

Preliminary Communication

A dinuclear triple bonded Ru–Ru compound: preparation and crystal structure of μ, μ' -1,2-phenylenediimine-(*N,N'*)-dicarbonylbis(triphenylphosphine)diruthenium(Ru–Ru) (I)

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Abstract

Reaction of $[\text{Ru}\{1,2\text{-C}_6\text{H}_4(\text{NH})_2\}(\text{PPh}_3)_3]$ (**1**) with CO in toluene at room temperature affords as one of the products the dinuclear complex *syn*- $[\text{Ru}_2\{\mu\text{-}1,2\text{-C}_6\text{H}_4(\text{NH})_2\}(\text{CO})_2(\text{PPh}_3)_2]$ (**2**). The crystal structure of **2** reveals it to be an unsaturated bimetallic species, with two $\text{Ru}(\text{CO})(\text{PPh}_3)$ moieties bridged by an $8e^-$ donor η^2 -diimine ligand in a tetrahedral-like fashion and involving a triple Ru–Ru bond.

The diimino ligand, $1,2\text{-C}_6\text{H}_4(\text{NH})_2$, when bonded through its N atoms can only be a four-electron donor when neutral, a six-electron donor when monoanionic, and an eight-electron donor when dianionic [1]. For σ -N bonded diimine ligands three possible coordination modes are shown in Fig. 1. Mode A is that usually found in transition metal complexes with 1,2-diimines, including some ruthenium compounds [2]. Mode B is known for some dinuclear compounds of Mo, Fe, and Ru [3,4], and the diimine bridge can further coordinate through C–C or C–N bonds [5]. Bridging mode C is found in compounds of silicon [6].

Dinuclear ruthenium complexes with a metal–metal bond order 2 or 3 with ligands other than carboxylates are scarce [7], the metal usually being in oxidation state +2 or +3 [8,9]. We now report the synthesis and X-ray structure of the first species with a Ru_2^{2+} core and a triple Ru–Ru bond bridged by 1,2-phenylenediimine showing the coordination mode B. This is the first species in which $1,2\text{-C}_6\text{H}_4(\text{NH})_2^{2-}$ bridges two metal atoms.

When CO is bubbled through a solution of $[\text{Ru}\{1,2\text{-C}_6\text{H}_4(\text{NH})_2\}(\text{PPh}_3)_3]$ (**1**) (2.5 g) in toluene (30 cm^3) at room temperature for 4 h, the crystalline complex

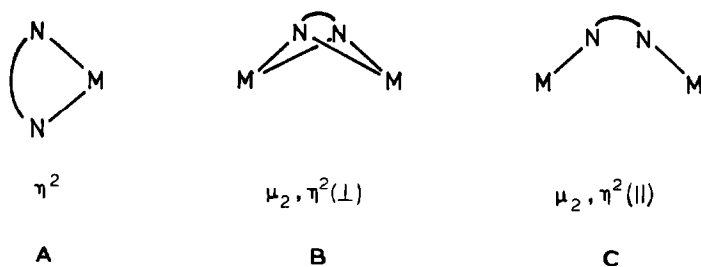


Fig. 1

[Ru{1,2-C₆H₄(NH)₂}₂](CO)(PPh₃)₂] (**2**) is obtained as the main product upon addition of light petroleum. When the reaction solution is chromatographed on an Al₂O₃ column (Brockmann activity II) and eluted with toluene, other compounds can be isolated in low yields: [Ru₂{μ-1,2-C₆H₄(NH)₂}₂](CO)₂(PPh₃)₂] (**2**) (15%, yellow fraction), [Ru{1,2-C₆H₄(NH)₂}₂](CO)₂(PPh₃)₂] (10%) and [Ru(CO)₃(PPh₃)₂] (5%). Compound **2**, an air stable yellow solid, was recrystallized from a toluene/light petroleum solution at room temperature and one of the crystals so obtained was used for the X-ray structural study.

Crystal data: (**2**) C₄₄H₃₆N₂O₂P₂Ru₂ · C₇H₈, *M* = 981.01, monoclinic, space group *P*2₁/*m*, *a* 10.502(2), *b* 25.443(4), *c* 10.011(2) Å, β 114.60(2)°, *Z* = 2, *V* 2432(1) Å³, *D*_x 1.339 g cm⁻³, λ(Mo-K_α) 0.71069 Å, μ(Mo-K_α) 7.10 cm⁻¹. Room temperature.

A Philips PW-1100 four circle diffractometer was employed. The unit-cell parameters were determined from 25 reflections and refined by least-squares. Intensities were collected with graphite monochromatized Mo-K_α radiation, using the ω-scan technique, scan width 1° and scan speed 0.03° s⁻¹. Three intensities checked every two hours showed no significant variations. 6032 reflections were measured in the range 2 ≤ θ ≤ 30° and 5000 were taken as observed by applying the condition *I* ≥ 2.5σ(*I*). Lorentz-polarization, but not absorption, corrections were made.

The structure was solved by direct methods, using the MULTAN system of computer programs. An E-map gave the positions of 10 heaviest atoms, and the remaining non-hydrogen atoms were located using the DIRDIF system. The structure was refined isotropically and anisotropically by full-matrix least-squares method, using the SHELX76 computer program. The function minimized was *w* ||*F*_o|| - ||*F*_c||², where *w* = (σ²(*F*_o) + 0.0104 ||*F*_o||²)⁻¹, *f*, *f*', and *f*'' were taken from International Tables of X-ray Crystallography. The position of 15 H atoms was computed and refined with an overall isotropic temperature factor, and anisotropically the remaining atoms. The final *R* factor was 0.068 (*R*_w = 0.082) for all observed reflections*.

The molecular structure of complex **2** is shown in Fig. 2, together with the most significant bond lengths and angles.

The diimine ligand bridging the two ruthenium atoms is planar and in the symmetry plane of the molecule; it can be regarded as in its dianionic form, in accord with the values of the C-C bond lengths, which lie between 1.377(12) and

* The authors will deposit a table of atomic coordinates and a full list of bond lengths and angles with the Cambridge Crystallographic Data Centre.

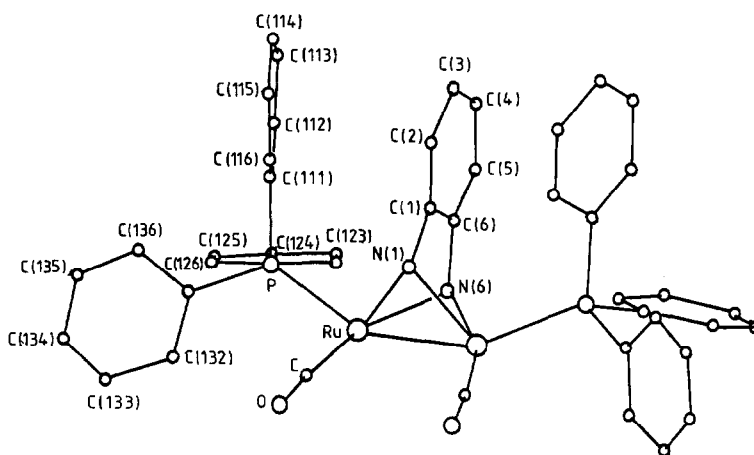


Fig. 2. The structure of $[\text{Ru}_2\{\mu\text{-}1,2\text{-C}_6\text{H}_4(\text{NH})_2\}(\text{CO})_2(\text{PPh}_3)_2]$ (**2**). Selected bond lengths (Å) and angles (°): Ru–Ru, 2.559(1); Ru–C, 1.858(5); Ru–N(1), 2.145(4); Ru–N(6), 2.156(4); Ru–P, 2.369(1); C–O, 1.120(7); N(1)–C(1), 1.396(10); N(6)–C(6), 1.467(9); C(1)–C(2), 1.393(10); C(2)–C(3), 1.445(15); C(3)–C(4), 1.420(11); C(4)–C(5), 1.392(13); C(5)–C(6), 1.377(12); C(1)–C(6), 1.461(7); Ru–N(1)–Ru, 73.26(2); N(1)–Ru–N(6), 69.41(1); Ru–C–O, 175.44(5); C–Ru–N(1), 97.56(2); C–Ru–N(6), 156.74(2); C–Ru–P, 98.23(1). Dihedral angle between two N_2Ru planes, 120.9(1).

1.461(7) Å, close to those in aromatic compounds [10]. This implies a +1 oxidation state for each ruthenium atom.

The C–N lengths, 1.396(10) and 1.467(9) Å, are consistent with single bonds; the difference of 0.071 Å between both C–N bonds is ascribed to the fact that N(6) lies *trans* to CO which strengthens the $\sigma(\text{Ru}\text{--}\text{N}(6))$ bond and lengthens the C–N(6) distance. The pale colour of compound **2** is also in accord with a dianionic form for diimine ligand, as all other compounds of this ligand in their neutral or mono-anionic forms are dark coloured. In order to complete the valence shells of the ruthenium atoms if the diimine ligand donates 8 electrons a triple bond character has to be assumed for Ru–Ru. This is supported by the short distance, 2.559(1) Å, between the two metal atoms, which is close to that of 2.553 Å for the triple metal–metal bond in $[\text{Ru}_2\text{H}_4\text{N}_2(\text{PPh}_3)_4]$ [11]. Compound **2** is obtained as the *syn*-isomer, which is the only stable structure in the crystalline form and in which the coordination spheres around both ruthenium atoms are least crowded.

Spectroscopic data: The infrared spectrum of solid **2**, in a KBr pellet, shows two $\bar{\nu}(\text{NH})$ bands at 3360w and 3325vw cm^{-1} , and that of a solution shows three bands at 2000vs, 1965m and 1930vs cm^{-1} corresponding to terminal $\bar{\nu}(\text{CO})$, rather than the two bands expected for the *syn*-isomer present in the solid state. This spectrum suggests that more than one isomer is present in solution of the complex in THF or aromatic hydrocarbons, as reported for related compounds [12], and presumably an equilibrium *syn*–*anti* is established. The ^1H NMR spectrum in C_6D_6 solution shows only resonances from aromatic and CH_3 (toluene) protons, those from NH not being accurately detected. The two PPh_3 ligands are equivalent, as indicated by the singlet (at 16.00 ppm relative to external 85% H_3PO_4) in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum at room temperature; this signal showed no splitting when the sample was cooled to 173 K in the hope of revealing the *syn*–*anti* equilibrium.

Reaction with trimethylphosphine. Compound **2** reacts readily with PMe_3 in boiling toluene to give an orange crystalline compound (yield 50%) which analyses for $[\text{Ru}_2\{1,2\text{-C}_6\text{H}_4(\text{NH})_2\}(\text{CO})_2(\text{PMe}_3)_2] \cdot \text{C}_6\text{H}_5\text{CH}_3$ (**3**), and this formulation is consistent with the ^1H NMR spectrum. The IR spectrum of a solid sample in a KBr pellet shows the characteristic absorptions at 3390vw for NH, at 1933vs and 1917vs for CO and at 945vs cm^{-1} for PMe_3 and there are no PPh_3 bands. In toluene solution there is only one $\bar{\nu}(\text{CO})$ at 1935vs cm^{-1} , and two possible structures must be considered: (a) one with the two CO ligands mutually *trans* and bonded to the same ruthenium atom (with both PMe_3 ligands bonded to the other Ru), and (b) the anti-isomer $[\text{Ru}_2(\mu\text{-diimine})(\text{CO})_2(\text{PMe}_3)_2]$, for which one of the expected $\bar{\nu}(\text{CO})$ bands is too weak to be observed. Whatever the structure may be two PMe_3 are equivalent in C_6D_6 solution, which shows only one singlet at 28.08 ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum assignable to coordinated phosphine [7].

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