Hydrogen Migration Reactions in the Dimetallic Fused-aromatic Complexes [(azulene)M$_2$H(CO)$_6$]$^+$

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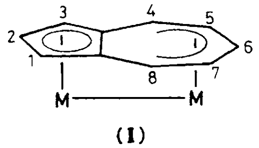
Stereospecific and regiospecific metal–ligand hydrogen migration reactions have been observed for the new complexes [(azul)M$_2$H(CO)$_5$L]$^+$ (azul = azulene or guaiazulene) together with a regiospecific low temperature photochemical substitution reaction of (azul)Mo$_2$(CO)$_6$ to give (azul)Mo$_2$(CO)$_5$L.

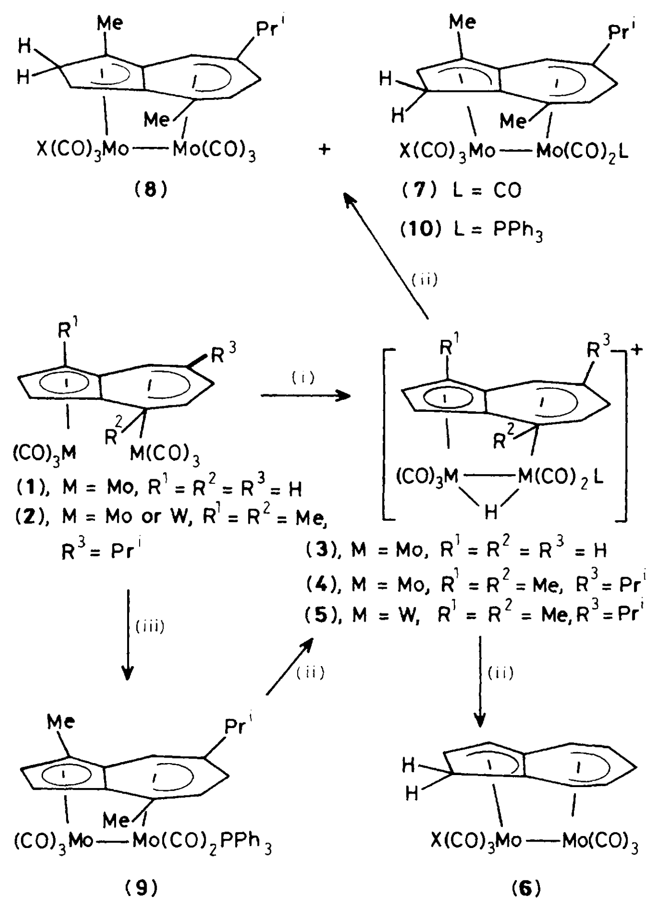
A key step in processes such as the hydrogenation or functionalisation of aromatics or polyaromatics involves metal-to-ligand migration. While migration reactions involving olefinic ligands have been extensively documented,[1] the position for aromatics is much less clear. There are only a few isolated reports of migration reactions involving arene ligands[2] and the position for cyclopentadienyl ligands is comparable.[3] Such migration reactions have been frequently inferred by identification of *endo* addition products.[4] However, in a number of cases where simple migration might be expected, detailed examination of products has revealed that other mechanisms are operative.[5] The strong implication of migration reactions in catalytic processes such as hydrogenation[6] makes the identification of clear examples important. In this paper we report an unexpected hydrogen migration reaction to a fused-aromatic ligand and demonstrate that the reaction is both regiospecific and stereospecific.

Although the unusual dimetallic complexes (I) have been known for a long time,[7] no systematic attempt has been made to study the chemistry of such systems. We are investigating the chemistry of these compounds as part of a study of the chemistry of polymetallic fused-aromatic systems.[8] Complexes containing the azulene ligand are particularly attractive for reactivity studies because the five- and seven-membered rings differentiate the two metals, allowing the regiospecificity of the reactions to be readily determined.

When the complexes (azul)M$_2$(CO)$_6$ (**1**) and (**2**) (azul = azulene or guaiazulene, M = Mo or W) are treated with a



(I)



Scheme 1. X = $CF_3CO_2^-$, L = CO or PPh_3, M = Mo or W. *Reagents and conditions*: (i) CF_3SO_3H, (ii) CF_3CO_2H, (iii) *hv*, PPh_3.

strong acid such as trifluoroacetic acid at low temperature (233 K), the hydrido complexes $[(azul)M_2H(CO)_6]^+$ (**3**)—(**5**) are formed in quantitative yield. (Scheme 1). In the case of tungsten, this product is thermally stable and can be observed at room temperature. The hydride region of the ^1H n.m.r. spectrum of this complex contains a doublet which can be assigned to satellites due to ^{183}W–H coupling and can be interpreted in terms of a hydride bridging two tungsten atoms with the two J_{WH} coupling constants coincidentally the same. A study of the J_{C-H} coupling constants shows that there is no agostic interaction involved in the complexes.

However, with the molybdenum complex, warming leads to hydrogen migration to the 5-membered azulene ring. In the case of $[(azulene)Mo_2H(CO)_6]^+$ a single product (**6**) is observed in which the migration occurs to the 1-position on the five-membered ring. The use of deuteriotrifluoroacetic acid demonstrates that the migration is stereospecific with no evidence for *endo*/*exo* scrambling. Further, the migration is not readily reversed and the added hydrogen is nonexchangeable (using D_2O) strengthening the case that the addition is *endo* with respect to the metal. The reaction is very different from the recently reported $(indenyl)Rh(C_2H_4)_2$ protonation reaction in which competitive *exo*- and *endo*-attack has been proposed.[9] In this case facile hydrogen exchange reactions led to multiple deuteriation, a completely different result from the reactions reported here.

These migration reactions are very like those proposed for the *endo* (with respect to the metal) protonation of $(C_8H_8)Mo(CO)_3$[10] in which the metal hydride was postulated. A cyclohexadienyl complex has also been observed as an intermediate in the more complex series of competitive migration reactions undergone by the molybdenum–arene/ethylene/hydride complex.[2] That the migration should occur for the dimeric complex and not for mononuclear compounds such as $(arene)Mo(CO)_3$ raises new questions about the potential of polymetallic species in the catalytic hydrogenation of aromatics. Not only is the migration regio- and stereospecific, but it is also dependent on the substitution pattern of the azulene ring. When guaiazulene is used in place of azulene, the same reaction is observed, but two isomers (**7**) and (**8**) are formed when the hydrogen migrates to the ring. During a period of hours isomerisation takes place and the single isomer (**7**) remains. A combination of 2-dimensional n.m.r. techniques have allowed the assignment of the structures of (**7**) and (**8**).†

The reaction is also sensitive to the nature of the counter-anion. Thus with trifluoromethanesulphonic acid (containing a less nucleophilic anion) no migration reaction is observed and the hydride complex is present at room temperature. Addition of the more nucleophilic trifluoroacetate anion however drives the migration reaction as previously indicated.

Other reactions of the complexes are also strongly dictated by the rings. Low temperature photolysis of the complex (**2**; M = Mo) at −40 °C in ether in the presence of PPh_3 quantitatively and exclusively substitutes the metal attached to the seven-membered ring to give (**9**). This may be compared with the indiscriminate high temperature thermal substitution reaction of (**2**; M = Mo) which generates low yields of monosubstituted products containing the phosphine on either metal.[11] Protonation of the product (**3**) however still leads to the migration reaction occurring to the five-membered ring complex (**10**).

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† *Spectroscopic data*: [azulene ring numbering as on structure (**I**)]. (**3**): ν_{CO} ($CHCl_3$) 2055m, 2006m, 1968s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) −6.17 (s, 1H), 4.80 (d, 2H, 4-, 8-H), 5.07 (d, 2H, 1-, 3-H), 5.19 (m, 2H, 5-, 7-H), 6.22 (m, 1H, 2-H), 6.93 (m, 1H, 6-H). (**4**): ν_{CO} ($CHCl_3$) 2049s, 2024m, 1989s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) −6.05 (s, 1H), 1.10 (d, 3H), 1.37 (d, 3H), 1.72 (s, 3H), 1.87 (s, 3H), 2.43 (sept., 1H), 4.49 (s, 1H, 4-H), 4.98 (d, 1H, 1- or 2-H), 5.23 (d, 1H, 7-H), 6.39 (d, 1H, 2- or 1-H), 6.82 (d, 1H, 6-H); ^{13}C n.m.r. δ (CD_2Cl_2) 11.96, 23.07, 23.42, 25.28 (4 × Me), 38.13 ($CHMe_2$), 74.69 (1), 81.47 (4), 88.94 (6), 98.57 (2), 99.86 (7), 210.06, 211.48, 216.98, 217.69, 217.90, 223.54 (6 × CO). (**5**): ^1H n.m.r. δ ($CDCl_3$) −10.74 (s and d with J_{W-H} 35 Hz, 1H), 1.13 (d, 3H), 1.37 (d, 3H), 1.91 (s, 3H), 2.09 (s, 3H), 2.53 (sept., 1H), 4.90 (s, 1H, 4-H), 5.15 (d, 1H, 7-H), 5.25 (d, 1H, 1- or 2-H), 6.05 (d, 1H, 2- or 1-H), 6.94 (d, 1H, 6-H). (**6**): ν_{CO} ($CHCl_3$) 2051w, 2003m, 1968s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 3.22 (d, 1H, 1-H{D}), 3.51 (d, 1H, 1-H), 4.60 (t, 1H, 6-H), 5.48 (t, 1H, 7-H), 5.59 (t, 1H, 5-H), 5.90 (d, 1H, 4-H), 6.10 (d, 1H, 8-H), 6.29 (m, 1H, 3-H), 6.65 (m, 1H, 2-H). (**7**): ν_{CO} 2039w, 2000m, 1970s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 1.37 (d, 3H), 1.48 (d, 3H), 2.21 (s, 3H), 2.84 (s, 3H), 3.12 (sept., 1H), 3.38 (d, 1H, 1-H{D}), 3.70 (d, 1H, 1-H), 5.79 (d, 1H, 7-H), 5.96 (s, 1H, 4-H), 6.03 (d, 1H, 6-H), 6.83 (d, 1H, 2-H); ^{13}C n.m.r. δ ($CDCl_3$) 13.00, 23.40, 24.51, 27.22 (4 × Me), 37.50 ($CHMe_2$), 41.77 (1), 89.41 (4), 97.76 (6), 98.55 (7), 141.20 (2), 201.00, 208.10 (6 × CO). (**8**): ν_{CO} ($CHCl_3$) 2049s, 2024m, 1989s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 1.40 (d, 3H), 1.43 (d, 3H), 2.08 (s, 3H), 2.49 (s, 3H), 2.94 (sept., 1H), 3.13 (d, 1H, 2-H{D}), 3.30 (d, 1H, 2-H), 4.89 (d, 1H, 7-H), 5.20 (d, 1H, 6-H), 5.50 (s, 1H, 4-H), 6.37 (s, 1H, 1-H). (**9**): ν_{CO} (Et_2O) 1971m, 1906s cm^{-1}; ^1H n.m.r. δ ($CDCl_3$) 0.69 (d, 3H), 1.06 (d, 3H), 1.32 (s, 3H), 1.55 (sept., 1H), 1.68 (s, 3H), 3.47 (d, 1H, 7-H), 3.91 (d, 1H, 1- or 2-H), 3.93 (s, 1H, 4-H), 5.22 (t, 1H, 6-H), 5.95 (d, 1H, (2- or 1-H), 7.35—7.70 (m, 15H); ^{13}C n.m.r. δ ($CDCl_3$) 12.38, 19.90, 24.80, 28.36 (4 × Me), 34.16 ($CHMe_2$), 65.35 (1- or 2-C), 71.38 (4), 88.60 (6), 90.39 (2- or 1-C), 97.83 (7), 128.2 (*meta*), 129.90 (*para*), 132.80 (*ortho*), 136.5 (*ipso*), 226.9 (5 × CO). (**10**): ^1H n.m.r. δ ($CDCl_3$) 1.35 (d, 3H), 1.42 (d, 3H), 2.10 (s, 3H), 2.20 (s, 3H), 2.75 (sept., 1H), 3.19 (d, 1H, 1-H{D}), 3.50 (d, 1H, 1-H), 4.99 (d, 1H, 7-H), 5.17 (d, 1H, 6-H), 5.74 (s, 1H, 4-H), 6.55 (s, 1H, 2-H), 7.1—7.8 (m, 15H).

These results suggest that hydrogen migrations in fused-aromatic/polymetallic complexes are observed where comparable migrations to simple monoaromatic complexes of the form (arene)M$(CO)_3$ are unknown. We are currently examining the extension of this reaction to more conventional fused-aromatics such as naphthalene and anthracene.

Finally, the contrast of this stereospecific migration with that reported for the rhodium–indenyl complex indicates the sensitivity of the migration reaction to the nature of the substrate. This sensitivity is further illustrated by the change in regioselectivity by simple change from azulene to guaiazulene.

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References

1 J. P. Collman, L. S. Hegedus, J. R. Norton, and R. G. Finke, 'Principles and Application of Organotransition Metal Chemistry,' University Science Books, 1987.

2 P. K. Rush, S. K. Noh, and M. Brookhart, *Organometallics*, 1986, **5**, 1745; H. E. Bunting, M. L. H. Green, and P. A. Newman, *J. Chem. Soc., Dalton Trans.*, 1988, 557.

3 F. W. S. Benfield and M. L. H. Green, *J. Chem. Soc., Dalton Trans.*, 1974, 1324; A. N. Nesmeyanov, N. A. Ustynyuk, L. G. Makarova, S. Andre, Y. A. Ustynyuk, L. N. Novikova, and Y. N. Luzikov, *J. Organomet. Chem.*, 1978, **154**, 45.

4 V. S. Leong and N. J. Cooper, *J. Am. Chem. Soc.*, 1988, **110**, 2644; W. P. Henry and R. D. Rieke, *ibid.*, 1983, **105**, 6314.

5 M. A. Wilmoth, R. J. Bernhardt, D. P. Eyman, and J. C. Huffman, *Organometallics*, 1986, **5**, 2559; J. P. Blaha and M. S. Wrighton, *J. Am. Chem. Soc.*, 1985, **107**, 2694.

6 K. Jonas, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 295.

7 R. Burton and G. Wilkinson, *Chem. Ind.* (*London*). 1958, 1205.

8 M. J. Begley, S. G. Puntambekar, and A. H. Wright, *J. Chem. Soc., Chem. Commun.*, 1987, 1251.

9 D. T. Clark, M. Mlekuz, B. G. Sayer, B. E. McCarry, and M. J. McGlinchey, *Organometallics*, 1987, 2201.

10 S. Winstein, H. D. Kaesz, C. G. Kreiter, and E. C. Friedrich, *J. Am. Chem. Soc.*, 1965, **87**, 3267.

11 F. A. Cotton, P. Lahuerta, and B. R. Stults, *Inorg. Chem.*, 1976, **15**, 1866.