Reaction of Dodecacarbonyltriruthenium with 7-Oxabicyclo[2.2.1]hept-5-en-2-yl Derivatives: Synthesis of (μ_3-η^2-Benzyne)-nonacarbonyldihydridotriruthenium and Derivatives

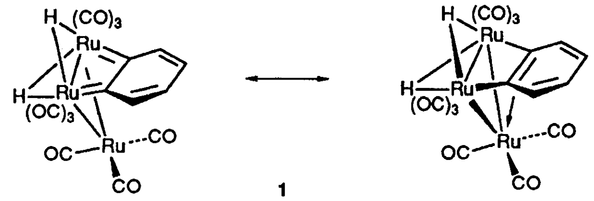
Edia Bonfantini and Pierre Vogel*

Section de Chimie de l'Université, 2, rue de la Barre, CH-1005 Lausanne, Switzerland

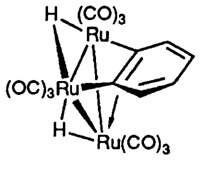
The thermal reaction of [$Ru_3(CO)_{12}$] with 7-oxabicyclo[2.2.1]hept-5-en-2-yl derivatives gave the corresponding [$Ru_3H_2(CO)_9$(7-oxabicyclo[2.2.1]hept-5-yn-2-yl)] clusters; treatment of the complex derived from 7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl benzoate with $(CH_3)_3SiOSO_2CF_3$ gave a mixture of [$Ru_3H_2(CO)_9$(benzyne)] and [$Ru_3H_2(CO)_9(C_6H_3$-$OCOC_6H_5)$].

Benzyne (1,2-didehydrobenzene) complexes of transition metal clusters have been proposed as models[1,2] for the species formed by dissociative chemisorption of benzene on metal surfaces. Transition metal complexes of benzyne such as [$Ir_2(CO)_2(\mu$-η^2-$C_6H_4)(\eta$-$C_5H_5)_2$],[3] [$Os_3H_2(CO)_9(\mu_3$-η^2-$C_6H_4)$][4,5] and other polynuclear complexes of osmium and ruthenium have been described.[2] In contrast with [$Os_3H_2(CO)_9(\mu_3$-η^2-$C_6H_4)$][4] that can be obtained on heating benzene with [$Os_3(CO)_{12}$], the thermal reaction of benzene with [$Ru_3(CO)_{12}$] did not afford [$Ru_3H_2(CO)_9$(benzyne)] **1**; instead a mixture of Ru_4 and Ru_6 clusters was obtained. None of these complexes incorporated the benzyne moiety.[6] To our knowledge, compound **1** has not been reported yet, although several analogues **2** incorporating bridging phosphido ligands are known.[2,7] We report here a synthesis of **1** which is based on the deoxygenation of [$Ru_3H_2(CO)_9(\mu_3$-η^2-7-oxabicyclo[2.2.1]hept-5-en-2-*endo*-yl benzoate)] **11**.

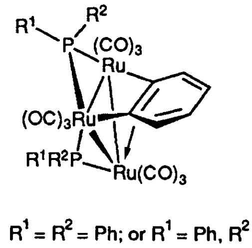
As for bicyclo[3.2.1]octa-2,6-diene which reacts with [$Ru_3(CO)_{12}$] to give the cluster **3**,[8] heating 7-oxabicyclo[2.2.1]hept-5-en-2-one **4**[9] with [$Ru_3(CO)_{12}$] in heptane at 95–100 °C under a flow of Ar afforded the corresponding [$Ru_3H_2(CO)_9$(alkyne)] complex **5** in 60% yield. Compound **5** was stable for several days on heating in $CDCl_3$ or C_6D_6 at 70 °C.† In [$^2H_8$]tetrahydrofuran ([$^2H_8$]THF) (70 °C, 2 days) **5** was decomposed and furnished catechol nearly quantitatively with precipitation of metallic species. The reaction was not significantly retarded on addition of $NaHCO_3$. Under the same conditions, **4** was not isomerized into catechol. Interestingly, the treatment of cluster **5** in benzene containing a small amount of CF_3CO_2H also led to catechol, even at 50 °C. With the more oxyphilic reagent $(CH_3)_3SiOSO_2CF_3$ (TMSOTf), **5** was rearranged at 7–20 °C (benzene) into the catechol derived cluster **6**. This compound was decomposed in [$^2H_8$]THF and afforded catechol quantitatively after 5 h at 20 °C (Scheme 1). The structure of **6** was suggested by its 250 MHz ^1H NMR spectrum in CD_2Cl_2 at −10 °C [δ_H 7.00, 6.45 (2d, 2 H, ^3J = 8 Hz), 6.03 (t, 1 H, ^3J = 8 Hz), 6.07 (br.s, OH), −12.75, −13.30 (2 br.s, 2 Ru–H–Ru)] which is similar to that reported for the analogous Os_3 cluster **7**.[11] The pK_a of **6** must be higher than that of H_2O as it was not soluble in a 5% aqueous solution of NaOH. Nevertheless, the OH signal in its ^1H NMR spectrum was exchanged on addition of D_2O. The other spectra were also consistent with structure **6** {ν_{CO}/cm^{-1} 2110, 2080, 2060 and 2010 cm^{-1}; ^{13}C NMR (62.9 MHz, CD_2Cl_2, −10 °C†) δ_C 202.2, 196.9 (CO), 183.8, 148.8, 100.2



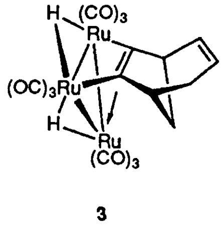
1



1′



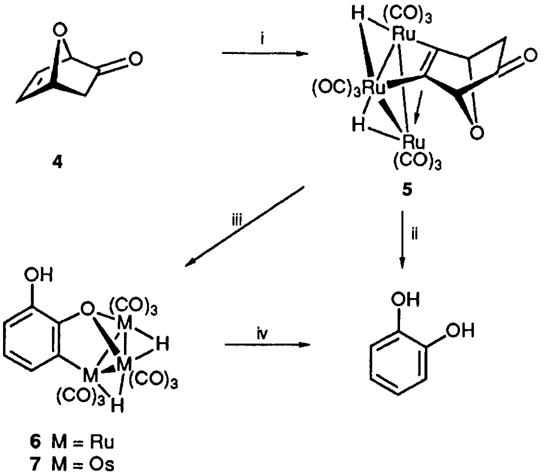
2 $R^1 = R^2$ = Ph; or R^1 = Ph, R^2 = ferrocenyl



3

---

† The gross structures of the alkyne clusters were deduced from their elemental analyses and spectral data. Details of the structure of the $Ru_3H_2(CO)_9$ moiety await single crystal X-ray diffraction studies.[10] Because only one stereoisomer is seen in the NMR spectra of **5**, **10** and **11**, we cannot yet exclude a structure with the two hydrido atoms bridging the pair of Ru atoms σ-linked to the alkyne ligand.

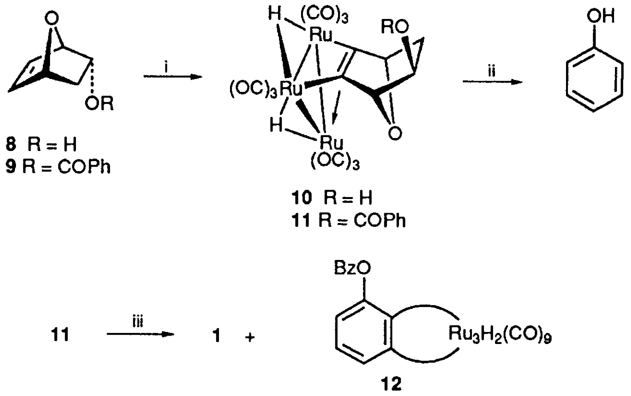


Scheme 1 *Conditions*: $[Ru_3(CO)_{12}]$, heptane, 95–100 °C, 4 h, 60%; ii, $[^2H_8]$THF, 70 °C, 2 days; or C_6D_6 + CF_3CO_3H, 50 °C, 2 days; iii, 1 equiv. TMSOTf, C_6H_6, 7–15 °C, 60%; iv, $[^2H_8]$THF, 20 °C, 5 h

(3m, quat. C), 153.1, 118.4 [2dd, ^1J(C,H) = 160, ^3J(C,H) = 10 Hz] and 113.5 [d, ^1J(C,H) = 162 Hz)]}.

Reduction of ketone **4** with $NaBH_4$ in MeOH gave the corresponding alcohol **8**[12] which was benzoylated [PhCOCl, pyridine, CH_2Cl_2, 4-dimethylaminopyridine (DMAP), 20 °C, 15 h] to give **9** (92%, m.p. 79–80 °C). Heating **8** or **9** with $[Ru_3(CO)_{12}]$ in heptane of 95–100 °C for 3–4 h gave the clusters **10** (35%) and **11** (50%), respectively (Scheme 2). In $[^2H_8]$THF at 70 °C, **10** and **11** were decomposed giving mixtures containing phenol. Treatment of **11** with TMSOTf (C_6H_6, 7–20 °C) gave a mixture of the Ru_3 clusters **1**, **12** and an unknown compound (probably a regioisomer of **12**). The aryne complexes **1** (7%) and **12** (33%) could be isolated and purified by flash column chromatography on silica gel. The structures of **1** and **12** were deduced from their elemental analyses and by comparison of their spectral data with those reported for analogous $[Os_3H_2(CO)_9(\text{aryne})]$ complexes.[4] While the formation of **12** corresponds to an isomerization of **11** with elimination of H_2O, reaction **11** → **1** implies deoxygenation (reduction) and benzoic acid elimination.

At 20 °C, the ^1H NMR (360 MHz) spectrum of **1** in CD_2Cl_2 displayed one broad singlet (δ_H −17.7) for the two hydrido protons.‡ At lower temperature, two broad singlets (δ_H −15.76, −19.78) were observed for these two protons, with a coalescence temperature T_C of 218 K. Line-shape analysis led to the following activation parameters: $\Delta H^‡$ = (32 ± 0.6 kJ mol^{-1} and $\Delta S^‡$ = −32 ± 2.5 J mol^{-1} K^{-1} [$\Delta G^‡$ (218 K) = 39.2 kJ mol^{-1}]. These parameters did not depend on the concentration (0.03–0.06 mol dm^{-3}) of **1**. Compared with the data reported for the hydride proton exchange in $[Os_3H_2(CO)_9(C_6H_4)]$ (T_C = 153 K, $\Delta G^‡$ = 28 kJ mol^{-1}),[13] the corresponding proton exchange was somewhat slower in the case of **1**. Fluxionality of the carbonyl ligands was also evident from the variable temperature ^{13}C NMR spectrum (CH_2Cl_2) of **1** which showed five signals for the carbonyl groups [δ_C 196.4 (1C), 193.7, 191.5, 190.1 and 188.4 (4 × 2C)] at 175 K and one broad line (δ_C 191.4) at 219 K. The aromatic carbon signals {δ_C 151.5 [dm, ^1J(C,H) = 160, ^3J(C,H) = 5 Hz], 140.8 (m) and 124.8 [dm, ^1J(C,H) = 160, ^3J(C,H) = 8 Hz)]} did not change between 175 and 219 K, thus proving the average C_s symmetry of **1**. Structure **1′** can be ruled out for **1** in CH_2Cl_2 solution. Possible exchange[14] of the hydrido and aromatic ring protons in **1** could not be detected below 100 °C, the temperature at which the complex decomposed.



Scheme 2 *Conditions*: i, $[Ru_3(CO)_{12}]$, heptane, 95–100 °C, 4 h; ii, $[^2H_8]$THF, 70 °C, 2 days; iii, 1 equiv. TMSOTf, C_6H_6, 7–20 °C, 1 h

Further experimental data must be collected before one can discuss the possible mechanisms of the processes reported here. Since the bicyclic alkenes **4**, **8** and **9** can be prepared optically pure in both enantiomeric forms,[14] our approach to the preparation of trinuclear ruthenium complexes might allow one to obtain some of these clusters in an optically pure form.

We thank Hoffmann-La Roche and Cie, AG Basel, the Fonds Herbette, Lausanne, and the Swiss National Science Foundation for financial support.

Received, 19th June 1991; Com. 1/03021C

References

1 E. L. Muetterties, *Pure Appl. Chem.*, 1982, **54**, 83.
2 S. A. R. Knox, B. R. Lloyd, D. A. V. Morton, S. M. Nicholls, A. G. Orpen, J. M. Viñas, M. Weber and G. K. Williams, *J. Organomet. Chem.*, 1990, **394**, 385 and references cited therein.
3 M. D. Rausch, R. G. Gastinger, S. A. Gardner, R. K. Brown and J. S. Wood, *J. Am. Chem. Soc.*, 1977, **99**, 7870.
4 A. J. Deeming and M. Underhill, *J. Chem. Soc., Dalton Trans.*, 1974, 1415; R. J. Groudsmit, B. F. G. Johnson, J. Lewis, P. R. Raithby and M. J. Rosales, *J. Chem. Soc., Dalton Trans.*, 1983, 2257.
5 M. A. Gallop, B. F. G. Johnson, J. Lewis, A. McCamley and R. N. Perutz, *J. Chem. Soc., Chem. Commun.*, 1988, 107.
6 C. R. Eady, B. F. G. Johnson and J. Lewis, *J. Chem. Soc. Dalton Trans.*, 1975, 2606; B. F. G. Johnson, R. D. Johnson and J. Lewis, *J. Chem. Soc., A*, 1968, 2865; see also: D. S. Bohle and H. Vahrenkamp, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 198; S. Bhaduri, K. Sharma and P. G. Jones, *J. Chem. Soc., Chem. Commun.*, 1987, 1769.
7 W. R. Cullen, S. T. Chacon, M. I. Bruce, F. W. B. Einstein and R. H. Jones, *Organometallics*, 1988, **7**, 2273; S. A. R. Knox, B. R. Lloyd, A. G. Orpen, J. M. Viñas and M. Weber, *J. Chem. Soc., Chem. Commun.*, 1987, 1498.
8 A. J. P. Domingos, B. F. G. Johnson and J. Lewis, *J. Organomet. Chem.*, 1972, **36**, C43; see also: F.-W. Grevels, J. G. A. Reuvers and J. Takats, *J. Am. Chem. Soc.*, 1981, **103**, 4069.
9 E. Vieira, and P. Vogel, *Helv. Chim. Acta*, 1982, **65**, 1700.
10 A. A. Pinkerton, Department of Chemistry, University of Toledo, Ohio, USA.
11 A. Kazi, A. Azam, A. J. Deeming, R. E. Kimber and P. R. Shukla, *J. Chem. Soc., Dalton Trans.*, 1976, 1853.
12 R. Saf, K. Faber, G. Penn and H. Griengl, *Tetrahedron*, 1988, **44**, 389.
13 A. Kazi, C. Azam, C. Choo Yin and A. J. Deeming, *J. Chem. Soc., Dalton Trans.*, 1978, 1201.
14 H. J. Kneuper, J. R. Shapley, *Organometallics*, 1987, **6**, 2455.
15 P. Vogel, D. Fattori, F. Gasparini and C. Le Drian, *Synlett.*, 1990, **1**, 173; J.-L. Reymond and P. Vogel, *Tetrahedron Asymmetry*, 1990, **1**, 729.

---

‡ Data for **1**: orange-yellow crystals, m.p. 85–90 °C (decomp.); IR ($CHCl_3$) ν/cm^{-1} 2105, 2075, 2055 and 2010; ^1H NMR (250 MHz, CD_2Cl_2, 25 °C) δ_H 7.90, 6.93 (2m, AA′XX′, 4 H) and −17.7 (s, 2H). Data for **12**: orange crystals, m.p. 102–103 °C; IR ($CHCl_3$) ν/cm^{-1} 2110, 2075, 2055, 2010 and 1730; ^1H NMR (250 MHz, $CDCl_3$) δ_H 8.23 (dm, J = 7.5 Hz, 2 H), 7.67 (tm, J = 7.5 Hz, 1 H), 7.54 (tm, J = 7.5 Hz, 2 H), 7.82 (dd, J = 7.5 Hz, 1.0, 1 H), 7.06 (t, J = 7.5 Hz), 6.93 (dd, J = 7.5, 1.0 Hz, 1 H) and −17.63 (br.s, 2 H); ^{13}C NMR (62.9 MHz, CH_2Cl_2, −10 °C) δ_C 191.3 (s, CO), 165.2, 163.7, 141.7, 137.1 (4s), 149.1, 133.9, 130.4, 128.7, 125.7, 117.4 [6d, ^1J(C,H) = 162 Hz].