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 $[Ru_3H_2(CC)_9(C_6H_3-OCOC_6H_5)]$.

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 $[Ir_2(CO)_2(\mu-\eta^2-C_6H_4)(\eta-C_5H_5)_2]$,³ $[Os_3H_2(CO)_9(\mu_3-\eta^2-C_6H_4)(\eta-C_5H_5)_2]$,⁴ $[Os_3H_2(CO)_9(\mu_3-Q_5H_5)]$,⁴ $[Os_3H_2(O)_9(\mu_3-Q_5H_5)]$,⁴ $[Os_3H_2(O)_9(\mu_3-Q_5)]$,⁴ $[Os_3H_2(O)_9(\mu_3-Q_5)]$,⁴ $[Os_3H_2(O)_9(\mu_3-Q_5)]$,⁴ $[Os_3H_2(O)_9(\mu_3-Q_5)]$,⁴ $[Os_3H_2(O)_9(\mu_3-Q_5)]$,⁴ $[Os_3H_2($ η^2 -C₆H₄)]^{4,5} and other polynuclear complexes of osmium and ruthenium have been described.² In contrast with [Os₃- $H_2(CO)_9(\mu_3-\eta^2-C_6H_4)]^4$ 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 Ru₄ and Ru₆ 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 $[Ru_3H_2(CO)_9(\mu_3-\eta^2-7-0xabi$ cyclo[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 4⁹ 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 CDCl₃ or C₆D₆ at 70 °C.† In [²H₈]tetrahydrofuran ([²H₈]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 NaHCO₃. Under the same conditions, 4 was not isomerized into catechol. Interestingly, the treatment of cluster 5 in benzene containing a small amount of CF₃CO₂H also led to catechol, even at 50 °C. With the more oxyphilic reagent (CH₃)₃SiOSO₂CF₃ (TMSOTf), 5 was rearranged at 7–20 °C (benzene) into the catechol derived cluster 6. This compound was decomposed in [²H₈]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 CD₂Cl₂ at -10 °C [$\delta_{\rm H}$ 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 Os₃ cluster **7**.¹¹ The pK_a of **6** must be higher than that of H₂O 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 D₂O. The other spectra were also consistent with structure **6** { $\nu_{\rm CO}$ /cm⁻¹ 2110, 2080, 2060 and 2010 cm⁻¹; ¹³C NMR (62.9 MHz, CD₂Cl₂, -10 °C†) $\delta_{\rm C}$ 202.2, 196.9 (CO), 183.8, 148.8, 100.2



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

[†] 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: [Ru₃(CO)₁₂], heptane, 95-100 °C, 4 h, 60%; ii, [²H₈]THF, 70 °C, 2 days; or C₆D₆ + CF₃CO₃H, 50 °C, 2 days; iii, 1 equiv. TMSOTf, C₆H₆, 7–15 °C, 60%; iv, [²H₈]THF, 20 °C, 5 h

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

Reduction of ketone 4 with NaBH₄ in MeOH gave the corresponding alcohol 812 which was benzoylated [PhCOCl, pyridine, CH₂Cl₂, 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 ^{[2}H₈]THF at 70 °C, 10 and 11 were decomposed giving mixtures containing phenol. Treatment of 11 with TMSOTf $(C_6H_6, 7-20 \degree C)$ gave a mixture of the Ru₃ 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 [Os₃H₂(CO)₉(aryne)] complexes.⁴ While the formation of 12 corresponds to an isomerization of 11 with elimination of H₂O, reaction $11 \rightarrow 1$ implies deoxygenation (reduction) and benzoic acid elimination.

At 20 °C, the ¹H NMR (360 MHz) spectrum of 1 in CD₂Cl₂ displayed one broad singlet ($\delta_{\rm H}$ -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: $\Delta H^{\ddagger} = (32 \pm 0.6 \text{ kJ})$ mol^{-1} and $\Delta S^{\ddagger} = -32 \pm 2.5$ J $mol^{-1} K^{-1} [\Delta G^{\ddagger} (218 \text{ K}) = 39.2$ kJ mol⁻¹]. These parameters did not depend on the concentration $(0.03-0.06 \text{ mol } dm^{-3})$ 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, $\Delta G^{\ddagger} = 28$ 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 (CH₂Cl₂) of 1 which showed five signals for the carbonyl groups [$\delta_{\rm C}$ 196.4 (1C), 193.7, 191.5, 190.1 and 188.4 $(4 \times 2C)$] at 175 K and one broad line (δ_{C} 191.4) at 219 K. The aromatic carbon signals { δ_{C} 151.5 [dm, ${}^{1}J(C,H) = 160, {}^{3}J(C,H) = 5$ Hz], 140.8 (m) and 124.8 [dm, ${}^{1}J(C,H) = 160, {}^{3}J(C,H) = 8 Hz$]} did not



Scheme 2 Conditions: i, $[Ru_3(CO)_{12}]$, heptane, 95–100 °C, 4 h; ii, $[^{2}H_{8}]THF$, 70 °C, 2 days; iii, 1 equiv. TMSOTf, $C_{6}H_{6}$, 7–20 °C, 1 h

change between 175 and 219 K, thus proving the average C_s symmetry of 1. Structure 1' can be ruled out for 1 in CH₂Cl₂ solution. Possible exchange¹⁴ of the hydrido and aromatic ring protons in 1 could not be detected below 100 °C, the temperature at which the complex decomposed.

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,
- 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.
- 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, , 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 (CHCl₃) v/cm⁻¹ 2105, 2075, 2055 and 2010; ¹H NMR (250 MHz, CD₂Cl₂, 25 °C) $\delta_{\rm H}$ 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 (CHCl₃) v/cm⁻¹ 2110, 2075, 2055, 2010 and 1730; ¹H NMR (250 MHz, CDCl₃) $\delta_{\rm H}$ 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)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); ¹³C NMR (62.9 MHz, 1) 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, ${}^{1}J(C,H) = 162 \text{ Hz}$].