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LETTER

Synthesis and solution state of $[(\mu\text{-dppf})(Cu(dppf))_2]X_2$ (dppf = 1,1′-bis(diphenylphosphino)ferrocene; $X = ClO_4^-$, BF_4^-)

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We have recently shown [1] that 1,1′-bis(diphenylphosphino)ferrocene (dppf) possesses a remarkable geometric flexibility in homoleptic Rh^I and Ir^I complexes, when they are dissolved in polar solvents. In particular, ^{31}P NMR data in CD_2Cl_2 revealed that dppf can act as a chelating and bridging ligand in the same molecular entity, with fast mutual interconversion of the two ligating modes.

The bridging ligating ability of dppf, albeit not common in its coordination chemistry, has been documented for $(\mu\text{-dppf})Au_2Cl_2$ [2] and for $(\mu\text{-dppf})[Mo(CO)_5]_2$ [3] on the basis of crystallographic data.

We report here on the synthesis and solution state of the title complexes, **1**, in which dppf behaves simultaneously as a chelating and a bridging ligand. The solid state molecular structure of its ClO_4^- salt is proven by X-ray single crystal analysis, as we have already preliminarily established [4].

Complexes **1** are prepared from $[Cu(CH_3CN)_4]X$ upon ligand displacement with excess of dppf in chlorinated solvents. The yield is essentially quantitative and the products, characterized by C, H, Fe and Cu elemental analyses, are obtained as yellow microcrystalline powders.

The $^{31}P\{^1H\}$ NMR spectra of both salts of the dimeric cationic complex display a temperature dependence, which is indicative of a chemical exchange process. In fact, both species exhibit in CD_3NO_2/CH_2Cl_2 (1:1 vol./vol.) at 27 °C a single broad resonance ($\nu_{1/2} = 60$ Hz at 36.23 MHz) centered at δ −7.8 ppm (versus external H_3PO_4 (85% wt./wt.)). Upon cooling, the peak broadens and at −40 °C it gives rise to an AB_2 multiplet centered at δ −6.0 and −8.5 ppm, with J_{PP} equal to 95 Hz. The same spectral behaviour is observed in a saturated nitromethane solution, operating at 80.9 MHz (Fig. 1). In these conditions the limit low-temperature spectrum is observed at −25 °C.

The low-temperature pattern displayed is consistent with the presence of chemically non-equivalent phosphorous ligands, apparently involved in bridging and chelating coordination modes. Thus, the solution state of **1** in nitromethane appears to be in close agreement with the X-ray single crystal structure without any solution-state related complication, previously observed for the related homoleptic complexes $[M(dppf)_2]^+$ (M = Rh, Ir) [1].

As to the exchange mechanism, we suggest that the dimeric complex undergoes at room temperature a very limited dissociation via bridge splitting into two monomeric species (eqn. (1)) able to undergo a kinetically easy mutual interconversion reaction.

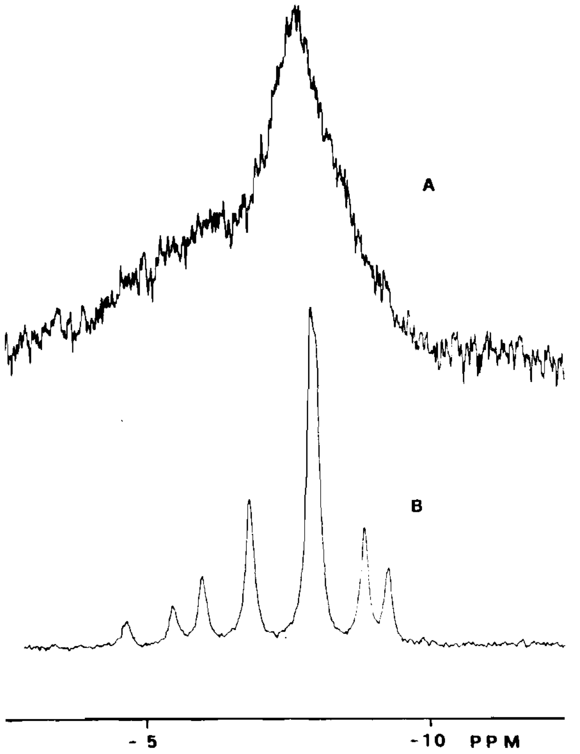

Fig. 1. $^{31}P\{^1H\}$ NMR spectrum at 80.9 MHz of $[(\mu\text{-dppf})(Cu(dppf))_2](BF_4)_2$ in CD_3NO_2: A, at 27 °C; B, at −25 °C.

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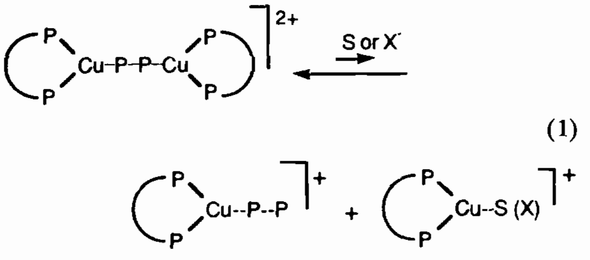

(1)

In view of the known biological antitumor activity of $(CuCl)_2(dppe)_3$ (dppe = 1,2-bis(diphenylphosphino)ethane) [5] and cytostatic activity of dppf against Eagle's KB cell line [6], the activity of **1** was also tested in preliminary experiments. The results appear very promising in that, not only does $[(\mu\text{-dppf})(Cu(dppf))_2](BF_4)_2$ possess an antitumor activity (ID_{50} 0.42 μM) [7] quite similar to that of *cis*-$[Pt(NH_3)_2Cl_2]$ (ID_{50} 0.37 μM), but it is much greater than that of free dppf (ID_{50} 17 μM) and of *cis*-$[Pt(dppf)Cl_2]$ (ID_{50} 61.7 μM) [6]. It is therefore apparent that the ligand and the metal center behave synergically in directing the metal–drug biological interaction. For this reason complexes **1** appear as promising subjects for extensive *in vitro* investigations as well as for bioinorganic work.

Experimental

Syntheses and manipulations of solutions were performed under a nitrogen atmosphere with standard Schlenk-line techniques. All solvents were dried by standard procedures. ^1H and $^{31}P\{^1H\}$ NMR spectra were recorded in CD_3NO_2 or CD_3NO_2/CH_2Cl_2 mixture with a JEOL 90-Q and a Bruker AC 200 spectrometer equipped with a variable temperature apparatus and were referenced to internal $SiMe_4$ and external H_3PO_4 (85% wt./wt.), respectively. 1,1′-Bis(diphenylphosphino)ferrocene(dppf) was from Strem Chemicals and was used as received.

Synthesis of $[Cu(CH_3CN)_4]X$ *(*$X = ClO_4^-$, BF_4^-*)*

$[Cu(H_2O)_6]X_2$, dissolved in anhydrous acetonitrile, was stirred at room temperature with a slight excess of metal copper (as turnings) until the colour of the solution had completely disappeared. The reaction mixture was filtered and the volume of the solution was reduced *in vacuo*. Addition of diethyl ether produced a white precipitate, which was collected by filtration and dried *in vacuo*.

Synthesis of $[(\mu\text{-dppf})(Cu(dppf))_2](BF_4)_2$

$[Cu(CH_3CN)_4]BF_4$ (0.283 g, 0.900 mmol) was added to a stirred solution of dppf (1.000 g, 1.804 mmol) in 1,2-dichloroethane (30 ml) at room temperature. After the reaction mixture became homogeneous, the resulting solution was heated to reflux for 30 min. The orange solution was then allowed to cool down to room temperature and then concentrated in a rotary evaporator to *c.* 10 ml. Upon the addition of toluene (40 ml), the product separated as a yellow powder and was recovered by filtration, washed with toluene, then Et_2O and dried under vacuum. The yield was 0.880 g (95%). The solid contained *c.* one molecule of DCE per molecule of complex as determined by ^1H NMR and confirmed by thermal and elemental analyses. *Anal.* Calc. for $C_{104}H_{88}B_2Cl_2Cu_2F_8Fe_3P_6$: C, 60.55; H, 4.30; Cu, 6.16; Fe, 8.12. Found: C, 60.32; H, 4.33; Cu, 6.10; Fe, 8.07%.

Heating of the solvated solid *in vacuo* at 120 °C to constant weight (*c.* 24 h) removed the crystallization solvent and afforded 0.795 g of pure complex. *Anal.* Calc. for $C_{102}H_{84}B_2Cu_2F_8Fe_3P_6$: C, 62.38; H, 4.31; Cu, 6.47; Fe, 8.53. Found: C, 62.84; H, 4.36; Cu, 6.40; Fe, 8.59%.

Synthesis of $[(\mu\text{-dppf})(Cu(dppf))_2](ClO_4)_2$ *(2)*

A CH_2Cl_2 solution (20 ml) containing dppf (0.540 g, 0.974 mmol) and $[Cu(CH_3CN)_4]ClO_4$ (0.159 g, 0.486 mmol) was stirred at room temperature for 3 h. The resulting orange solution was then evaporated almost to dryness. The oily residue was redissolved in the minimum volume of CH_2Cl_2. Upon addition of toluene and cooling in the refrigerator the product precipitated as a yellow microcrystalline powder. The solid, recovered by filtration, washed with toluene and Et_2O, was dried under vacuum to give 0.490 g of pure product. Orange crystals analysing as $C_{102}H_{84}Cl_2Cu_2Fe_3O_8P_6$ could be obtained upon solvent evaporation from nitromethane solutions. *Anal.* Calc.: C, 61.59; H, 4.26. Found: C, 61.34; H, 4.20%.

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