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Preliminary communication

PYRAZOLATE BRIDGED RUTHENIUM(I) COMPLEXES. A CONVENIENT SYNTHESIS OF RUTHENIUM(I) COMPOUNDS. THE X-RAY STRUCTURE OF BIS-μ-(3,5-DIMETHYLPYRAZOLATE)BIS(TRICARBONYL-RUTHENIUM(I)) (*Ru–Ru*)

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Summary

$RuCl_3 \cdot nH_2O$ reacts with carbon monoxide in boiling 2-methoxyethanol to give a solution which upon treatment with pyrazole-type ligands (HPz) in the presence of zinc and carbon monoxide yields the complexes $[Ru(\mu\text{-Pz})(CO)_3]_2$. This provides an easy high-yield route to ruthenium(I) complexes. In the crystal structure of $[Ru(\mu\text{-dpmz})(CO)_3]_2$ (dpmz = 3,5-dimethylpyrazolate) the Ru_2N_4 framework adopts a boat conformation with a Ru–Ru distance of 2.705(2) Å.

Although the first ruthenium(I) compound $[RuCp(CO)_2]_2$ was reported in 1962 [1], relatively few complexes with ruthenium in this oxidation state compared with those for ruthenium(II) or ruthenium(III) [2,3] have appeared. The relative lack of attention to ruthenium(I) compounds may be due to the non-availability of a good general synthetic method. Apart from $[RuCp(CO)_2]_2$ [4] and carboxylate complexes of the type $[Ru(\mu\text{-RCO}_2)(CO)_2(L)]_2$ [5], whose syntheses are well established, most of the other known ruthenium(I) compounds were obtained in low yields, generally as by-products of reactions of $Ru_3(CO)_{12}$ or other triruthenium clusters [2,3a,6], or were made by use of special ligands; e.g. the complexes $[Ru(\mu\text{-Cl})(CO)_2(PR_3)]_2$ can only be obtained using phosphines containing at least two t-butyl groups [7]. Dinuclear ruthenium(I) complexes have, however, been postulated as intermediates in some homogeneously catalysed reactions [8].

In view of the ability of pyrazolates to act as strongly bound yet flexible bridging ligands capable of maintaining two metal fragments in close proximity, both within and beyond the requirements of metal–metal interactions [9–11] we decided to try to make complexes containing the $Ru_2(\mu\text{-Pz})_2$ framework. We also had in mind

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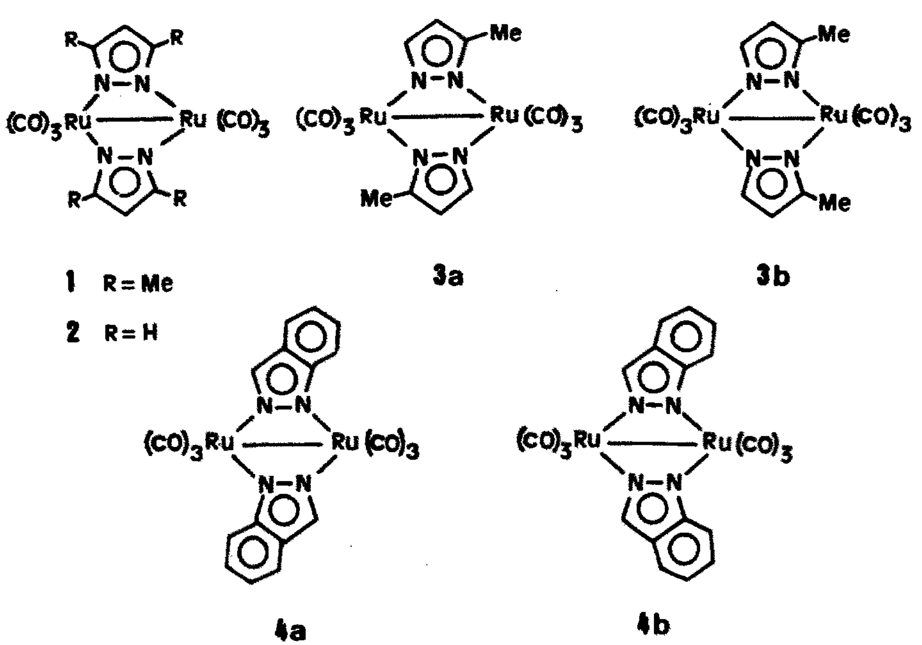

SCHEME 1

that there are very few pyrazolate complexes of ruthenium [11–13], and none at all of ruthenium(I).

It is well known that the yellow solution prepared by treating $RuCl_3 \cdot nH_2O$ with carbon monoxide in refluxing 2-methoxyethanol is a good source of mononuclear ruthenium(II) carbonyl compounds [2,3,14], and that zinc reduction of the mixture of chlorocarbonyl species contained in that solution produces $Ru_3(CO)_{12}$ [15]. We thus carried out the zinc reduction of the yellow solution in the presence of carbon monoxide and pyrazole-type (HPz) ligands in order to examine the ability of these ligands to trap the ruthenium(I) intermediates in the reduction. We obtained medium to excellent yields of the white or pale-yellow, air-stable, ruthenium(I) complexes **1** (85%), **2** (56%), **3** (81%), and **4** (74%) (see Scheme 1). Interestingly they do not lose carbon monoxide (even under vacuum), in contrast to the analogous carboxylate complexes $[Ru(\mu\text{-}RCO_2)(CO)_3]_2$ which undergo spontaneous decarbonylation to give polymeric $[Ru(\mu\text{-}RCO_2)(CO)_2]_n$ [5].

The new complexes were characterized by microanalysis, molecular weight measurements, and ^1H NMR and IR spectroscopy *. Their ^1H NMR spectra are as

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* All compounds gave satisfactory microanalyses (C,H,N) and molecular weights (osmometrically in chloroform). ^1H NMR (200 MHz, δ, ppm): **1** ($CDCl_3$): 5.60 (s, 1H), 2.10 (s, 6H); **2** ($CDCl_3$): 7.19 (d, J 2.1 Hz, 2H), 6.07 (t, J 2.1, 1H); **3a**+**3b** ($(CD_3)_2CO$): 7.10 (d, J 1.9 Hz, 1H), 7.08 (d, J 1.9 Hz, 1H), 5.76 (virtual t, J 1.9 Hz, 2H), 2.10 (s, 6H); **4** ($CDCl_3$), only the peaks of the major component of the mixture are given since most of those of the minor component are overlapped with them: 7.80 (d, J 1.0 Hz, 1H), 7.57 (dt, J 7.6, 1.0 Hz, 1H), 7.53 (dd, J 8.7, 1.0 Hz, 1H), 7.28 (ddd, J 8.7, 7.7, 1.0 Hz, 1H), 7.00 (ddd, J 7.7, 7.6, 1.0 Hz, 1H). ν(CO) (hexane, cm^{-1}): **1**: 2089m, 2057s, 2013vs, 1998m(sh), 1971w, 1964w; **2**: 2094m, 2063s, 2018vs, 2005m(sh), 1982w, 1969w; **3**, 2091m, 2059s, 2015vs, 2001m(sh), 1982w, 1966w; **4**, 2094s, 2066s, 2019vs, 2006m(sh), 1972w, 1953w.

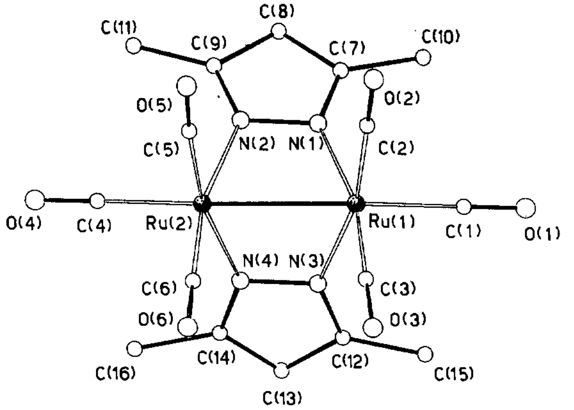

Fig. 1. View of the structure of the complex $[Ru(\mu\text{-dmpz})(CO)_3]_2$ (1) with the atomic numbering scheme. Important bond distances (Å): Ru(1)–Ru(2) 2.705(2), Ru(1)–N(1) 2.071(8), Ru(1)–N(3) 2.090(13), Ru(2)–N(2) 2.081(8), Ru(2)–N(4) 2.088(11), Ru(1)–C(1), 1.93(2), Ru(1)–C(2) 1.87(2), Ru(1)–C(3) 1.84 (2), Ru(2)–C(4) 1.97(2), Ru(2)–C(5) 1.84(2), Ru(2)–C(6) 1.87(2).

expected, those of complexes **3** and **4** showing the presence of the two possible isomers **a** and **b** (see Scheme 1) in a 1/1 ratio for complex **3** and a 4.6/1 ratio for complex **4**, but we cannot say whether **4a** or **4b** is the major component of the mixture. All the complexes show the same pattern of carbonyl absorptions in their IR spectra, with no differences between the spectra of isomers **a** and **b**.

We also tried the reaction of $Ru_3(CO)_{12}$ with various amounts of pyrazole-type ligands, but only in the case of 3,5-dimethylpyrazole (Hdmpz), and using a 1/3 mole did we obtain a complex of the type $[Ru(\mu\text{-dpmz})(CO)_3]_2$ (**1**) (80% yield, after column chromatography on silica gel to separate it from some unchanged $Ru_3(CO)_{12}$ and the new compound $Ru_3(\mu\text{-dmpz})(\mu\text{-H})(CO)_{10}$ (6%) *). When other pyrazoles (pyrazole, 3-methylpyrazole or indazole) were used mixtures of $Ru_3(CO)_{12}$, $[Ru(\mu\text{-Pz})(CO)_3]_2$ and $Ru_3(\mu\text{-Pz})(\mu\text{-H})(CO)_{10}$, in various proportions were recognised as products by IR and ^1H NMR spectroscopy, but they were not isolated.

The structure of complex **1** was determined by X-ray diffraction ** and is shown in Fig. 1. Two ruthenium atoms, at a distance of 2.705(2) Å, consistent with a metal–metal bond, are doubly bridged by two 3,5-dimethylpyrazolate ligands coor-

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* $Ru_3(\mu\text{-dmpz})(\mu\text{-H})(CO)_{10}$: ^1H NMR (200 MHz, $CDCl_3$, δ, ppm): 5.66 (s, 1H), 1.98 (s, 6H), −13.28 (s, 1H). IR: ν(CO), hexane, cm^{-1}): 2102w, 2063s, 2052s, 2035m(sh), 2020s, 2007m, 1993m(sh).

** Crystal data for **1**: $C_{16}H_{14}N_4O_6Ru_2$, $M = 560.45$, monoclinic, space group $P2_1/n$, a 15.388(7), b 10.497(5), c 13.706(5) Å, β 110.32(2)°, V 2076(2) Å^3, $Z = 4$, D_c 1.793 g cm^{-3}, $F(000) = 1096$, λ 0.71069 Å, μ(Mo-K_α) 14.64 cm^{-1}. The intensities of 3773 independent reflections were collected on a Siemens AED diffractometer (with θ in the range 3–25°) using the $\theta/2\theta$ scan technique and the Nb-filtered Mo-K_α radiation. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares on the basis of 1987 observed reflections $[I > 2\sigma(I)]$ with anisotropical thermal parameters for the non hydrogen atoms. All hydrogen atoms were placed at their geometrically calculated positions and introduced in the final structure factor calculation. Final R and R_w values 0.056 and 0.069. The atomic coordinates for this work are available on request from the authors or from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by full literature citation for this communication.

dinated through their nitrogen atoms. Each Ru atom is in an octahedral arrangement, being bonded to three carbon atoms from terminal carbonyls, the other Ru atom, and two nitrogen atoms from two bridging ligands. The Ru–Ru distance is comparable with those found in other binuclear Ru^I–Ru^I complexes with bridging ligands, such as $[Ru(\mu\text{-}Br)(CO)_2(PBu^t_3)]_2$, 2.672 (2) Å [7c], and $[Ru(\mu\text{-}C_3H_7CO_2)$-$(CO)_2(PBu^t_3]_2$, 2.728(1) Å [7d], but is longer than that found in $\{Ru(\mu\text{-}Cl)(CO)_2$-$[PBu^t_2(p\text{-}tol)]\}_2$, 2.632 Å [7a]. The two pyrazolate rings are nearly orthogonal, the dihedral angle between them being 94.4(4)°. The Ru_2N_4 framework adopts a boat conformation, with the Ru(1) and Ru(2) atoms 1.38 Å above the mean plane through the four nitrogen atoms and a dihedral angle of 91.3(2)° between the mean planes through Ru(1),Ru(2),N(1),N(2) and Ru(1),Ru(2),N(3),N(4).

This work has provided a new route to ruthenium(I) complexes starting from $RuCl_3 \cdot nH_2O$, the cheapest starting material for ruthenium compounds, and has also extended the chemistry of the pyrazolate ligands. The synthetic strategy reported in this communication may have wider implications for the preparation of ruthenium(I) complexes with other binucleating ligands, a possibility that we are now investigating. Further work on the reactivity of these dinuclear ruthenium(I) complexes is in progress.

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Note added in proof: After submission of this manuscript Bruce et al. have published the isolation of the trinuclear complexes $Ru_3(\mu\text{-Pz})(\mu\text{-H})(CO)_{10}$ (Pz = pz, dmpz, $3,5\text{-}(CF_3)_2pz$) from reactions of $Ru_3(CO)_{12}$ with the appropriate pyrazole ligands in a 1/1, $Ru_3(CO)_{12}$/HPz mole ratio: M.I. Bruce, M.G. Humphrey, M.R. Snow, E.R.T. Tiekink and R.C. Wallis, J. Organomet. Chem., 314 (1986) 311.

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