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Preliminary communication

NOVEL *triangulo*-DIPLATINUM-IRON AND ISOMERIC *triangulo*-PLATINUM-PALLADIUM-IRON COMPLEXES, $[Pt_2Fe(Ph_2PCH_2PPh_2)_2(CO)_4]$ AND $[PtPdFe(Ph_2PCH_2PPh_2)_2(CO)_4]$, AND OTHER RELATED MIXED-METAL CLUSTERS

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Summary

The complexes $[Pt_2Fe(dppm)_2(CO)_4]$ and $[PtPdFe(dppm)_2(CO)_4]$ (dppm = $Ph_2PCH_2PPh_2$) have been prepared by treating $[Pt_2Cl_2(dppm)_2]$ and $[PtPdCl_2(dppm)_2]$, respectively, with $Na_2[Fe(CO)_4]$; the structures of the products in solution were established by ^1H, ^{13}C, ^{31}P and ^{195}Pt NMR spectroscopy, and $[PtPdFe(dppm)_2(CO)_4]$ was shown to exist as an isomeric mixture.

Despite the widespread use of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [1] (dppm = bis(diphenylphosphino)methane) as a reagent for the synthesis of a wide range of complexes [2], only two mixed-metal complexes based upon the dimeric platinum skeleton $\{Pt_2(dppm)_2\}$ have been reported, viz. $[Pt_2(SnCl_3)_2(\mu\text{-dppm})_2]$ and $[Pt_2Cl(SnCl_3)(\mu\text{-dppm})_2]$ [3]. Braunstein's recent report [4] of the reaction between $[Pd_2Cl_2(\mu\text{-dppm})_2]$ and $Na[Mn(CO)_5]$ to yield the complex $[Pd_2Mn_2(dppm)_2(CO)_9]$ (1), which possesses a *triangulo*-Pd_2Mn skeleton with a terminal $\{Mn(CO)_5\}$ group pendant upon one of the palladium atoms, prompts us to report the results of our study of the reactions of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ [1] or $[PtPdCl_2(\mu\text{-dppm})_2]$ [5] with $Na_2[Fe(CO)_4]$.

Treatment of $[Pt_2Cl_2(\mu\text{-dppm})_2]$ with $Na_2[Fe(CO)_4]\cdot 1.5C_4H_8O_2$ in tetrahydrofuran produced red crystals of $[Pt_2Fe(dppm)_2(CO)_4]$ in better than 80% yield. Multinuclear (^1H, ^{13}C, ^{31}P and ^{195}Pt) magnetic resonance spectroscopic

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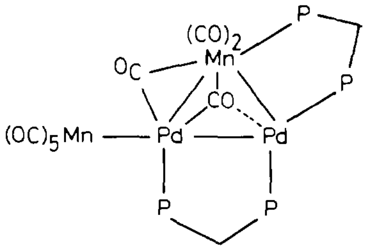
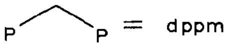
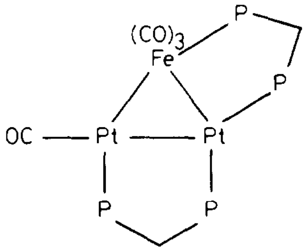
studies of this complex in CD_2Cl_2 or tetrahydrofuran solution unambiguously establish its structure as **2**, as will be demonstrated.



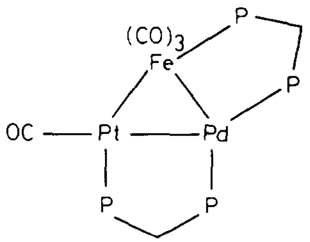
(1)





(2)

In the related reaction between $[PtPdCl_2(\mu\text{-dppm})_2]$ and $Na_2[Fe(CO)_4] \cdot 1.5C_4H_8O_2$, a red product $[PtPdFe(dppm)_2(CO)_4]$ was obtained in good (>80%) yield; this was shown to be an isomeric mixture (approximately 1/1) of complexes **3** and **4**, but all attempts to separate these complexes have been thus far unsuccessful (perhaps not surprisingly, in view of their similar physical properties).



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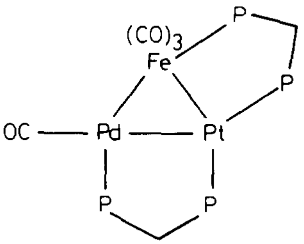
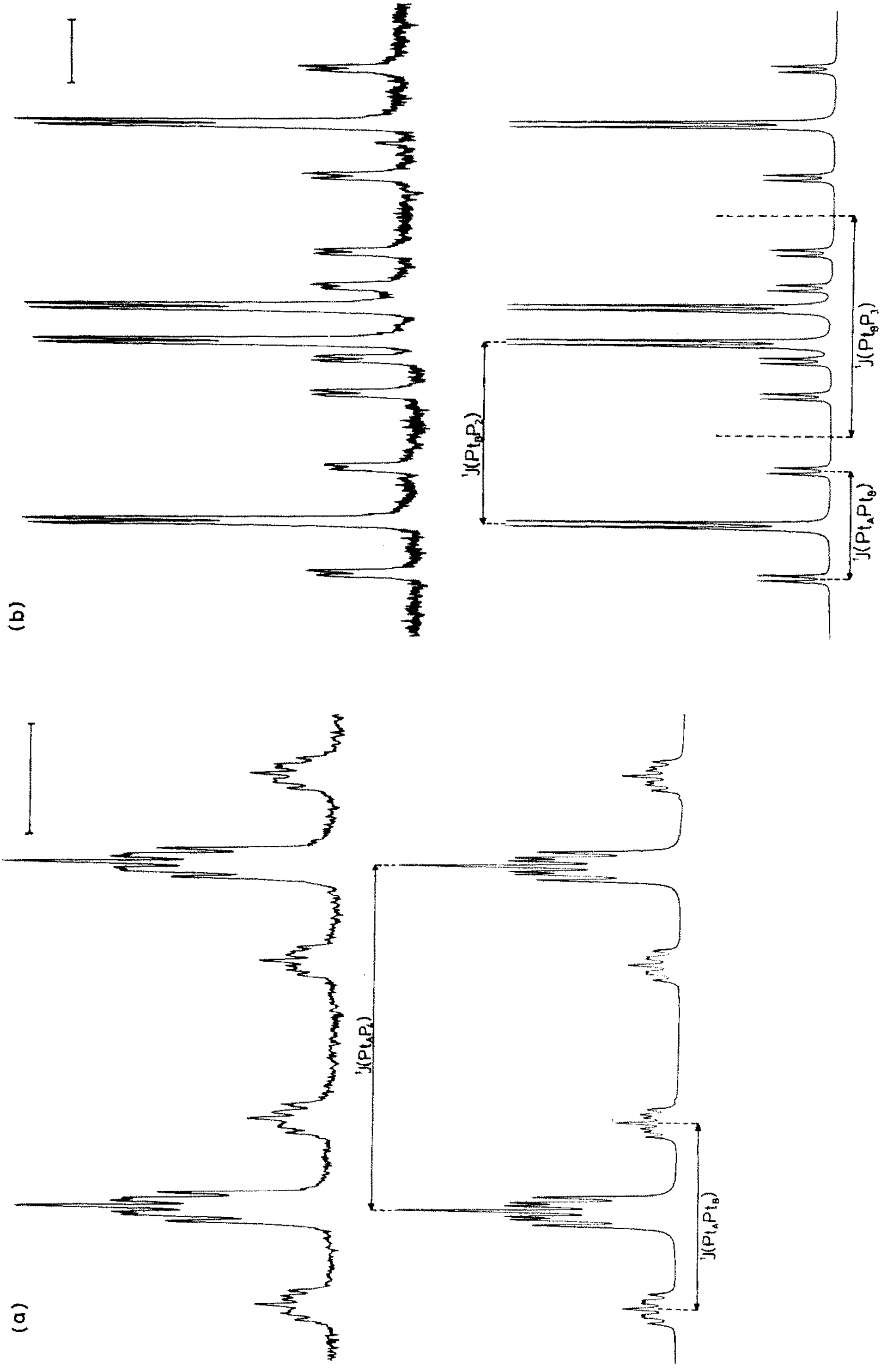
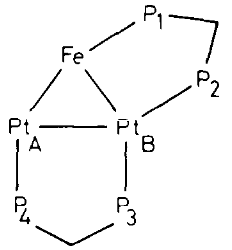


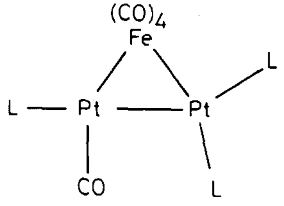
(4)

The ^{195}Pt NMR spectrum of **2** shows two discrete platinum resonances (see Fig. 1): the low field signal, Pt_A, is a doublet ($^1J(Pt_AP_4)$ 3186 Hz) due to coupling with one directly bonded phosphorus atom, P_4 (see **5**), whereas the high field signal, Pt_B, is a doublet of doublets ($^1J(Pt_BP_3)$ 4387 Hz, $^1J(Pt_BP_2)$ 2923 Hz) due to coupling with the two directly bonded phosphorus atoms, P(2) and P(3). The weaker satellites on the Pt_A and Pt_B peaks are due to the isotopomer containing two ^{195}Pt atoms (cf. [6]), and correspond to a $^1J(PtPt)$ coupling of 1730 Hz, whereas the fine structure is due to various $^2J(PtP)$ couplings (which have been fully assigned). The computer simulation [7] of the ^{195}Pt spectrum (Fig. 1) demonstrates the validity of the assignments. The ^{31}P spectrum of **2** shows four discrete ^{31}P resonances, and is extremely complex. However, using the data from the analysis of the ^{195}Pt NMR spectrum to identify each of the peaks, a complete analysis in terms of structure **2** was possible, yielding all the values of $^1J(PtP)$, $^2J(PtP)$, $^2J(PP)$ and $^3J(PP)$ for the molecule. In addition, the ^1H NMR spectrum of **2** confirmed the presence of two different CH_2 groups, and was again completely anal-


(a)
$^1J(Pt_AP_1)$
$^1J(Pt_APt_B)$
(b)
$^1J(Pt_BP_2)$
$^1J(Pt_APt_B)$
$^1J(Pt_BP_3)$



(5)



(6 ; L = P(OPh)3)

ysed in terms of skeleton 5. The ^{195}Pt, ^{31}P and ^{1}H spectra of the isomeric mixture of 3 and 4 were predictably more complex than those of 2, showing two, eight and four discrete resonances due to Pt, P and CH_2, respectively. However, the spectral analysis was routine, following the pattern established for 2. The terminal nature of the four carbonyl groups was confirmed by the ^{13}C NMR spectrum of 2, which showed only one CO directly bonded to platinum (δ(C) 197.4 ppm; ^{1}J(PtC) 1504 Hz). The IR spectrum of 2 in CH_2Cl_2 showed bands at 2030vw and 1995s cm^{-1} (ν(CO)$_{Pt}$) and 1930s, 1885s and 1850s cm^{-1} (ν(CO)$_{Fe}$); that of the isomeric mixture of 3 and 4 was similar, except that the highest frequency CO stretch was a doublet (2010s and 1995s cm^{-1}) due to ν(CO)$_{Pd}$ and ν(CO)$_{Pt}$. The deduced structures of 2—4 are similar to that of the complex $[Pt_2Fe\{P(OPh)_3\}_3(CO)_5]$ (6) [8], which was prepared in very low yield (8.5%) by treating $[Pt\{P(OPh)_3\}_4]$ with $[Fe_2(CO)_9]$ [9].

It is of interest that, both the reaction of $[Pd_2Cl_2(\mu\text{-dppm})_2]$ with $[Mn(CO)_5]^-$ and the reaction between $[Pt_2Cl_2(\mu\text{-dppm})_2]$ and $[Fe(CO)_4]^{2-}$, the $\{M_2(\mu\text{-dppm})_2\}$ (M = Pt or Pd) skeleton is disrupted, with one of the M—P bonds being cleaved in favour of an Fe—P bond. However, the reaction of $[PdPtCl_2(\mu\text{-dppm})_2]$ shows that the Pt—P and the Pd—P bonds are cleaved with equal probability, suggesting that kinetic (rather than thermodynamic) control is occurring. In contrast with the manganese system, the iron complexes are formed in near quantitative yield (presumably since only one nucleophilic attack on the $\{Pt_2(dppm)_2\}$ skeleton is required for the formation of 2), with the reaction stopping at the 1/1 stage. Moreover, 2 satisfies the normal electronic requirements of the platinum and iron atoms (cf. 6) without the formation of bridging carbonyls. We have also prepared $[Pt_2Ru(dppm)_2(CO)_4]$ and $[Pt_2Os(dppm)_2(CO)_4]$ by related reactions, and found them to possess structures analogous to 2.

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Fig. 1. ^{195}Pt $\{^{1}$H$\}$ NMR spectra (85.69 MHz) of $[Pt_2Fe(dppm)_2(CO)_4]$ in tetrahydrofuran (D_2O lock). Figure a illsutrates the low field signal (δ(Pt$_A$) 790 ppm) together with its computer simulation. Figure b illustrates the high field signal (δ(Pt$_B$) 497 ppm) also with its computer simulation. Pt chemical shifts are measured relative to a frequency of 21.4 MHz on a hypothetical NMR machine for which the ^{1}H TMS frequency is 100 MHz. The bars on the diagrams represent 1000 Hz.

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