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The Dichlorobis(triphenylphosphine)ruthenium(II) Dimer

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A recent communication to this journal [1] prompts us to report further details concerning characterization of an isolated $[RuCl_2(PPh_3)_2]_2$ complex [2, 3]. The authors of the recent communication [1] were clearly not aware of our communication [2], which was published some three months prior to submission of their article. We had noted [2] isolation of $[RuX_2L_2]_2$ complexes (X = Cl or Br; L = PPh_3 or $AsPh_3$) and had alluded to the accompanying AB pattern of the ^{31}P–{H} NMR spectra for the $[RuCl_2P_2]_2$ complex (P = PPh_3).

Of major interest, however, is that the product (**1**) isolated by Vriends *et al.* [1], although also giving an AB pattern in the ^{31}P NMR, is not the chloride-bridged $[RuCl_2P_2]_2$ dimer, as claimed. Complex **1** was prepared from $RuCl_2P_3$ by reaction with what was said to be catalytic amounts of 2-pyridyl ketones, C_5H_4N–COR (R = H, CH_3, Ph) [1]. We find that the complex prepared using 2-acetylpyridine is a six-coordinate monomer $RuCl_2P_2(C_5H_4N\text{-}COCH_3)$, containing chelated 2-acetylpyridine. Vriends *et al.* reported that **1** was a purple dimer almost insoluble in benzene or toluene, and showed in $CDCl_3$ from *room temperature to 60 °C* an AB pattern (δ_A 43.6 and δ_B 38.8 ppm, downfield from 85% H_3PO_4) with J_{PP} = 35 Hz [1]. Further, a bridge-cleaving reaction with PPh_3 to give $RuCl_2P_3$ did not occur, and reaction with CO was said to yield dimeric $[RuCl_2(CO)P_2]_2$ [1]. Our complex (**2**), prepared by

$$RuCl_3P_2 + 0.5H_2 \rightarrow RuCl_2P_2 + H^+ + Cl^- \qquad (1)$$

the H_2 reduction of $RuCl_3P_2$ in NN′-dimethylacetamide (DMA) according to equation (1) [3, 4] is isolated as a red-brown dimer (correct elemental analysis; mol. wt. by cryoscopy in benzene 1200, calc. 1392; terminal ν(Ru–Cl) at 320 cm^{-1}), which is readily soluble in benzene or toluene. The ^{31}P NMR AB pattern is sharpened and resolved *only at low temperatures*, and at –70 °C in toluene δ_A = 58.8 and δ_B = 53.0 ppm downfield from H_3PO_4, with J_{PP} = 41.5 Hz, very different to the parameters reported for complex **1** [1]. Also in contrast to **1**, toluene solutions of **2** readily react with PPh_3 to give $RuCl_2(PPh_3)_3$ (readily monitored by visible spectroscopy [5]), and with CO to give a $RuCl_2(CO)_2P_2$ species [6]. After dissolution in CH_2Cl_2 at room temperature, **2** is converted into the insoluble almost black, polymeric $[RuCl_2P_2]_n$ complex [7], which presumably contains six-coordinate octahedral ruthenium(II). Solutions of **2** are also much more oxygen-sensitive than corresponding solutions of **1**. We also find that **2** is readily converted into **1** by treatment with 2-pyridyl ketones.

The ^{31}P spectral data of our isolated biphosphine species are identical to those measured by others [8, 9] and ourselves for a species detected in solutions of $RuCl_2P_3$, and formed by dissociation of PPh_3 from this species. Vriends *et al.* [7] present a ^{31}P NMR spectrum of $RuCl_2P_3$ at –97 °C showing no AB pattern (Fig. 1b in ref. [1]). However, their spectrum shows a signal for free PPh_3 which is much too intense, and triphenylphosphine oxide is also present. These anomalies were not explained. Excess phosphine will inhibit dissociation of phosphine from $RuCl_2P_3$, and this would account for the non-detection of $[RuCl_2P_2]_2$. A low-temperature ^{31}P NMR spectrum of the tetrakis(triphenylphosphine) complex, $RuCl_2P_4$, would resemble that of Fig. 1b reported by the Dutch workers.

We thus synthesized complex **1** according to the reported procedure [1] and find its ^{31}P NMR data to be as reported. A comparison of the IR spectra of **1** and **2** reveals extra weak bands at 1550 and 730 cm^{-1} for the former, and we considered first that these could be, respectively, the C–C stretch and C–H out-of-plane deformation characteristic of an *ortho*-metallated complex [5, 10]. Such a complex, which could give rise to an AB ^{31}P NMR pattern, could be formed according to reaction (2):

$$[RuCl_2(PPh_3)_2]_2 \rightarrow$$

$$\underset{\mathbf{3}}{\{HRuCl_2[o\text{-}C_6H_4(PPh_2)](PPh_3)\}_2} \rightarrow$$

$$\underset{\mathbf{4}}{\{RuCl_2[o\text{-}C_6H_4(PPh_2)](PPh_3)\}_2} + H_2 \qquad (2)$$

We were unable, however, to detect a hydride ligand by IR or high field ^1H NMR, thus ruling out **3**, and we could not detect the evolution of H_2 that would be required for formation of **4**. This complex would also be a ruthenium(III) species and some coupling between the metal centres would have to be invoked to account for the diamagnetism that we have measured for both **1** and **2** complexes. A number of other structures involving *ortho*-metallation can be formulated; triply-bridged chloride species were

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considered [9] but, since there are two chlorides per ruthenium, this implies an unsymmetrical structure and a more complex ^{31}P NMR would be expected. Conductivity data ruled out ionic species.

Closer examination of complex **1** that we prepared revealed that it did contain small amounts of nitrogen. We had initially considered this to be due to residual traces of the pyridyl ketone, since nitrogen was said to be absent [1]. However, we have now demonstrated that the synthesis of **1** is *not* catalytic in ketone but involves a 1:1 stoichiometric reaction between $RuCl_2P_3$ and, for example, 2-acetylpyridine. This is readily shown by a spectrophotometric titration of the rapid reaction in $CHCl_3$, **1** having a visible absorption maximum at 580 nm, while undissociated $RuCl_2P_3$ has absorption maxima at 480 and 750 nm [11], and $[RuCl_2P_2]_2$ has a broad maximum at about 500 nm. The absorption at 580 nm increases to a maximum with added acetylpyridine concentration at a 1:1 ratio with the ruthenium. The elemental analysis is consistent with an empirical formula $RuCl_2(PPh_3)_2(C_7H_7NO)$ [calc. for $C_{43}H_{37}NoCl_2P_2$-Ru; C, 63.1; H, 4.5; N, 1.7; Cl, 8.7. Found C, 62.2; H, 4.6; N, 1.6; Cl, 7.8%], and we measured cryoscopically an average molecular weight of 800 in 1,2-dibromoethane which shows the complex to be monomeric [calc. 817], although Vriends *et al.* [1] reported an osmometric molecular weight of 1277. Proton NMR readily confirms the presence of one acetylpyridine per two triphenylphosphines in the complex. Further, the methyl resonance of the acetyl group (τ 7.60) is shifted about 0.2 ppm upfield from that of the free ligand, while the 6-H of the pyridine ring (τ0.46) is shifted about 0.9 ppm downfield, and these data strongly suggest that the acetylpyridine is chelated via the carbonyl and nitrogen. The lack of an IR band in the 1700–1800 cm^{-1} region also shows coordination via the acetyl carbonyl; several bands in the 1550–1600 cm^{-1} region could be attributed to ν(CO), and bands at 1020, 780, 730, and 620 cm^{-1} are likely due to the coordinated pyridine [12]. A ^{31}P NMR AB pattern results from either *cis* or *trans* chloride isomers of a $RuCl_2(PPh_3)_2(C_7H_7NO)$ complex containing *cis* phosphines; the six-coordinate chelate structure also explains more readily the non-fluxional behavior at ambient conditions. We favor slightly the *trans*-isomer due to the dominance of a single band at 325 cm^{-1} [ν(Ru-Cl)] in the 400–250 cm^{-1} region, although the exact nature of **1** will be elucidated by X-ray analysis which is reported to be underway [1]. Our complex **2** is certainly the $[RuCl_2(PPh_3)_2]_2$ dimer, presumably with square pyramidal geometry at the ruthenium.

Vriends *et al.* [1] also report ^{31}P NMR data for the species produced *in situ* in DMA by H_2 reduction of $RuCl_3P_2$, equation (1); a single broad resonance at 55.7 ppm (from 20 to -10 °C) was tentatively attributed to $RuCl_2P_2(DMA)$. The ^{31}P NMR spectrum of $[RuCl_2P_2]_2$ (our complex **2**) in DMA at 25 °C is a sharp singlet at 64.9 ppm and this we attribute [3] to $RuCl_2P_2(DMA)_2$ by analogy with other such six-coordinate complexes [7]. On adding excess chloride to the $[RuCl_2P_2]_2$/DMA system, the singlet is shifted to 48.1 ppm; visible spectral measurements [13] indicate formation of a dimer, possibly a triple chloro-bridged species such as $Ru_2Cl_5(PPh_3)_4^-$. The *in situ* species formed according to equation (1) does contain excess chloride, and the broad resonance at 55.7 ppm [1] could result from an exchanging equilibrium mixture of $RuCl_2P_2(DMA)_2$ and the pentachloro dimer.

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