Syntheses of Metallabenzynes from an Allenylcarbene Complex

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The chemistry of transition metal-containing metallabenzynes has attracted considerable attention both experimentally and theoretically. In contrast, the chemistry of the related compounds, metallallabenzenes, is much less developed, 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=CCSiMe$_3$ in wet benzene. 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=CCMe$_3$ and HC=CH(OMe)Ph$_2$ were used. 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=CCSiMe$_3$ 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(≡C=CH$_2$)(C≡CC(SiMe$_3$)=CH)$_2$Cl(PPh$_3$)$_3$. 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$_3$)$_2$ with HC=CCPh. The X-ray as well as the NMR data suggest that the compound can be best described as an η$_1$-allenylcarbene complex.

The allenylcarbene complex OsCl$_2$(≡CPh-η$_1$-CH=CH≡C=CHPh)(PPh$_3$)$_2$ (2) was obtained as a green precipitate by treatment of the vinylidene complex OsCl$_2$(≡C=CHPh)(PPh$_3$)$_2$ with HC=CCPh in benzene (eq 1). The complex could also be prepared from the one-pot reaction of OsCl$_2$(PPh$_3$)$_3$ with HC=CCPh in benzene, where 2 is presumably formed from the cycloaddition reaction of HC=CCPh with OsCl$_2$(≡C=CHPh)(PPh$_3$)$_2$ generated in situ. Grubbs et al. have recently reported the related ruthenium η$_1$-vinylcarbene complex RuCl$_2$(η$_1$-PhC≡CPh)(H$_2$IMes) from the reaction of PhC≡CPh with RuCl$_2$(η$_1$=CPh)(PCy$_3$)(H$_2$IMes) [H$_2$IMes = 1,3-dimesityl-4,5-dihydroimidazol-2-ylidene].

Complex 2 has been characterized by elemental analysis, MS, and NMR spectroscopy. 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$_2$Ph)(CO)(P$_3$Pr$_2$$_2$) (1.887(9) Å) and OsCl$_2$(≡CHPh)(CO)(P$_3$Pr$_2$$_2$) (1.892(3) Å). The bond distances of Os−C(2) (2.067(11) Å) and Os−C(3) (2.167(11) Å) are comparable to the values reported for typical Os−C single bonds and are similar to the Os−C(allene) bond distances in OsCl(C(3)≡CHPh)(η$_2$-C$_2$H$_4$≡C≡CHPh)(PPh$_3$)$_2$. The C−C bond distances within the metallacycle (C(2)−C(3) = 1.441(15) Å, C(3)−C(4) = 1.437(15) Å) are comparable, indicating the presence of substantial π-electron delocalization. On the basis of the structural data, this complex can be described as an η$_1$-allenylcarbene complex with contributions from limiting structures such as 2, 2A (which most closely resembles the actual structure), and 2B. The structural features associated with Os, C(2), C(3), and C(4), are similar to those of RuCl$_2$(η$_1$-PhC≡CPh)(H$_2$IMes), where the C−C bond distances within the metallacycle are observed at 1.437(6) and 1.409(6) Å.

The solid-state structure is fully supported by the solution NMR (31P, 1H, and 13C) spectroscopic data. In particular, the 31P{1H} NMR spectrum (in CD$_2$Cl$_2$) at 210 K showed two doublets at −8.3 and −32.3 ppm with a 2J(PP) of 329.1 Hz, and the 13C{1H} NMR spectrum (in CD$_2$Cl$_2$) 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 31P{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=CCPh is interesting, as allenylcarbene complexes have often been proposed as the key intermediates in metal-catalyzed polymerization of terminal alkynes. However, very few such complexes have been previously isolated. The reactions of 2 with alkynes were carried out to see if osmabenzenes can be obtained. When 2 was treated with HC=CCPh in CH$_2$Cl$_2$, most of the HC=CCPh was polymerized, and a...
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 NEt₃, osmabenzyne 3 was produced as the major species detectable by ³¹P NMR (eq 2), although the reaction is slow and takes a day to go to completion. The reaction also produced oligomers of HC=CHPh 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 osmabenzyne from the reactions of 2 with other alkynes such as HC≡CSiMe₃ or aliphatic terminal alkynes under similar conditions were unsuccessful.

The promoting effect of NEt₃ in the production of osmabenzyne 3 from the reaction of 2 with H≡CPh led us to speculate that 3 may be formed from an acetylide intermediate. To test this hypothesis, we have treated 2 with (PPh₃)AuC≡CPh in the presence of HNEt₃Cl. We were pleased to learn that the reaction quickly produced the expected 3 (Scheme 1). In the absence of HNEt₃Cl, 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 osmabenzyynes using other gold(I) acetylide derivatives. Thus, treatment of 3 with HNEt₃Cl, the reaction also produced oligomers of HC≡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 osmabenzyne from the reactions of 2 with other alkynes such as HC≡CSiMe₃ or aliphatic terminal alkynes under similar conditions were unsuccessful.

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