Journal of Organometallic Chemistry, 342 (1988) C33–C37
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Crystal structure and fluxionality of the chiral cluster $[HRu_3(C{\equiv}CBu^t)(CO)_7(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$). A novel racemization mechanism

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(Received November 20th, 1987)

Abstract

The variable temperature ^1H, ^{13}C and ^{31}P NMR spectra of the complex $[HRu_3(C{\equiv}CBu^t)(CO)_7(dppm)]$ (dppm = $Ph_2PCH_2PPh_2$), which crystallizes as an ordered racemic array of the two enantiomers, reveals a fluxional behaviour induced by the diphosphine, involving racemization via acetylide rotation and concurrent hydride migration.

The production of chiral clusters for asymmetric catalysis is an important goal of modern organometallic chemistry [1]. As the chirality of a cluster must come from its frame and not from a chiral ligand, two main synthetic strategies can in principle be adopted, involving: (a) a building up of heterometallic clusters in which each vertex of the polyhedron bears a different transition metal or main group element [2,3]; (b) a conversion of a homometallic symmetrical species into a chiral cluster via incorporation of suitable ligands [4].

Most of the chiral clusters obtained by routes (a) and (b) exhibit fluxional behaviour which unfortunately causes racemization even on the NMR time scale, so preventing any attempt to resolve the racemic mixture. Thus the heterometallic tetrahedral clusters $[(RC{\equiv}CR')\{CpNiCo(CO)_3\}]$ undergo racemization via formal rotation for the Ni–Co and C≡C bond vectors [3a], whereas the homometallic tetrahedral species $[RCCo_3(CO)_7(arphos)]$ (arphos = $Ph_2AsCH_2CH_2PPh_2$) loses its

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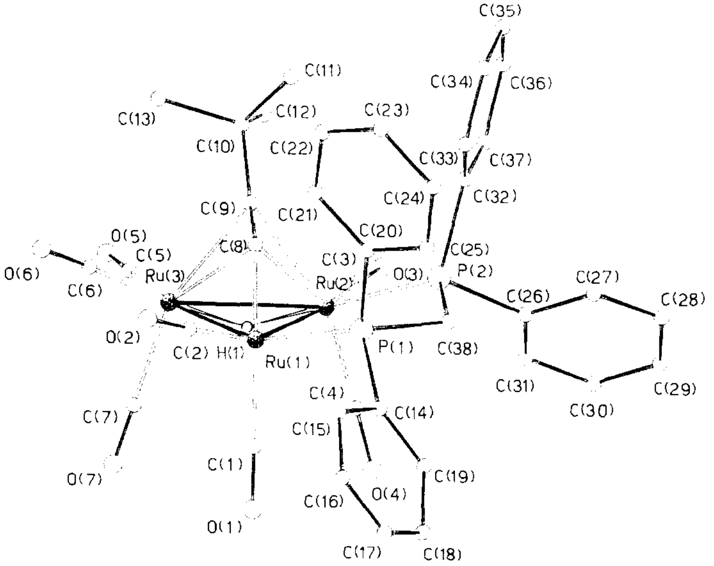

Fig. 1. View of the structure of the complex **1** with the atomic numbering scheme. Selected bond distances (Å): Ru(1)–Ru(2) 2.783(4), Ru(1)–Ru(3) 2.781(3), Ru(2)–Ru(3) 2.787(5), Ru(1)–P(1) 2.266(4), Ru(2)–P(2) 2.303(4), Ru(1)–C(8) 1.964(9), Ru(2)–C(8) 2.197(7), Ru(2)–C(9) 2.309(7), Ru(3)–C(8) 2.215(10), Ru(3)–C(9) 2.286(10), C(8)–C(9) 1.285(12).

stereochemical integrity via migration of the arsenic terminus between cobalt atoms [4b]. Replacement of arphos by $Me_2PCH_2PPh_2$ gives the complex $[RCCo_3(CO)_7(Ph_2PCH_2PMe_2)]$, whose NMR spectrum reveals irreversible coordination of the diphosphine, i.e. the absence of racemization on the NMR time scale [4a].

These results prompted us to synthesize $[HRu_3(CO)_7(dppm)(C_2Bu^t)]$ (**1**) [5*] (starting from $[HRu_3(CO)_9(C_2Bu^t)]$ (**2**), in which the chirality is induced by the bridging diphosphine ligand, with the aim of obtaining a rather rigid chiral system.

The structure of **1**, shown in Fig. 1, was determined by a single crystal X-ray analysis [6 *]. It involves (i) an equilateral triangle of Ru atoms; (ii) seven terminal carbonyls (two bonded to Ru(1) and Ru(2), three bonded to Ru(3)); (iii) a C_2Bu^t ligand interacting with all three metals (in a σ-fashion to Ru(1) and in a π-fashion to Ru(2) and Ru(3)); (iv) a dppm ligand bridging the Ru(1)–Ru(2) edge; and (v) a hydride bridging the Ru(2)–Ru(3) edge. The structure of **1** can be regarded as derived from that of the starting compound **2** [7] by replacement of two equatorial carbonyls on Ru(1) and Ru(2) by the bridging dppm ligand. This substitution leaves the Ru_3C_2 core practically unaltered, excepting that some of the carbonyls and the hydride ligand undergo slight deviations because of the hindrance of the bulky dppm. By virtue of the presence of a glide in the space group *C*2/*c*, both enantiomers are present in the crystal structure.

In solutions of **1** the presence of the diphosphine does, as expected, block the axial-equatorial CO site exchange at Ru(1) (σ-bound to acetylide), which is the

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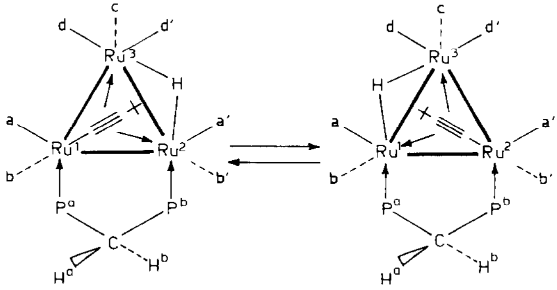
* This and other references marked with asterisks indicate notes occurring in the list of references.

lowest energy independent CO-scrambling process observed both in **2** [8] ($\Delta G^\ddagger$ 13.2 kcal/mol) and in $[HRu_3(CO)_8(PPh_3)(C_2Bu^t)]$ [9] ($\Delta G^\ddagger$ 11.8 kcal/mol). However, the presence of the bridging ligand promotes a new, concentration independent, fluxional behaviour ($\Delta G^\ddagger$ 13.8 kcal/mol or 57.8 kJ/mol, obtained from the ^{31}P coalescence), namely acetylide rotation and the contemporary hydride transfer, as depicted in the scheme. The process, which can be identified from the variable temperature ^{1}H, ^{13}C and ^{31}P NMR spectra, equalizes (see the scheme) P^a and P^b, Ru^1 and Ru^2, the carbonyls a and a′, b and b′, d and d′, but not H^a and H^b, and so leads to racemization of the cluster on the NMR time scale.



Scheme 1. $\Delta G^\ddagger = 13.8$ kcal/mol

The main NMR results are:

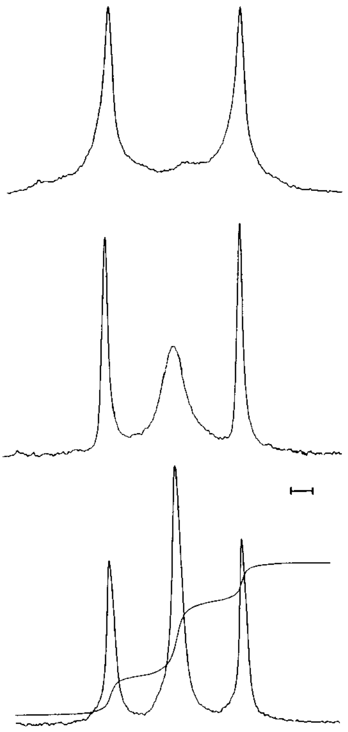


Fig. 2. ^{1}H NMR spectra in the hydride region at various temperatures: from the top to the bottom, 253, 293, 313 K. The bar represents 5 Hz.

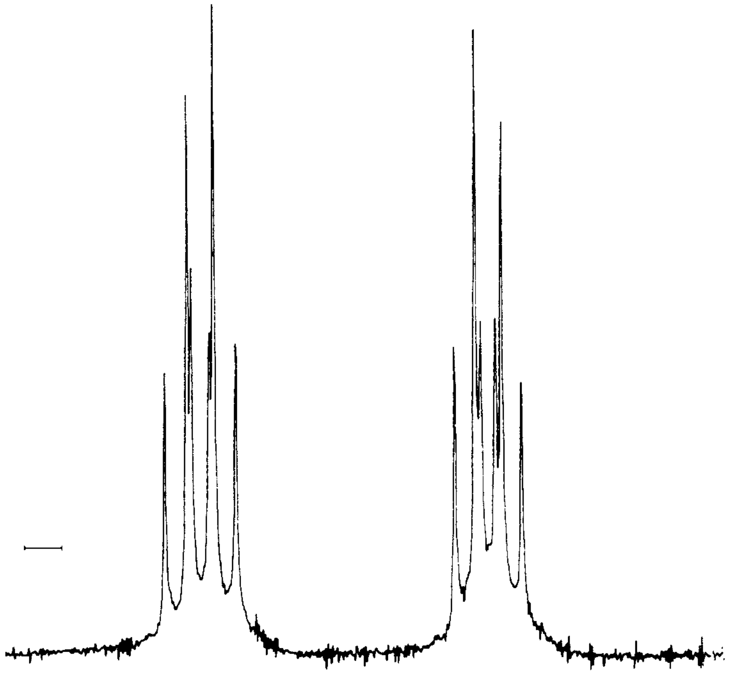


Fig. 3. ^{1}H NMR spectrum in the methylene region at 303 K, emphasizing the non equivalence of H^a and H^b. The bar represents 20 Hz.

(1) The two P atoms, which exhibit a well resolved ^{31}P AB pattern (^2J(PP) 55 Hz, $\Delta\delta$ 519 Hz) at 233 K, become equivalent at 313 K, giving a single peak.

(2) As shown in Fig. 2, the hydride is strongly coupled only with the adjacent phosphorus, giving a doublet at 233 K (ABX system: ^2J(AX) 33, ^4J(BX) 0 Hz). As the temperature is increased and $[\delta(A) - \delta(B)] \rightarrow 0$, the doublet tends to a triplet (A_2X system at 313 K), the observed splitting being $\frac{1}{2}[J(AX) + J(BX)]$ [10*].

(3) The two protons of the methylene bridge of the diphosphine are inequivalent over the range of temperatures examined, giving two doublets of triplets (geminal couplings ^2J(HH) 14, ^2J(HP) 11 and 12 Hz; Fig. 3) and suggesting that the diphosphine is rigidly anchored to one side of the cluster.

(4) The ^{13}C{^{1}H} NMR spectrum at 233 K shows seven doublets (J(PC) 7–17 Hz), corresponding to the seven different carbonyls of the rigid system. These collapse in four broadened peaks at 273 K (intensity ratio 2/2/2/1; this pattern is maintained at 293 K), as required by the proposed fluxional mechanism.

This process, which requires a facile interchange of the σ- and π-bonds between the bridged ruthenium atoms, concerted with hydride transfer, has not to our knowledge been observed previously for an acetylide ligand. Previous reports of similar phenomena on metal triangles involved benzyne [11], alkyne [12], vinylidene [12a,c], or alkenyl [13] ligands. In particular in $[HOs_3(CO)_{10}(PhC{=}CHPh)$ such a σ–π interchange, but without H migration, takes place for the alkenyl ligand, the activation energy being 11.3 kcal/mol [13b].

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5 Experimental: To a stirred solution of **2** (0.2 g, 0.31 mmol) in hexane (50 ml) under N_2 were added dppm (0.2 g, 0.5 mmol) and Me_3NO (0.05 g, 0.67 mmol). After a few minutes, reflux, the solution was filtered and reduced to small volume in vacuo. Unchanged **2** (30%), **1** (50%), and an unidentified orange product were separated by preparative TLC (Kieselgel; light petroleum/ethyl ether). Recrystallization of **1** from hexane/chloroform gave yellow crystals suitable for X-ray analysis. **1** IR (hexane): 2062vs, 2009vs, 1996vs, 1983m, 1958m, 1939m cm^{-1}; NMR ($CDCl_3$; coupling constants are given in the text); ^1H: δ (ppm) at 303 K, 7.65–7.36 (m, 20H, Ph), 4.21 (dt, 1H, CH_2), 3.41 (dt, 1H, CH_2), 0.94 (s, 9H, Me), -19.85 (t, 1H, μ-H); ^{13}C: δ (ppm) at 233 K (carbonyl region, assignments on the basis of the ref. 8 and 9) 191.1 (d′ of the scheme), 192.3 (d), 198.4 (a′), 199.6 (a), 202.3 (c), 206.5 (b′), 207.9 (b); $^{31}P\{^1H\}$: δ (ppm) at 233 K, 30.6 (d, P close to μ-H, unambiguously deduced from $^1H\{^{31}P\}$ spectra), 36.7 (d, P far from μ-H).

6 *Crystal data*: $C_{38}H_{32}O_7P_2Ru_3$ (**1**), $M = 965.82$, monoclinic, space group $C2/c$, a 35.555(12), b 14.023(7), c 20.144(8) Å, β 120.71(3)°, $Z = 8$, V 8635(7) $Å^3$, D_{calc} 1.486 g cm^{-3}, μ(Mo-K_α) 11.29 cm^{-1}. The structural analysis was based on 5190 observed ($I \geqslant 2\sigma(I)$) reflections (8104 unique measured reflections) collected on a Siemens AED diffractometer using Mo-K_α ($\lambda = 0.71069$ Å) radiation with θ in the range 3–26°. The structure was solved by direct and Fourier methods and refined by full-matrix least-squares to R and R_w values of 0.0542 and 0.0715, respectively. All non hydrogen atoms were refined anisotropically. The hydride was located clearly in the ΔF map and refined isotropically; other hydrogen atoms were placed at their geometrically calculated positions and introduced in the final calculations, but not refined. Some residual peaks found in the final ΔF map were attributable to the presence of solvent molecules (probably hexane) disordered and distributed over several positions, so that neither the sure nature of the solvent nor the number of molecules could be determined. All crystal data refer to complex **1** without solvent molecules. A table of atomic coordinates and a complete table of bond angles and distances have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW.

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