), 2.167(11); Os(1)−C(4), 1.894(9); C(1)−C(2), 1.316(16); C(2)−C(3), 1.441(15); C(3)−C(4), 1.437(15); C(2)−C(3)−C(4), 115.9(10); C(2)−Os(1)−C(4), 75.9(4); C(1)−C(2)−C(3), 139.5(11).



2



2A



2B

The solid-state structure is fully supported by the solution NMR (^{31}P, ^1H, and ^{13}C) spectroscopic data. In particular, the $^{31}P\{^1H\}$ NMR spectrum (in CD_2Cl_2) at 210 K showed two doublets at −8.3 and −32.3 ppm with a $^2J(PP)$ of 329.1 Hz, and the $^{13}C\{^1H\}$ NMR spectrum (in CD_2Cl_2) showed the three Os-bound carbon signals at 249.8 (CPh), 136.6 (C), and 36.1 (CH) ppm. At room temperature, the complex is fluxional, and the $^{31}P\{^1H\}$ NMR spectrum showed two broad singlets at −8.4 and −28.1 ppm.

Formation of allenylcarbene **2** from the reaction of **1** with $HC\equiv CPh$ is interesting, as allenylcarbene complexes have often been proposed as the key intermediates in metal-catalyzed polymerization of terminal alkynes.[12] However, very few such complexes have been previously isolated. [13]

The reactions of **2** with alkynes were carried out to see if osmabenzynes can be obtained. When **2** was treated with $HC\equiv CPh$ in CH_2Cl_2, most of the $HC\equiv CPh$ was polymerized, and a

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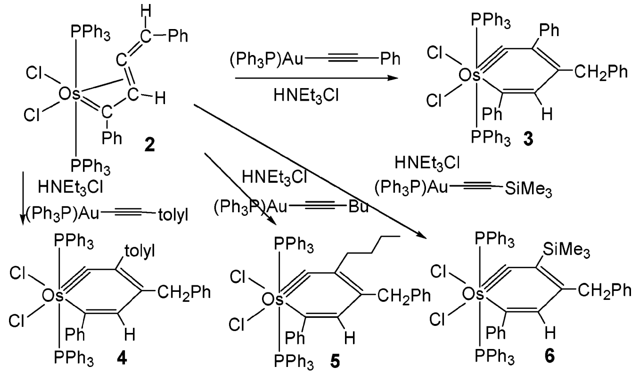
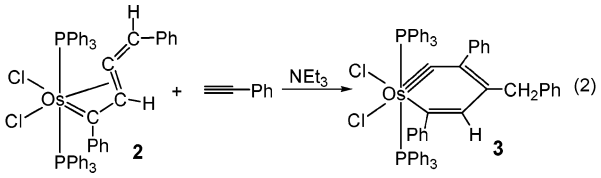
Scheme 1



mixture of phosphorus-containing species was produced. The expected osmabenzyne was produced in only trace amount, if any. Interestingly, when the reaction was performed in the presence of NEt_3, osmabenzyne **3** was produced as the major species detectable by ^{31}P NMR (eq 2), although the reaction is slow and takes a day to go to completion. The reaction also produced oligomers of $HC{\equiv}CPh$ and other unidentified phosphorus-containing species, which can cause difficulty in the isolation of pure samples of **3** from the reaction mixture. Our attempts to obtain osmabenzynes from the reactions of **2** with other alkynes such as $HC{\equiv}CSiMe_3$ or aliphatic terminal alkynes under similar conditions were unsuccessful.



(2)

The promoting effect of NEt_3 in the production of osmabenzyne **3** from the reaction of **2** with $H{\equiv}CPh$ led us to speculate that **3** may be formed from an acetylide intermediate. To test this hypothesis, we have treated **2** with $(PPh_3)AuC{\equiv}CPh$[14] in the presence of $HNEt_3Cl$. We were pleased to learn that the reaction quickly produced the expected **3** (Scheme 1). In the absence of $HNEt_3Cl$, the reaction also produced **3**, but the rate was slow and other unidentified species were also formed, as one might expect.

The chemistry can be extended to prepare new osmabenzynes using other gold(I) acetylide derivatives. Thus, treatment of **2** with $(PPh_3)AuC{\equiv}C$-tolyl produced the tolyl-containing osmabenzyne **4**, treatment with $(PPh_3)AuC{\equiv}C$-*n*-Bu produced the *n*-Bu-containing osmabenzyne **5**, and treatment with $(PPh_3)AuC{\equiv}CSiMe_3$ produced the $SiMe_3$-containing osmabenzyne **6**. Most of the reactions are completed in less than 3 h. It is noted that the reported preparation of the osmabenzyne complex $Os({\equiv}CC(SiMe_3){=}C(CH_3)C(SiMe_3){=}CH)Cl_2(PPh_3)_2$ from the reaction of $OsCl_2(PPh_3)_3$ with $HC{\equiv}CSiMe_3$ takes 5 days.

All the new osmabenzynes have been characterized by elemental analysis, MS, and NMR spectroscopy.[8] The structures of **3**−**5** have been confirmed by X-ray diffraction.[8] The structural features of the metallacycles are very similar to those of reported ones.[4] The NMR (^{31}P, ^{1}H, and ^{13}C) spectroscopic data are fully consistent with the solid-state structures.

The detailed mechanism for the formation of **3**−**6** in the reactions of **2** with $(PPh_3)AuC{\equiv}CR$ in the presence of $HNEt_3Cl$ is not very clear yet. It is possible that reactions of **2** with $(PPh_3)AuC{\equiv}CR$ may initially produce the acetylide complexes $OsCl(C{\equiv}CR)({=}CPh\text{-}\eta^2\text{-}CH{=}C{=}CHPh)(PPh_3)_2$ or allenylcarbene osmium complexes with a coordinated gold acetylide, which react with $HNEt_3Cl$ to give osmabenzynes. Apparently, the γ-carbon of the allenylcarbene ligand attacked at the β-carbon atom of the acetylide ligands in the cyclization reaction. At this stage, we are not sure whether the intramolecular cyclization reactions proceed before or after the protonation of the terminal CHPh group. Alkynyl transfer from gold to rhenium has been reported recently.[15] Intramolecular coupling of alkenylcarbene and acetylide ligands has been proposed for the formation of a novel osmium isometallabenzene.[2b]

In summary, we have developed a more efficient synthetic route to prepare osmabenzynes starting from an allenylcarbene complex. The new method allows us to obtain metallabenzynes with various substituents in short reaction time under mild reaction conditions. Extension of the chemistry to prepare metallabenzynes with other metals and substituents is in progress.

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Supporting Information Available: Experimental procedures and characterization data (PDF); X-ray crystallographic files (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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