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Reactions of $[\text{Ru}_2\{\mu\text{-}1,2\text{-(NH)}_2\text{C}_6\text{H}_4\}(\text{CO})_4(\text{PPh}_3)_2]$ with H^+ , NO^+ and group 11 metal fragments. Syntheses of trinuclear Ru_2M ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) and pentanuclear Ru_4Au clusters

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Abstract

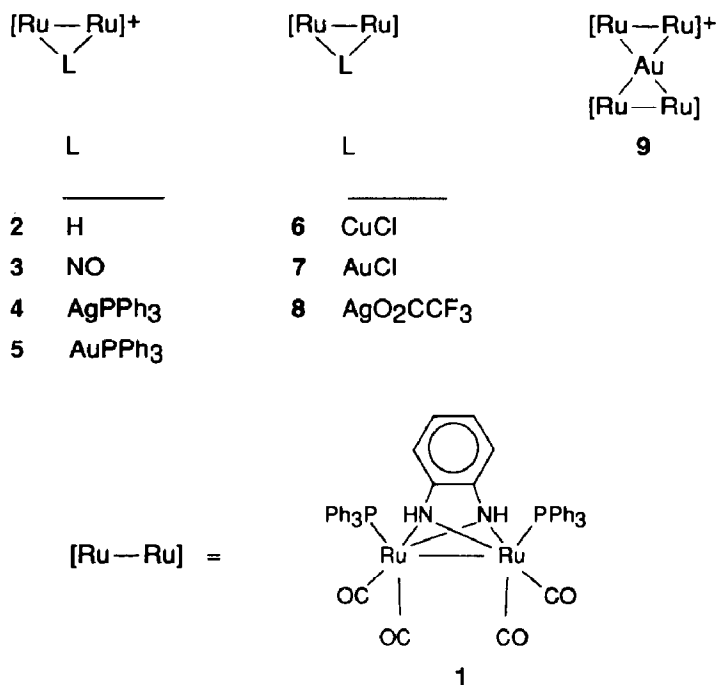
The complex $[\text{Ru}_2\{\mu\text{-dib}\}(\text{CO})_4(\text{PPh}_3)_2]$ (**1**) (dib = 1,2-(NH)₂C₆H₄) reacts with Lewis acids (H^+ , NO^+ , MX, MPPh_3^+) to give cationic $[\text{Ru}_2(\mu\text{-L})(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)_2]^+$ (L = H (**2**), NO (**3**), Ag(PPh₃) (**4**), Au(PPh₃) (**5**)), and neutral $[\text{Ru}_2(\mu\text{-L})(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)_2]$ (L = CuCl (**6**), AuCl (**7**), AgO₂CCF₃ (**8**)) complexes. The pentanuclear compound $[\text{Ru}_4(\mu_4\text{-Au})(\mu\text{-dib})_2(\text{CO})_8(\text{PPh}_3)_4]\text{PF}_6$ has been prepared by reaction of complexes **1** and **7** in the presence of TlPF₆. These compounds react with an excess of base (RNH₂ or PPh₃) to regenerate complex **1**.

Introduction

We recently described [1] the synthesis and crystal structure of $[\text{Ru}_2(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)_2]$ (**1**) (dib = 1,2-diiminobenzene; 1,2-(NH)₂C₆H₄). This complex is unique because it is the first binuclear ruthenium(I) complex containing 1,2-diiminobenzene as a 6-electron bridging ligand and also because it has the shortest Ru–Ru distance (2.560(1) Å) ever reported for a ruthenium(I) dimer [2]. Other binuclear complexes containing 1,2-diiminobenzene derivatives as bridging ligands have been reported for iron [3], molybdenum [4], and rhodium [5,6], and with 1,8-diiminonaphthalene for rhodium [5–8], iridium [6] and ruthenium [2a,9]. We thought it of interest to study the reactivity of Ru–Ru bond of complex **1** towards Lewis acids, having in mind that the ruthenium(I) dimer $[\text{Ru}_2(\mu\text{-dmpz})_2(\text{CO})_6]$ (dmpz = 3,5-dimethylpirazolate), which has a Ru–Ru distance of 2.705(2) Å, does not react with sulfuric acid or with the metallic fragments $[\text{MPPh}_3]^+$ (M = Ag, Au) [2b]. We now report the syntheses of bi-, tri- and penta-nuclear complexes formed by the reaction of various Lewis acids with complex **1**.

Results and discussion

Reactions of $[\text{Ru}_2(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)_2]$ (**1**) with HBF₄ or NOBF₄ in tetrahydrofuran (THF) at room temperature gave, in 30 min, yellow precipitates of $[\text{Ru}_2(\mu\text{-}$



Scheme 1

$L(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)_2\text{BF}_4$ ($L = \text{H}$ (2) or NO (3)) (Scheme 1). The IR spectrum of 2 displays the expected $\nu(\text{NH})$ (3320 m, cm^{-1} , Nujol mull) and $\nu(\text{CO})$ (2066 vs, 2050 m, 2002 vs, cm^{-1} , CH_2Cl_2 solution) absorptions for a complex of C_{2v} symmetry, with the $\nu(\text{CO})$ bands at higher frequencies than those for the starting material 1 (1999 vs, 1965 m, 1929 vs, cm^{-1} , THF solution). These data are consistent with an oxidation at the metal centres. Further evidence for the formation of a new bridge between the ruthenium atoms is provided by the ^1H and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of 2, which show a triplet at $\delta -8.90$ ppm ($J(\text{P}-\text{H})$ 42 Hz) and a singlet at $\delta 37.0$ ppm, respectively.

The nitrosyl complex 3 is insoluble in all common solvents, and this prevented a detailed spectroscopic study. However, its IR spectrum in Nujol mull is very similar to that of complex 2, but shows in addition a weak absorption at 1815 cm^{-1} that can be tentatively assigned to the $\nu(\text{NO})$ stretching vibration. Although this value of $\nu(\text{NO})$ lies within the range normally assigned to terminal rather than to bridging nitrosyls [10], we have no doubt about the bridging character of the NO ligand in complex 3 because the analogous complex $[\text{Ru}_2(\mu\text{-NO})(\mu\text{-din})(\text{CO})_4(\text{PPh}_3)_2]\text{BF}_4$ ($\text{din} = 1,8\text{-diiminonaphthalene}$), which is more soluble and exhibits the same IR spectrum in Nujol mull as complex 3, shows a singlet resonance in its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at $\delta 37,7$ ppm [11]. Interestingly, although CO is isoelectronic with NO^+ , complex 1 was recovered unchanged after treatment with CO at 10 atm for 2 h.

When other cationic species like the silver and gold fragments $[\text{MPPh}_3]^+$ ($M = \text{Ag}, \text{Au}$), prepared in situ from AgBF_4 and PPh_3 or from $[\text{AuCl}(\text{PPh}_3)]$ and TIPF_6 , were allowed to react with complex 1 in THF, yellow precipitates of the salts $[\text{Ru}_2(\mu\text{-MPPH}_3)(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)_2] \text{PF}_6$ ($M = \text{Ag}$ (4), Au (5)) (Scheme 1) were obtained.

As expected, their IR spectra (see Experimental) show the three $\nu(\text{CO})$ bands shifted to higher frequencies compared with those for compound **1**. The $^{31}\text{P}\{^1\text{H}\}$ NMR of **5** consists of a doublet and a triplet at δ 37.0 and 56.0 ppm, respectively ($^3J(\text{P}-\text{P})$ 42.7 Hz), confirming the triangular arrangement of the metals. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of **4** is more complicated owing to ^{31}P coupling to ^{107}Ag and ^{109}Ag (51.8 and 48.2% natural abundance, respectively, $I = 1/2$), showing an apparent doublet of doublets for the Ru-bonded phosphine, δ 34.3 ppm [$^3J(\text{P}-\text{P}) = 38$ Hz, $^2J(\text{P}-^{107}\text{Ag}) \approx ^2J(\text{P}-^{109}\text{Ag}) = 55$ Hz] and a broad, unresolved signal at δ 10.4 ppm, assignable to the Ag-bonded phosphine. It has been reported [8] that the cations $[\text{MPPh}_3]^+$ ($\text{M} = \text{Cu}, \text{Ag}, \text{Au}$) react with the dirhodium complex $[\text{Rh}_2(\mu\text{-din})(\text{CO})_2(\text{PPh}_3)_2]$ to give trinuclear complexes in which the group 11 metal fragments are attached to both rhodium atoms. However, in this case the initial rhodium compound is a 32-electron compound for which no Rh–Rh bond has to be assumed, whereas compound **1** is a 34-electron complex and the presence of a Ru–Ru bond has to be assumed in order to account for its diamagnetism.

The reactions of CuCl , $[\text{AuCl}(\text{tht})]$ ($\text{tht} = \text{tetrahydrothiophene}$) and AgO_2CCF_3 with complex **1** gave greenish-yellow precipitates of the neutral complexes $[\text{Ru}_2(\mu\text{-L})(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)_2]$ ($\text{L} = \text{CuCl}$ (**6**), AuCl (**7**), AgO_2CCF_3 (**8**)) (Scheme 1). Their IR spectra (Nujol mulls) show the same pattern and similar values for the $\nu(\text{CO})$ absorptions as complexes **4** and **5**, suggesting the formation of trinuclear compounds. The small difference between the values of $\nu_{\text{sym}}(\text{CO}_2)$ (1467 s, cm^{-1}) and $\nu_{\text{asym}}(\text{CO}_2)$ (1673 s, cm^{-1}) for the silver-trifluoroacetate complex indicates that the trifluoroacetate ligand chelates the silver atom through both oxygens [12]. The same coordination mode has been found in the dirhodium-silver complex $[\text{Rh}_2(\mu\text{-AgO}_2\text{CCF}_3)(\text{C}_5\text{H}_5)_2(\mu\text{-CO})(\mu\text{-dppm})]$, which was characterized by X-ray diffraction [13]. Only compound **8** was soluble enough for an NMR study; its $^{31}\text{P}\{^1\text{H}\}$ spectrum shows an apparent doublet at δ 32.6 ppm ($^2J(\text{P}-^{107}\text{Ag}) \approx ^2J(\text{P}-^{109}\text{Ag}) = 39$ Hz) which confirms the triangular structure.

These new compounds (**2–8**) can be regarded as three-centre two-electron bond complexes, in which an empty orbital of the bridging atom accepts electron density from the original Ru–Ru bond.

The reaction of equimolecular amounts of complexes **1** and **7** in the presence of TlPF_6 led to isolation of the pentanuclear compound $[\text{Ru}_4(\mu_4\text{-Au})(\mu\text{-dib})_2(\text{CO})_8(\text{PPh}_3)_4]\text{PF}_6$ (**9**). Care must be taken that the sample of complex **7** used is free from tetrahydrothiophene, which is released during its preparation from complex **1** and $[\text{AuCl}(\text{tht})]$, because the reaction of two moles of complex **1** with $[\text{AuCl}(\text{tht})]$, in the presence of TlPF_6 gave the trinuclear complex $[\text{Ru}_2(\mu\text{-AuPPh}_3)(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)_2]\text{PF}_6$ (**5**) as the only well characterized product. Since this complex contains three PPh_3 ligands, probably the released tetrahydrothiophene displaces one of the PPh_3 ligands from compound **1**, so leading to a mixture of complex **5** and $[\text{Ru}_2(\mu\text{-dib})(\text{CO})_4(\text{PPh}_3)(\text{tht})]$, although the latter could not be obtained pure. The IR spectrum of complex **9** shows three $\nu(\text{CO})$ absorptions at slightly higher wavenumbers than those for **1** (see Experimental). Its $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum is a singlet over the range -50 to 25°C . The analytical and spectroscopic data for **9** led us to propose for this complex the pentanuclear structure shown in Scheme 1, that of a five-centre-four electron bond Ru_4Au cluster. All the attempts to obtain crystals suitable for X-ray analysis were unsuccessful. No clusters of nuclearity higher than three containing copper or silver could be prepared. A cluster

[Ru₂(μ-H)(μ-dib)(CO)₄(PPh₃)₂]BF₄ (2)

Aqueous HBF₄ (0.2 cm³, 32%, 0.7 mmol) was added to a solution of [Ru₂(μ-dib)(CO)₄(PPh₃)₂] · C₆H₅CH₃ (50 mg, 0.048 mmol) in THF (3 cm³) and the mixture stirred for 30 min. Hexane (3 cm³) was added and the yellow solid was filtered off, washed with THF and with hexane, and dried in vacuo (37 mg, 75%). (Found: C, 53.9; H, 3.9; N, 2.6. C₄₆H₃₇BF₄N₂O₄P₂Ru₂ calcd.: C, 53.5; H, 3.6; N, 2.7%.) IR (cm⁻¹): 3320 m, ν(NH) (Nujol); 2066 vs, 2050 m, 2002 vs, ν(CO) (CH₂Cl₂ solution); 1055 vs(br) ν(BF₄) (Nujol). Λ_m(Me₂CO) = 106.51 ohm⁻¹ cm² mol⁻¹. ¹H NMR (Me₂CO-*d*₆): 7.70(m, PPh₃), 5.0(s, 4H, C₆H₄), 4.82(s, br, NH), -8.90(t, *J*(P-H) = 42 Hz, (μ-H)). ³¹P{¹H} NMR (Me₂CO-*d*₆): 37.04(s, RuP).

[Ru₂(μ-NO)(μ-dib)(CO)₄(PPh₃)₂]BF₄ (3)

A solution of NOBF₄ (20 mg, 0.17 mmol) in 3 cm³ of tht was added to a solution of [Ru₂(μ-dib)(CO)₄(PPh₃)₂] · C₆H₅CH₃ (100 mg, 0.096 mmol) in 4 cm³ of dichloromethane. The colour changed from yellow to green as a yellow solid progressively separated. The mixture was stirred for 20 min, and the solid was filtered off, washed with diethyl ether, and vacuum dried (50 mg, 49%). (Found: C, 51.9; H, 3.6; N, 3.7. C₄₆H₃₆BF₄N₃O₅P₂Ru₂ calcd.: C, 52.0; H, 3.4; N, 4.0%.) IR (Nujol, cm⁻¹): 3328 s, ν(NH); 2065 vs, 2048 vs, 2000 vs, 1970 m(sh), ν(CO); 1815 w, ν(NO); 1070 vs, ν(BF₄). The compound is not soluble enough for NMR analysis.

[Ru₂(μ-AgPPh₃)(μ-dib)(CO)₄(PPh₃)₂]BF₄ (4)

AgBF₄ (19 mg, 0.097 mmol) was added to a solution of [Ru₂(μ-dib)(CO)₄(PPh₃)₂] · C₆H₅CH₃ (100 mg, 0.096 mmol) and PPh₃ (26 mg, 0.099 mmol) in THF (10 cm³). A pale yellow precipitate separated. The mixture was stirred for 40 min and the solid was filtered off, washed with diethyl ether (2 × 5 cm³), and vacuum dried (110 mg, 82%). (Found: C, 55.0; H, 3.9; N, 2.1. C₆₄H₅₁AgBF₄N₂O₄P₃Ru₂ calcd.: C, 54.8; H, 3.7; N, 2.0%.) IR (cm⁻¹): 3360 sh, 3340 m, ν(NH) (Nujol); 2013 s, 1993 s, 1948 vs, ν(CO) (CH₂Cl₂ solution). ³¹P{¹H} NMR 34.3 (apparent dd, *J*(P-P) = 38 Hz, *J*(³¹P-¹⁰⁷Ag) ≈ *J*(³¹P-¹⁰⁹Ag) = 55 Hz, (2P, RuP)), 10.4 (br, 1P, AgP). ¹H NMR (Me₂CO-*d*₆): 7.40 (m, PPh₃), 4.88 (m, 4H, C₆H₄), 4.52 (s, br, 2H, NH).

[Ru₂(μ-AuPPh₃)(μ-dib)(CO)₄(PPh₃)₂]PF₆ (5)

[AuCl(PPh₃)] (17 mg, 0.034 mmol) and TlPF₆ (15 mg, 0.043 mmol) were added to a solution of [Ru₂(μ-dib)(CO)₄(PPh₃)₂] · C₆H₅CH₃ (35 mg, 0.034 mmol) in THF (3 cm³) and the mixture was stirred for 1 h. The solution was filtered and hexane (10 cm³) added. After 2 h the yellow precipitate was collected, washed with hexane, and vacuum dried (44 mg, 85%). (Found: C, 51.0; H, 3.8; N, 1.7. C₆₄H₅₁AuF₆N₂O₄P₄Ru₂ calcd.: C, 49.6; H, 3.3; N, 1.8%.) IR (cm⁻¹): 3348 m, ν(NH) (Nujol); 2023 s, 2003 s, 1956 vs, ν(CO) (CH₂Cl₂ solution), 838 s, ν(PF₆) (Nujol). ³¹P{¹H} NMR (Me₂CO-*d*₆): 56.0 (t, 1P, AuP), 37.0 (d, 2P, RuP, *J*(P-P) = 42.7 Hz).

[Ru₂(μ-CuCl)(μ-dib)(CO)₄(PPh₃)₂] (6)

CuCl (5 mg, 0.05 mmol) was added to a solution of [Ru₂(μ-dib)(CO)₄(PPh₃)₂] · C₆H₅CH₃ (50 mg, 0.048 mmol) in THF (3 cm³). The mixture was stirred for 12 h during which a greenish-yellow precipitate was formed. This was filtered off, washed with THF and with hexane, and vacuum dried (45 mg, 90%). (Found: C, 52.7; H,

3.3; N, 2.2. $C_{46}H_{36}ClCuN_2O_4P_2Ru_2$ calcd.: C, 52.9; H, 3.4; N, 2.6%) IR (cm^{-1}): 3290 w, $\nu(NH)$ (Nujol); 2007 s, 1989 s, 1948 vs, $\nu(CO)$ (CH_2Cl_2 solution). The compound is not soluble enough for NMR analysis

[Ru₂(μ -AuCl)(μ -dib)(CO)₄(PPh₃)₂] (7)

[AuCl(tht)] (25 mg, 0.079 mmol) was added to a solution of $[Ru_2(\mu-dib)(CO)_4(PPh_3)_2] \cdot C_6H_5CH_3$ (50 mg, 0.048 mmol) in THF (3 cm^3) and the mixture stirred for 1 h. The greenish-yellow solid formed was washed with THF and vacuum dried (45 mg, 80%). (Found: C, 46.6; H, 3.7; N, 2.1. $C_{46}H_{36}AuClN_2O_4P_2Ru_2$ calcd.: C, 46.9; H, 3.1; N, 2.4%.) IR (cm^{-1}): 3340 vw, 3290 w, $\nu(NH)$ (Nujol); 2012 s, 1998 s, 1957 vs, $\nu(CO)$ (CH_2Cl_2 solution). The compound is not soluble enough for NMR analysis.

[Ru₂(μ -AgO₂CCF₃)(μ -dib)(CO)₄(PPh₃)₂] (8)

A mixture of $[Ru_2(\mu-dib)(CO)_4(PPh_3)_2] \cdot C_6H_5CH_3$ (75 mg, 0.072 mmol), AgO₂CCF₃ (18 mg, 0.08 mmol) and CH_2Cl_2 (5 cm^3) was stirred for 10 min, with protection from light (aluminium foil). Addition of hexane (5 cm^3) afforded a greenish-yellow solid, which was washed with hexane (2 \times 5 cm^3) and vacuum dried (60 mg, 78%). (Found: C, 49.8; H, 3.3; N, 2.2. $C_{48}H_{36}AgF_3N_2O_6P_2Ru_2$ calcd.: C, 49.5; H, 3.1; N, 2.4%.) IR (cm^{-1}): 3354 w, $\nu(NH)$; 1673 vs, 1467 vs, $\nu(CF_3CO_2)$ (Nujol); 2012 s, 1997s, 1959 s, $\nu(CO)$ (CH_2Cl_2 solution). ¹H NMR ($CDCl_3$): 7.30 (m, PPh₃), 4.80 (AA'BB', 4H, C₆H₄), 3.74 (s, 2H, NH). ³¹P{¹H} NMR ($CDCl_3$): 32.6 (apparent d, $J(^{31}P-^{107}Ag) \approx J(^{31}P-^{109}Ag) = 39$ Hz).

[Ru₄(μ_4 -Au)(μ -dib)₂(CO)₈(PPh₃)₄]PF₆ (9)

A mixture of $[Ru_2(\mu-dib)(CO)_4(PPh_3)_2] \cdot C_6H_5CH_3$ (35 mg, 0.034 mmol), $[Ru_2(\mu-AuCl)(\mu-dib)(CO)_4(PPh_3)_2]$ (40 mg, 0.034 mmol), THF (3 cm^3), and TlPF₆ (20 mg, 0.057 mmol) was stirred for 3 h. The solution was filtered and hexane (2 cm^3) was added to give dark-yellow crystals (35 mg). Addition of an excess of hexane to the mother liquor gave a further 25 mg of the crystals (total yield, 73%). (Found: C, 50.3; H, 3.8; N, 2.3. $C_{92}H_{72}AuF_6N_4O_8P_5Ru_4$ calcd.: C, 49.5; H, 3.2; N, 2.5%.) IR (cm^{-1}): 3330 vw, 3280 w, $\nu(NH)$ (Nujol); 2000 vs, 1957 s, 1934 w, $\nu(CO)$ (THF solution); 842 vs, $\nu(PF_6)$ (Nujol). ³¹P{¹H} NMR (Me_2CO-d_6): 40.0 (s, RuP).

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