Detection of a Ruthenabenzene, Ruthenaphenoxide, and Ruthenaphenanthrene Oxide: The First Metalla Aromatics of a Second-Row Transition Metal

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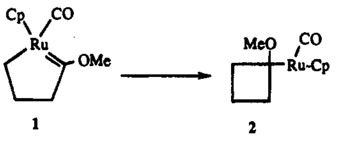
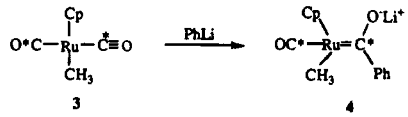
Although theory predicts[1] potential aromaticity and therefore unusual stability for some transition metal metallabenzenes, most examples of such heteroaromatics have simply been inferred from reaction products;[2] to date the only recorded examples of stable transition metal heteroaromatics not stabilized by coordination of the π-system to another metal[3] are limited to two third-row metals, osmium[4] and iridium.[5,6]

We have been interested for some time in the carbene migratory insertion reaction, a reaction which is probably responsible for the decomposition of unstable transition metal heteroaromatics. In the course of our work, we have found that the ruthenium alkyl substituted carbene complex **1** undergoes migratory insertion to **2** at least 10^7 times slower than its iron analogue.[8]

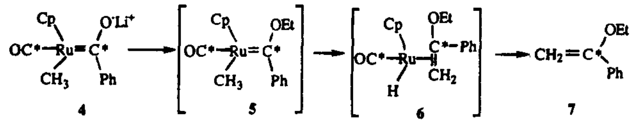


This suggested the possibility that a 2-alkoxy-substituted ruthenabenzene might be stable enough for observation and possible isolation. At this time we report evidence for formation of a 2-ethoxy-substituted ruthenabenzene **15**, a molecule which, although unstable above −30 °C, is significantly more stable to decomposition by migratory insertion than either its acyclic analogue **5** or the ruthenaphenanthrene **10**. We also report observation of the progenitors to **15** and **10**, ruthenaphenoxide **14** and ruthenaphenanthrene oxide **9**.

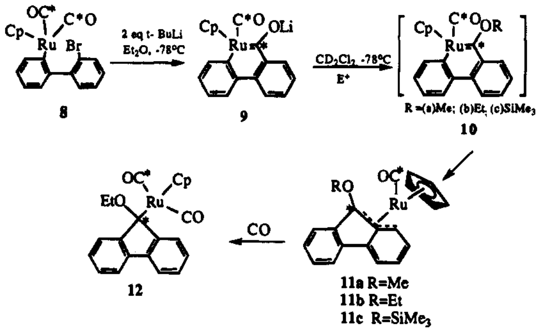
Scheme 1



Scheme 2



Scheme 3



As the precursor to a model carbene complex, lithium enolate **4**[9] (enriched with ^{13}C to enhance the carbene NMR signal) was prepared as shown in Scheme 1. At −90 °C this enolate showed five broad but distinct ^{13}C resonances between δ 291 and 296 [in the same region as the carbene complex **1** (δ 325 ppm) and its benzannelated analogue (δ 294 ppm)].[8] These different resonances, which are believed to arise from lithium aggregates, will be discussed in more detail in the full paper. The enolate, which was stable to 0 °C, was treated with $Et_3O^+BF_4^-$ at −78 °C in CD_2Cl_2 and the subsequent reaction monitored with both ^1H and ^{13}C NMR. Alkylation proceeded at a reasonable rate at −40 °C (half-life of about 2 h) with concomitant formation of the metal hydride **6**. During the alkylation, we could find no evidence of new resonances that could be assigned to the alkoxy-substituted carbene complex **5** (Scheme 2). Upon further warming, **6** slowly decomposed to the free vinyl ether **7**. By addition of 12-crown-4, complex **4** could be alkylated below −70 °C, but again, no transients were detected; only **6** was observed.

If the ring containing ruthenium in ruthenaphenanthrene **10** has significant aromatic character, its migratory insertion should be retarded. The ^{13}C-enriched ruthenaphenanthrene oxide **9** (stable to 0 °C) was therefore prepared as shown in Scheme 3. As in **4**, the ^{13}C resonance of the "carbene" carbon of the metallaenolate (**9**)[9] appeared as a multiplet centered at about δ 292 ppm. The metallaenolate **9** was treated with $Et_3O^+BF_4^-$ at −78 °C, and the reaction mixture was warmed and monitored with ^1H and ^{13}C NMR. In a very clean reaction, alkylation occurred at about −50 °C, but again, we could find no evidence for a carbene−metallacyclic intermediate; only the rearranged π-benzyl complex **11b** was observed. The structure of **11b** was confirmed by comparison with **11a**[11] and by trapping with CO

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[1] Thorn, D. L.; Hoffmann, R. *Nouv. J. de Chimie.* **1979**, *3*, 39.

[2] (a) Ferede, R.; Allison, N. T. *Organometallics* **1983**, *2*, 463. (b) Ferede, R.; Hinton, J. F.; Korfmacher, W. A.; Freeman, J. P.; Allison, N. T. *Organometallics* **1985**, *4*, 614. (c) Mike, C. A.; Ferede, R.; Allison, N. T. *Organometallics* **1988**, *7*, 1457. (d) Cantrell, R. D.; Shevlin, P. B. *J. Am. Chem. Soc.* **1989**, *111*, 2348.

[3] (a) Kralik, M. S; Rheingold, A. L.; Ernst, R. D. *Organometallics* **1987**, *6*, 2612. (b) Lin, W.; Wilson, S. R.; Girolami, G. S. *J. Chem. Soc., Chem. Commun.* **1993**, 284. (c) Bosch, H. W.; Hund, H. U.; Nietlispach, D.; Salzer, A. *Organometallics* **1992**, *11*, 2087.

[4] Elliott, G. P.; Roper, W. R.; Waters, J. M. *J. Chem. Soc., Chem. Commun.* **1982**, 811.

[5] (a) Bleeke, J. R.; Peng, W. J.; Xie, Y. F.; Chiang, M. Y. *Organometallics* **1990**, *9*, 1113. (b) Bleeke, J. R.; Xie, Y. F.; Bass, L.; Chiang, M. Y. *J. Am. Chem. Soc.* **1991**, *113*, 4703. (c) Bleeke, J. R. *Acc. Chem. Res.* **1991**, *24*, 271. (d) Bleeke, J. R.; Bass, L. A.; Xie, Y. F.; Chiang, M. Y. *J. Am. Chem. Soc.* **1992**, *114*, 4213. (e) Bleeke, J. R.; Behm, R.; Xie, Y. F.; Clayton, T. W., Jr.; Robinson, K. D. *J. Am. Chem. Soc.* **1994**, *116*, 4093.

[6] An interesting stable diazatungstabenzene has recently been reported by Templeton.[7]

[7] Feng, S. G.; White, P. S.; Templeton, J. L. *Organometallics* **1993**, *12*, 1765.

[8] (a) Trace, R. L.; Sanchez, J.; Yang, J.; Yin, J. G.; Jones, W. M. *Organometallics* **1992**, *11*, 1440. (b) Yang, J.; Yin, J. G.; Abboud, K. A.; Jones, W. M. *Organometallics* **1994**, *13*, 971.

[9] Complexes **4**, **9**, and **14** are represented in their enolate forms because the ^{13}C chemical shifts of their "carbene" carbons are significantly further downfield than is typical of neutral acyl complexes[10] (the negative charge would normally be expected to cause an upfield shift) and because of the similar chemical shifts of **14** and **15**. However, at this time we know of no way to quantitatively assess the relative importance of enolate and acyl resonance forms in any of these intermediates.

[10] For examples, see: (a) Lisko, J. R.; Jones, W. M. *Organometallics* **1986**, *5*, 1890–1896. (b) Lisko, J. R.; Jones, W. M. *Organometallics* **1985**, *4*, 612–614. (c) Manganiello, F. J.; Oon, S. M.; Radcliffe, M. D.; Jones, W. M. *Organometallics* **1985**, *4*, 1069–1072.

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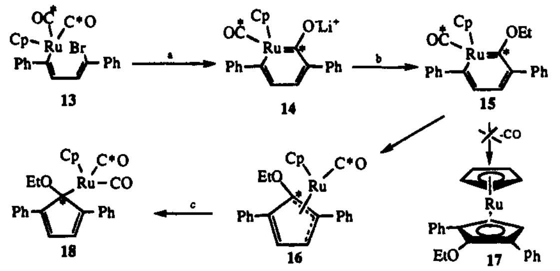
Scheme 4[a]



[a] (a) 2 eq of *t*-BuLi, −78 °C; (b) $Et_3O^+BF_4^-$, CD_2Cl_2, −78 °C; (c) CO.

to give **12**, which could be isolated and characterized. In this case, the alkylation temperature could not be lowered by addition of crown ether due to formation of a viscous material that could not be satisfactorily monitored by NMR. However, ruthenaphenanthrene oxide **9** was successfully silylated below −70 °C with trimethylsilyl chloride, although, even at this temperature, rapid rearrangement to the corresponding π-benzyl complex occurred and no transients could be detected. From these results it is clear that combining the strength of the carbon−ruthenium double bond, the stabilizing effect of an alkoxy substituent, and possible aromaticity in the ruthenaphenanthrene is not sufficient to prevent migratory insertion at −50 °C when R = Et or at −70 °C when R = $SiMe_3$, the lowest temperatures at which we were able to effect alkylation or silylation.

It is well-known that aromatic stabilization in benzene is significantly more pronounced than in the central ring of phenanthrene. This suggests the possibility that ruthenabenzene may enjoy similar stabilization compared to ruthenaphenanthrene with concomitant retardation of decomposition by migratory insertion. In order to explore this possibility, the ^{13}C-enriched lithium enolate **14** was prepared as outlined in Scheme 4 by a method similar to that previously described.[2] Similar to **4** and **9**, the intermediate lithium salt **14** is stable to about 0 °C, decomposing to a complex mixture of products, and its "carbene" ^{13}C resonance appeared at δ 293, in this case as a broad singlet.[9,12] However, unlike **4** and **9**, alkylation of **14** with $Et_3O^+BF_4^-$ at low temperature (ca. −70 °C) did not show initial formation of the π-allyl complex **16** or ruthenacene **17** (from loss of an additional CO), but instead, new resonances appeared, including a new sharp peak at δ 291. The resonance at δ 291 is believed to be due to C2 of the ruthenabenzene **15**. As this peak increased in intensity, resonances assigned to the enolate disappeared with a concomitant increase in the intensity of new peaks in the ^{13}C NMR spectrum at δ 201.2 (terminal CO), 152−126 (aromatic and vinyl), 89.01 (Cp), 76.23 (OCH_2), and 12.50 (CH_3). Similarly, in the ^1H NMR spectrum, new resonances appeared at δ 1.50 (ethoxy methyl), 4.56−4.75 (ethoxy methylene), and 5.32 (Cp). Vinyl and phenyl hydrogens appeared as a complex multiplet between δ 7.40 and 7.80. The ruthenabenzene is reasonably stable at −50 °C but cleanly rearranged at −30 °C to the π-allyl complex **16**. This complex was stable to about 0 °C. In the absence of a trapping ligand, **16** decomposed to unidentified products. However, in the presence of added CO, it was cleanly converted to the σ complex **18**, which was stable enough for complete characterization. Conversion of the ruthenabenzene **15** to **16** showed good first-order kinetics at −30 °C with a rate constant of $(3.72 \pm 0.09) \times 10^{-4}\ s^{-1}$.

From these results we conclude that a ruthenabenzene, a ruthenaphenoxide and a ruthenaphenanthrene oxide have been formed and that the ruthenabenzene decomposes by carbene migratory insertion. However, this process is significantly slower in **15** than in either the acyclic complex **5** or the ruthenaphenanthrene **10**. The simplest explanation for this rate retardation is stabilization of the ruthenabenzene by aromaticity. Chemical reactions of **15** and synthesis of other metallabenzenes are under active investigation.

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(11) Complex **9** could not be methylated ($Me_3O^+BF_4^-$) at −50 °C, but unlike **11b**, the rearranged complex **11a** was stable enough for isolation at −20 °C (as a dark red solid) and complete characterization at ambient temperature.

(12) Upon addition of the alkylating agent at −78 °C the broad enolate resonance shifted from δ 293 to 274.0. This shift is presumably due to replacement of the lithium cation by Et_3O^+.