

*Journal of Organometallic Chemistry*, 376 (1989) C23–C25  
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands  
JOM 20186PC

### Preliminary communication

---

## $\mu$ -Amido complexes of ruthenium carbonyl. Asymmetric versus symmetric bridging preference of the monodeprotonated derivatives of 1,2-arenediamines. Crystal structure of $[\text{Ru}_3(\mu\text{-H})(\mu\text{-H}_3\text{N}_2\text{-4,5-Me}_2\text{-1,2-phenylene})]$

Javier A. Cabeza <sup>\*</sup>, Victor Riera,

*Departamento de Química Organometálica, Facultad de Química, Universidad de Oviedo, E-33071 Oviedo (Spain)*

Maria Angela Pellinghelli and Antonio Tiripicchio <sup>\*</sup>

*Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffraattometrica del C.N.R., Viale delle Scienze, I-43100 Parma (Italy)*

(Received May 25th, 1989)

### Abstract

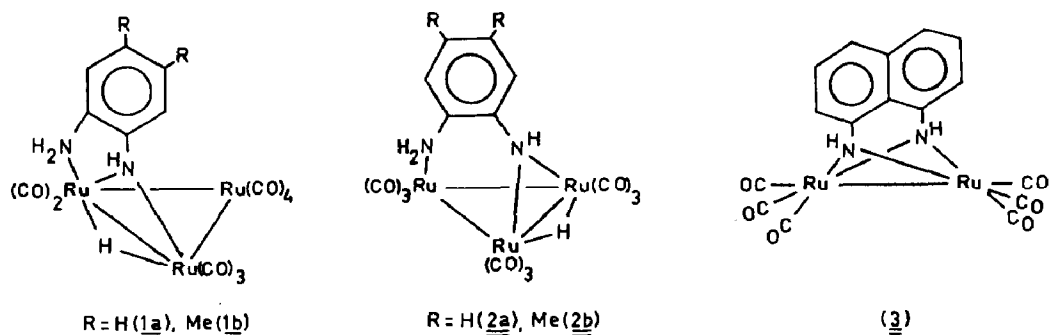
$[\text{Ru}_3(\text{CO})_{12}]$  reacts with 1,2-arenediamines ( $\text{H}_4\text{N}_2$  arene), under CO, to give the very asymmetric clusters  $[\text{Ru}_3(\mu\text{-H})(\mu\text{-H}_3\text{N}_2\text{ arene})(\text{CO})_9]$  (arene = 1,2-phenylene (**1a**) or 4,5-Me<sub>2</sub>-1,2-phenylene (**1b**)) in which the three Ru atoms bear two, three, and four CO ligands, respectively. Under similar conditions, reaction of  $[\text{Ru}_3(\text{CO})_{12}]$  with 1,8-diaminonaphthalene ( $\text{H}_4\text{N}_2$  naph) leads to break up of the cluster framework to give the binuclear ruthenium(I) compound  $[\text{Ru}_2(\mu\text{-H}_2\text{N}_2\text{ naph})(\text{CO})_6]$  (**3**). The crystal structure of compound **1b** has been determined by an X-ray diffraction study.

---

The ability of difunctional ligands to act as flexible bridges, within and beyond the requirements of metal-metal interactions, in polynuclear transition metal complexes is a matter of considerable interest. Among such ligands, arenediamines have been very little studied [1], but give binuclear complexes with the dideprotonated (diimine) form of the diamine symmetrically bridging the two metals; e.g. in rhodium and iridium complexes [2]. In addition,  $[\text{Ru}_3(\text{CO})_{12}]$  reacts with arylamines to give compounds [3] which are catalyst precursors for the hydrogenation of olefins [4] or for carbonylation of nitrobenzene to give phenylisocyanate [5]. We now report some reactions of  $[\text{Ru}_3(\text{CO})_{12}]$  with 1,2-arenediamines and 1,8-diaminonaphthalene.

---

<sup>\*</sup> Reference number with asterisk indicates a note in the list of references.



Scheme 1

The reaction of  $[Ru_3(CO)_{12}]$  with an excess of 1,2-diaminobenzene or 1,2-diamino-4,5-dimethylbenzene in refluxing toluene under CO [6\*] gives the orange asymmetric clusters **1a** or **1b** quantitatively [7\*], rather than the symmetric **2a** and **2b** (Scheme 1). A crystal structure determination for **1b** (Fig. 1) [8\*] shows that the monodeprotonated form of the initial diamine is bridging and chelating two ruthenium atoms, resulting in a very asymmetric trinuclear cluster. This is unex-

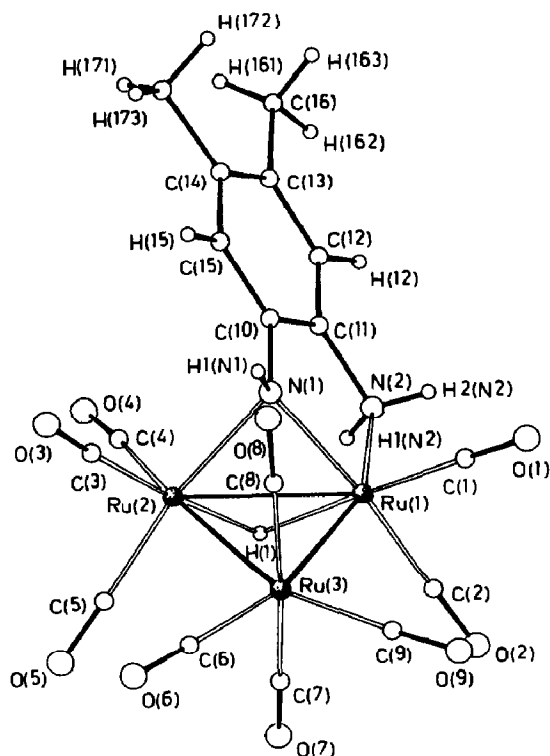


Fig. 1. Perspective view of the structure of the compound **1b**. Selected bond distances (Å) and angles (°): Ru(1)–Ru(2) 2.777(1), Ru(1)–Ru(3) 2.788(1), Ru(2)–Ru(3) 2.816(1), Ru(1)–N(1) 2.093(4), Ru(1)–N(2) 2.208(5), Ru(2)–N(1) 2.140(4), N(1)–C(10) 1.433(6), N(2)–C(11) 1.470(7); Ru(2)–Ru(1)–Ru(3) 60.8(1), Ru(1)–Ru(3) 59.8(1), Ru(1)–Ru(3)–Ru(2) 59.4(1), Ru(1)–N(1)–Ru(2) 82.0(1), Ru(1)–N(1)–C(10) 113.9(3), Ru(2)–N(1)–C(10) 117.5(3), N(1)–Ru(1)–N(2) 79.1(2), Ru(1)–N(2)–C(11) 110.1(3).

pected, because all the known triruthenium clusters having related nitrogen-containing ligands (e.g., 7-azaindolate [9]) are symmetric. Although complexes having neutral [10] or dideprotonated [2,11] 1,2-aryldiamines are known, as far as we are aware this is the first report of complexes containing monodeprotonated derivatives of these ligands.

[Ru<sub>3</sub>(CO)<sub>12</sub>] reacts with an excess of 1,8-diaminonaphthalene in refluxing toluene under CO [6\*] to give the binuclear pale-yellow ruthenium(I) compound **3** quantitatively [12\*]. This is one of the very few high-yield syntheses of ruthenium(I) compounds [13,14]. The oxidation state one is still uncommon for ruthenium. The structure we suggest for **3** is based on analytical and spectroscopic data [12\*]. A study of its reactions is in progress.

We thank the Dirección General de Investigación Científica y Técnica (Spain) and the Ministero della Pubblica Istruzione (Italy) for support.

## References

- 1 D.A. House, in G. Wilkinson, R.D. Gillard and J.A. McCleverty (Eds.), *Comprehensive Coordination Chemistry*, Vol. 2, Pergamon, Oxford 1987, p. 59.
- 2 L.A. Oro, M.J. Fernández, J. Modrego, C. Foces-Foces and F.H. Cano, *Angew. Chem. Int. Ed. Engl.*, 23 (1984) 913; L.A. Oro, M.J. Fernández, J. Modrego and J.M. López, *J. Organomet. Chem.*, 287 (1985) 409.
- 3 E. Sappa and L. Milone, *J. Organomet. Chem.*, 61 (1973) 383.
- 4 J.A. Smieja, J.E. Gozum and W.L. Gladfelter, *Organometallics*, 5 (1986) 2154.
- 5 A. Basu, S. Baduri and J. Khwaja, *J. Organomet. Chem.*, 319 (1987) C28.
- 6 When these reactions were carried out under nitrogen, in the absence of CO, dark-brown, air-sensitive solids were obtained. Their microanalyses suggest that they are polymers with a formula such as  $[\{\text{Ru}(\text{CO})_2(\mu\text{-diimine})\text{Ru}(\text{CO})_2\}(\mu\text{-diamine})]_n$ , but their insolubility and instability prevented any other structural analysis.
- 7 [Ru<sub>3</sub>(CO)<sub>12</sub>] (200 mg, 0.3 mmol) and the corresponding diamine (0.9 mmol) in refluxing toluene, under CO, for 10 h. Chromatography on silica gel (toluene). **1a**: Correct elemental analysis (C, H, N); FAB MS (*m/z*): 663 (*M*<sup>+</sup>) and the successive loss of nine CO groups; IR (cm<sup>-1</sup>): ν(NH) (nujol) 3362m, 3332s, 3283s; ν(CO) (hexane) 2082m, 2043s, 2001s, 1993s, 1981m, 1941; <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm, *J* in Hz): δ(CH) 7.24 (d, *J* 7.6, 1H), 7.17 (t, *J* 7.6, 1H), 7.05 (d, *J* 7.6, 1H); δ(NH) 5.68 (s, 1H), 4.67, 4.29 (AB system, *J* 12, 2H); δ(μ-H) -12.41 (s). **1b**: Correct elemental analysis (C, H, N); FAB MS: 691 (*M*<sup>+</sup>) and the successive loss of nine CO groups; (cm<sup>-1</sup>) IR ν(NH) (nujol) 3373m, 3342s, 3290s; ν(CO) (hexane) 2091m, 2052s, 2008s, 1994s, 1980m, 1943m; <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ(CH) 6.99 (s, 1H), 6.77 (s, 1H), 2.22 (s, 3H), 2.14 (s, 3H); δ(NH) 5.64 (s, 1H), 4.54, 4.15 (AB system, *J* 12, 2H); δ(μ-H) -12.30 (s).
- 8 **1b**: triclinic,  $\bar{P}1$ , *Z* = 2, *a* 9.447(3), *b* 14.510(6), *c* 9.357(4) Å, α 95.57(1), β 113.55(1), γ 100.22(1)°; *V* 1136.9(8) Å<sup>3</sup>, *M* 691.50, *D*<sub>c</sub> = 2.020 g cm<sup>-3</sup>; Siemens AED diffractometer (Mo-*K*<sub>α</sub>), μ 19.78 cm<sup>-1</sup>; 3 < θ < 27°, 4968 unique reflections, 4192 observed with *I* > 2σ(*I*), *R* = 0.0436, *R*<sub>w</sub> = 0.0575. Further details of the crystal structure analysis may be obtained from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW (UK), on quoting the names of authors and the journal citation.
- 9 J.A. Cabeza, L.A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Chem. Soc. Dalton Trans.*, (1988) 1437.
- 10 G.J. Grant and D.T. Royer, *J. Am. Chem. Soc.*, 103 (1981) 868.
- 11 R. Obeso-Rosete, D.J. Cole-Hamilton and G. Wilkinson, *J. Chem. Soc. Dalton Trans.*, (1979) 1618.
- 12 [Ru<sub>3</sub>(CO)<sub>12</sub>] (200 mg, 0.3 mmol) and 1,8-diaminonaphthalene (143 mg, 0.9 mmol) in refluxing toluene, under CO, for 12 h. Chromatography on silica gel (toluene). **3**: Correct elemental analysis (C, H, N); FAB MS (*m/z*): 526 (*M*<sup>+</sup>) and the successive loss of six CO groups; IR (cm<sup>-1</sup>): ν(NH) (nujol) 3348m, 3332w; ν(CO) (hexane) 2084w, 2059m, 2009m, 1994s, 1940w; <sup>1</sup>H NMR (CDCl<sub>3</sub>) (ppm, *J* in Hz): δ 7.50 (d, *J* 7.5, 1H), 7.19 (t, *J* 7.5, 1H), 7.08 (d, *J* 7.5, 1H), 5.14 (s, br, NH).
- 13 J.A. Cabeza, C. Landázuri, L.A. Oro, A. Tiripicchio and M. Tiripicchio-Camellini, *J. Organomet. Chem.*, 322 (1987) C16.
- 14 P.L. Andreu, J.A. Cabeza, V. Riera, F. Robert and Y. Jeannin, *J. Organomet. Chem.*, 372 (1989) C15.