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Chelating and bridging behaviour of bidentate P,P or P,As ligands (L–L) in $HRu_3(C{\equiv}CBu^t)(CO)_7(L–L)$ as indicated by ^1H, ^{13}C and ^{31}P NMR spectroscopy

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Abstract

The reactions of the cluster $HRu_3(C{\equiv}CBu^t)(CO)_9$ (**1**) with the bidentate ligands $Ph_2PCH_2CH_2EPh_2$ (E = P, dppe; E = As, dppae), in the presence of Me_3NO, give the complexes $HRu_3(C{\equiv}CBu^t)(CO)_7(Ph_2PCH_2CH_2EPh_2)$, as two isomers, which have been separated by TLC. In the first isomer, the ligand chelates the ruthenium atom opposite to the bridging hydride (1,1-derivative), whereas, in the second, it bridges a hydride-free edge (1,2-derivative). In contrast the rather rigid diphosphine *cis*-$Ph_2PCH{=}CHPPh_2$ (c-dppet) gives only the 1,1-derivative. When chelating, the ligands do not show any significant fluxional behaviour, but when they are bridging there is interconversion between axial and equatorial positions.

Introduction

Symmetrical or asymmetrical bidentate ligands are useful for stabilizing bimetallic and cluster frameworks [1] (relevant to homogeneous catalytic applications involving reversible metal–metal bond cleavage) or for inducing chirality even in suitable homometallic clusters [2,3].

We have recently obtained the cluster $HRu_3(C{\equiv}CBu^t)(CO)_7(\mu\text{-dppm})$ (**4a**), as the only product from the reaction of $HRu_3(C{\equiv}CBu^t)(CO)_9$ (**1**) with dppm (dppm = $Ph_2PCH_2PPh_2$). In this chiral complex **4a**, which crystallizes as an ordered

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racemic array of the two enantiomers, the dppm ligand bridges a Ru–Ru hydride-free edge [3]. In solution, the presence of the diphosphine blocks the axial–equatorial CO site exchange at Ru(1) (σ-bound to the acetylide) as expected, but promotes a new, concentration-independent, fluxional behaviour, involving acetylide rotation and concurrent hydride migration from one phosphine-free edge to the other.

With the aim of examining the effect of the chain length of the diphosphine on the dynamic behaviour in solution and, possibly, of producing chiral clusters not liable to fluxionality, we treated the parent cluster **1** with $Ph_2PCH_2CH_2EPh_2$ (E = P, dppe; E = As, dppae) and with *cis*-$Ph_2PCH{=}CHPPh_2$ (c-dppet), obtaining mono- (**2**) and disubstitution derivatives (**3** and **4**). This paper deals with the synthesis and characterization of these compounds and with their behaviour in solution as revealed by multinuclear NMR spectroscopy.

Whereas dppae and c-dppet are rather unusual ligands in cluster chemistry, dppe has been widely used and has been found to chelate or to bridge metal centers, particularly in ruthenium [4–8] and osmium [9–11] clusters.

Experimental

Synthesis, purification and analysis of the products

Cluster **1** was prepared and purified by established methods [12]. Diphosphines and dppae were commercial products (Strem Chemicals) and were used as received after purity checks. Anhydrous Me_3NO was obtained by sublimation in vacuo of the commercial dihydrate (Fluka). The reactions were performed in conventional three necked flasks equipped with gas inlet and water condenser. Hydrocarbon solvents (C. Erba) were distilled over sodium and reactions were carried out under dry nitrogen. The reaction mixtures were evaporated to small volume under reduced pressure and the products separated on TLC preparative plates (Kieselgel P.F., Merck; eluents: light petroleum and ethyl ether). Attempts to crystallize some of the products from heptane/chloroform mixtures gave crystalline aggregates unsuitable for X-ray diffraction studies.

Elemental analyses were performed with a Perkin–Elmer 204 automatic analyzer (C, H) and a Leeman ICP 2.5 plasma emission spectrometer (P). IR spectra were recorded in NaCl cells on a Perkin–Elmer 580B instrument. Room temperature ^1H and ^{31}P NMR spectra were registered on a Jeol JNM GX 270 FT spectrometer (Torino); variable temperature ^1H, ^{13}C and ^{31}P NMR spectra were recorded on a Bruker CXP 200 FT instrument (Parma). ^{13}C NMR spectra (natural abundance) were obtained for $CDCl_3$ solutions containing ca. 0.05 mol dm^{-3} $Cr(acac)_3$ as shiftless relaxation reagent.

Reaction of 1 with dppe

Treatment of **1** (0.2 g) with a small molar excess of dppe (0.2 g) and Me_3NO (0.05 g) in refluxing heptane (50 ml) for a few minutes gave unchanged **1** (10%), $HRu_3(C{\equiv}CBu^t)(CO)_8$(dppe-*P*) (complex **2b**, 5%), $HRu_3(C{\equiv}CBu^t)(CO)_7$(dppe-*P*,*P*) (**3b**, 30%), $HRu_3(C{\equiv}CBu^t)(CO)_7(\mu$-dppe) (**4b**, 35%), and a little unidentified orange oily product. Complex **2b**, yellow. Found: C, 47.0; H, 3.6. $C_{40}H_{34}O_8P_2Ru_3$ calcd.: C, 47.7; H, 3.4%; IR ν(CO) (hexane/chloroform): 2076s, 2055vs, 2024vs, 2018s and 1975m cm^{-1}; ^1H NMR ($CDCl_3$, room temperature): δ 2.67, 2.00 (m, 4H, $2CH_2$),

Table 1

Characterization data for compounds **3** [a] and **4** [b]

Complex	Color	Analysis [c] (%)			ν(CO) [d] (cm^{-1})	^1H (δ,ppm) [e] J (Hz)	^{31}P(δ,ppm) [f]
		C	H	P			
3b(dppe-*P*,*P*)	dark-yellow	48.3 (47.8)	3.7 (3.5)	6.0 (6.3)	2064s,2044vs 1998vs,1976s	2.72,2.07(m,4H,2CH_2) 1.62(s,9H,Bu^t) −21.40(t,1H,μ-H, ^3J(HP) 1.5)	89.3
3c(dppae-*P*,*As*)	dark-yellow	46.2 (45.7)	3.8 (3.3)	2.7 (3.0)	2062s,2044vs 1999vs,1988s	2.47(m,4H,2CH_2) 1.58(s,9H,Bu^t) −21.31(d,1H,μ-H, ^3J(HP) 1.0)	93.4
3d(c-dppet-*P*,*P*)	dark-yellow	48.5 (47.9)	3.6 (3.3)	6.1 (6.3)	2064s,2044vs 2000vs,1978s	1.25(s,2H,2CH) 1.62(s,9H,Bu^t) −21.32(t,1H,μ-H, ^3J(HP) 1.3)	94.0
4b(μ-dppe)	dark-yellow	47.4 (47.8)	3.1 (3.5)	5.1 (6.3)	2065vs,2044m 2018vs, 2014m(sh) 1999vs,1988m 1958m,1939m	2.76(m,4H,2CH_2) 1.57(s,9H,Bu^t)	
Equatorial isomer (45%) [h]						−20.41(dd,1H,μ-H) [g] ^2J(HP) 35.0, ^3J(HP) 1.6	56.4 [g] 35.5
Axial isomer (55%) [h]						−20.89(dd,1H,μ-H) [g] ^2J(HP) 6.3, ^3J(HP) 1.1	60.2 [g] 42.8
4c(μ-dppae)	dark-yellow	46.0 (45.7)	3.6 (3.3)	2.8 (3.0)	2065vs,2044m 2014m, 1999vs(br) 1985m(sh), 1959m,1940m	2.65(m,4H,2CH_2) 1.52(s,9H,Bu^t)	
Equatorial isomer (15%) [h]						−20.97(d,1H,μ-H) [g] ^3J(HP) 1.2	54.8 [g]
Axial isomer (85%) [h]						−20.86(d,1H,μ-H) [g] ^3J(HP) 1.0	61.2 [g]

[a] Containing chelating diphosphine. [b] Containing bridging diphosphine. [c] Calculated values are given in parentheses. [d] Hexane/chloroform solution. [e] $CDCl_3$ solution; $SiMe_4$ as internal reference. [f] $CDCl_3$ solution; positive chemical shifts are downfield relative to external 85%-H_3PO_4. [g] 233 K. [h] See discussion.

1.42 (s, 9H, Bu^t), −21.19 (d, 1H, μ-H, ^3J(HP) 1.5 Hz). Characterization data for **3b** and **4b** are given in Table 1.

Reaction of ***1*** *with dppae*

Use of the procedure described above gave the following products: unchanged **1** (20%), a mixture of $HRu_3(C{\equiv}CBu^t)(CO)_8$(dppae-*P*), and $HRu_3(C{\equiv}CBu^t)(CO)_8$-(dppae-*As*) (complexes **2c** and **2c′**, 5%), $HRu_3(C{\equiv}CBu^t)(CO)_7$(dppae-P,As) (**3c**, 20%), $HRu_3(C{\equiv}CBu^t)(CO)_7$($\mu$-dppae) (**4c**, 30%), and two unidentified yellow compounds. Solid mixture of **2c** and **2c′**, yellow. Found: C, 46.2; H, 3.5. $C_{40}H_{34}AsO_8PRu_3$ calcd.: C, 45.7; H, 3.3%; IR ν(CO) (hexane/chloroform): 2077s, 2054vs, 2018vs, 2008s and 1974m cm^{-1}; ^1H NMR ($CDCl_3$, room temperature): δ 2.13, 2.02 (m, 4H, 2CH_2), 1.29 and 1.31 (s, 9H, Bu^t), −21.19 (s) and −21.21 (d, ^3J(HP) 1.2 Hz)(1H, μ-H). Characterization data for **3c** and **4c** are given in Table 1.

Reaction of 1 with c-dppet

The same procedure gave the following: unchanged **1** (5%), $HRu_3(C{\equiv}CBu^t)(CO)_7$(c-dppet-*P*,*P*) (**3d**, 40%) and an unidentified pink derivative. Characterization data for **3d** are given in Table 1.

Reaction of 1 with t-dppet

Treatment of **1** with *trans*-bis(diphenylphosphino)ethylene (t-dppet) under the same conditions gave unchanged **1** (15%), $HRu_3(C{\equiv}CBu^t)(CO)_8$(t-dppet-*P*) (**2e**, 5%) and an unidentified red derivative. Complex **2e**, yellow: Found: C, 48.2; H, 3.6. $C_{40}H_{32}O_8P_2Ru_3$ calcd.: C, 47.8; H, 3.2%; IR ν(CO) (hexane/chloroform): at 2070s, 2055vs, 2014vs, 2006s and 1972m cm^{-1}; ^1H NMR ($CDCl_3$, room temperature): δ 1.56 (m, 2H, 2CH), 1.27 (s, 9H, Bu^t), −20.80 (broad, 1H, μ-H).

Results and discussion

The reactions of complex **1** with $Ph_2PCH_2CH_2EPh_2$ (E = P, dppe; E = As, dppae) give the bridged complexes **4** (1,2-derivatives) as the major products along with the chelate complexes **3** and trace amounts of the complexes **2** in which the ligands are monodentate. The suggested structures of compounds **3** and **4** are shown in Fig. 1. Table 1 shows the characterization data for complexes **3** and **4**; corresponding data for **2** are presented in the Experimental section.

In complexes **2** (obtained in low yields also with t-dppet), one donor atom of the ligands must be coordinated to Ru(1) (σ-bound to the acetylide) in view of the similarity of the IR spectra with those of well established $HRu_3(C{\equiv}CBu^t)(CO)_8(L)$ derivatives [13–15]. Moreover the low ^1H–^{31}P coupling constants for coupling between the bridging hydride and the coordinating P are typical of an interaction through three bonds [13].

In complexes **3**, which can be obtained also with c-dppet as ligand, the bidentate ligands chelate the Ru(1) atom of the species depicted in Fig. 1. Supporting evidence for the chelating behaviour comes from the appearance of weakly P-coupled hydride signals (a triplet for dppe and c-dppet and a doublet for dppae) and low-field singlets in the ^{31}P NMR spectra. The large downfield shifts exhibited by these complexes must be a consequence of the formation of five-membered chelate rings [16].

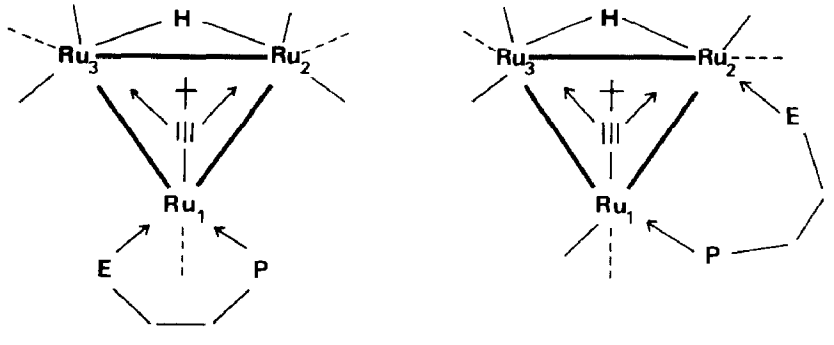

Fig. 1. Outline structure of compounds **3** (1,1-derivative) and **4** (1,2-derivative); P = PPh_2, E = $AsPh_2$ or PPh_2; — — — axial positions, ——— equatorial positions (carbonyls are omitted).

In terms of this view the chelating ligands must occupy two equivalent equatorial positions, thus maintaining, in the case of dppe and c-dppet, the symmetry plane perpendicular to the metal triangle. The ^{13}C NMR spectrum of **3b**, recorded at 233 K, shows four peaks at 207.9, 203.9, 194.2 and 193.6 ppm, in the intensity ratio 1/2/2/2, as required for the suggested structure. The highest frequency resonance is easily assigned to the unique axial CO on Ru(1), whereas the equivalent axial CO's on Ru(2) and Ru(3) are probably responsible for the peak at 203.9 ppm, in view of the fact that, in this type of complexes, the axial ^{13}CO shift is generally downfield from the equatorial one at a given metal atom [13]. Consequently the other two peaks are attributable to the two pairs of equatorial CO's on Ru(2) and Ru(3). As the temperature is raised to 303 K the three two-carbonyl resonances merge into a broad band, indicating the onset of axial–equatorial exchange at Ru(2) and Ru(3), while the one-carbonyl high-frequency peak remains unchanged.

The complex **3c** exhibits very similar behaviour: the only difference consists in the appearance of additional resonances arising from the inherent asymmetry of the chelating ligand dppae, which makes this chelate compound chiral. The low-temperature limiting spectrum (233 K) shows peaks at 208.0 (axial Ru(1)), 203.9, 203.7 (axial Ru(2) and Ru(3)), 194.1, 193.5, 192.8 (equatorial Ru(2) and Ru(3)).

A bridged structure is suggested for complexes **4**, as shown in Fig. 1 (1,2-derivative). Only one isomer is depicted in this scheme (the equatorial one), but there is spectroscopic evidence for the presence in solution of the axial isomer also. In fact, as indicated in the table, both **4b** and **4c** show two sets of signals in the ^1H and ^{31}P spectra, at 233 K. As the temperature is raised to 313 K the peaks broaden, without reaching coalescence, and the peak area ratios remain virtually unchanged. In the case of 1,2-dppe derivative **4b**, whose ^1H NMR spectrum in the hydride region is shown in Fig. 2, the first set of signals in the table (the left hand peaks in Fig. 2) is attributed to the equatorial isomer, which possesses a *trans*-H–Ru–P configuration, responsible for the rather high value of $^2J(HP)$. Whereas the existence of equatorial/axial isomerism at Ru(2) seems likely in the light of the $^2J(HP)$ values, this is not possible for Ru(1); nevertheless, since in these compounds the localized scrambling on Ru(1) has a lower activation barrier [13], it is reasonable to think that when P on Ru(1) moves to the axial position it pulls along the other P on Ru(2).

The low values of $J(HP)$ found for the 1,2-dppae derivative **4c** clearly indicate that phosphorus is bound to the ruthenium atom opposite to the hydride. No appreciable amounts of the other isomer were obtained. The attribution of the

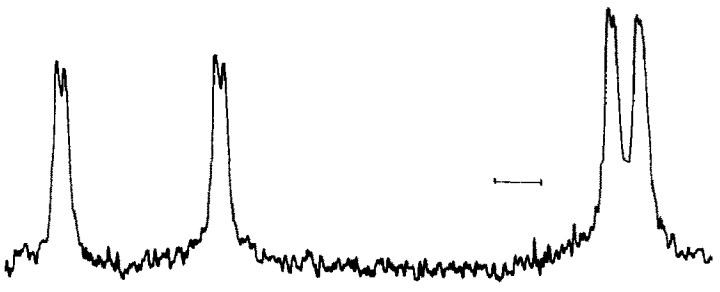

Fig. 2. ^1H NMR spectrum in the hydride region for of **4b** (1,2-dppe derivative) at 233 K. The bar represent 10 Hz.

equatorial/axial isomers of **4c** was made by comparing the ^{31}P chemical shifts with those of **4b**.

The ^{13}C NMR spectra of **4b** and **4c** are not particularly revealing; they present four sets of partially overlapping peaks, practically unaffected by temperature (from 233 to 303 K). In the case of **4c**, for which the axial isomer predominates (85%), the spectrum is less complicated and the peaks (or groups of peaks) are at 205.4, 201.8, 197.0 and 192.3 ppm, the integration ratios being 1/2/2/2.

We conclude that the length and the shape of the chains in these bidentate P,P or P,As ligands strongly influence their coordinative ability towards the cluster used. Thus whereas dppm [3] gives only the 1,2-isomer and, while remaining rigidly anchored at the equatorial positions (short chain), promotes acetylide fluxionality, both dppe and dppae give the chelate 1,1- and the bridged 1,2-derivatives, and when bridging are involved in localized scrambling processes by virtue of the length and the flexibility of their chains. In contrast, the rather rigid chain of c-dppet causes this ligand to form only the 1,1-derivative.

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