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Bis(dimethylphosphino)methane Complexes of Ruthenium Carbonyl

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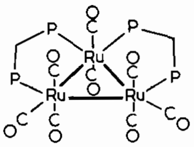
Abstract

Reaction of $Me_2PCH_2PMe_2$ with $[Ru_3(CO)_{12}]$ in a 1:1 or 2:1 ratio in the presence of $[(Ph_3P)_2N]CN$ catalyst gives $[Ru_3(CO)_{10}(\mu\text{-}Me_2PCH_2PMe_2)]$ and $[Ru_3(CO)_8(\mu\text{-}Me_2PCH_2PMe_2)_2]$ respectively. The complexes were characterized by elemental analysis, IR and ^1H and ^{31}P NMR spectroscopies.

Introduction

The ligand bis(diphenylphosphino)methane, dppm, has been used extensively to bridge between two metal centres and hence to discourage dissociation of binuclear or trinuclear complexes [1, 2]. Bis(dimethylphosphino)methane, dmpm, has been studied much less, though it has considerable potential; we know of no reported cluster complexes of this ligand. Although dmpm is more difficult to prepare and handle than dppm, the lower steric bulk of the methyl substituents compared to the phenyl substituents of dppm can lead to enhanced reactivity and different stereochemistries and coordination numbers for dmpm complexes [3, 4]. We have studied the reactions of dmpm with $[Ru_3(CO)_{12}]$ in order to compare them with the known reactions of dppm [5, 6] and to prepare useful precursors for organometallic cluster synthesis.

Results and Discussion



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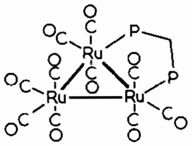

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The ligand dmpm reacts with $[Ru_3(CO)_{12}]$ slowly at room temperature but only low yields of $[Ru_3(CO)_{10}(dmpm)]$, **1**, or $[Ru_3(CO)_8(dmpm)_2]$, **2**, could be isolated. Much faster reaction occurred in the presence of the catalyst $[(Ph_3P)_2N]CN$, as found recently for many other substitution reactions of $[Ru_3(CO)_{12}]$ [7] and, by using the appropriate stoichiometry, complexes **1** and **2** could be isolated in good yield. It was not possible to substitute more than two dmpm ligands onto $[Ru_3(CO)_{12}]$.

The complexes were characterized by elemental analysis and by IR and NMR spectroscopy. For complex **1**, the IR spectrum in the carbonyl region (Experimental section) was very similar to that of $[Ru_3(CO)_{10}(\mu\text{-dppm})]$ [5, 6]. In the ^1H NMR spectrum, the resonance due to the $C\underline{H}_2P_2$ protons occcurred as a triplet at δ 3.34 ppm, $^2J(PH) = 10$ Hz and, in the ^{31}P NMR spectrum, the chemical shift for the phosphorus atoms (δ −15.3 ppm) was in the region expected for bridging, rather than chelating, dmpm [3, 4]. Together, these data strongly support structure **1**, with the μ-dmpm ligand in the equatorial plane, since an axially substituted μ-dmpm ligand would have non-equivalent $CH^aH^bP_2$ protons.

For complex **2**, the ^1H NMR spectrum contained a triplet due to the CH_2P_2 protons at δ 3.04 ppm, $^2J(PH) = 10$ Hz. Again, this is only consistent with the two μ-dmpm ligands being in the equatorial plane. There is then a mirror plane, at least on the NMR time scale, containing the skeletal $Ru_3P_4C_2$ atoms and the $C\underline{H}_2P_2$ protons are equivalent. As expected for this stereochemistry, the CH_3P protons gave two doublets in the ^1H NMR spectrum and two signals were observed in the ^{31}P NMR spectrum (Fig. 1). The ^{31}P NMR spectrum occurred as an AA′BB′ multiplet, and the ^{31}P chemical shifts were both in the μ-dmpm region [3, 4].

Both complexes **1** and **2** are orange solids, which are reasonably stable in air, and their properties are under investigation. Although the structures of **1** and **2** are analogous to those of the known dppm complexes, it is probable that the lower steric effects of the ligands will lead to enhanced reactivity.

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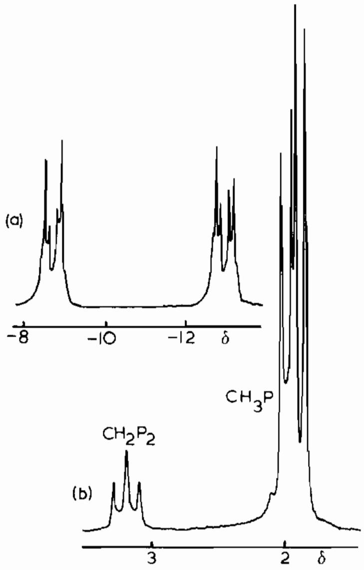

Fig. 1. NMR spectra of [$Ru_3(CO)_8(\mu\text{-dmpm})_2$]. (a) ^{31}P {^1H} spectrum (121.5 MHz); (b) ^1H spectrum (100 MHz).

Experimental

General techniques and ligand syntheses have been described elsewhere [3, 4].

[$Ru_3(CO)_{10}(\mu\text{-dmpm})$]

$Ru_3(CO)_{12}$ (0.30 mmol, 192 mg) was dissolved in freshly distilled THF (50 ml). To the stirring orange solution under N_2 atmosphere, dmpm (0.05 ml, 0.30 mmol) was added. Immediately the colour began to darken and some bubbling was observed. The catalyst , [PPN] [CN] [8] (8.9 mg, 0.015 mmol) was dissolved in $CHCl_3$ (1 ml) and added to the dark orange stirring solution. After 1 h of stirring at room temperature, the solvent was removed by rotary evaporation leaving a brown–orange powder. The powder was dissolved in CH_2Cl_2 and pentane was added dropwise until a light brown precipitate formed. The solution was filtered and more pentane was added to the filtrate until some crystal formation was observed. Cooling in an ice bath for 1 h gave large needle-like orange crystals; 85% yield. Only 8% yield was obtained without [PPN] [CN]. Melting point: 140 °C (dec.). IR in cyclohexane: 2078(m), 2010(sh), 2000(s), 1998(sh), 1985(sh), 1978(w), 1965(w), 1960(m). NMR in $CDCl_3$: ^1H, 1.94 [m, $^2J(PH) + {}^4J(PH) = 9$ Hz, $\underline{Me}P$]; 3.34 [t, $^2J(PH) =$ 10 Hz, $C\underline{H}_2P_2$]; ^{31}P, −15.3 [s]. MS: Envelope centered at m/e 720. Calc. for [$^{102}Ru_3(CO)_{10}(dmpm)$], 722. *Anal.* Calc. for $C_{15}H_{14}O_{10}P_2Ru_3$: C, 25.2; H, 2.0. Found: C, 25.3; H, 2.1%.

Monitoring of the above reaction mixture by solution IR showed that the reaction in the presence of catalyst was complete within 5 min, and good yields can be obtained after such short reaction times.

[$Ru_3(CO)_8(\mu\text{-dmpm})_2$]

$Ru_3(CO)_{12}$ (0.30 mmol, 192 mg) was dissolved in freshly distilled THF (50 ml). To the stirring orange solution under N_2 atmosphere, dmpm (0.15 ml, 0.90 mmol) was added. Immediately, the colour darkened and considerable bubbling was observed. The catalyst [PPN] [CN] (89 mg, 0.15 mmol) was added and the mixture was left to stir at room temperature for 1 h. The solvent was removed by rotary evaporation leaving a deep orange oil. The oil was dissolved in CH_2Cl_2 and passed through a florisil column. Pentane was added dropwise to the collected solution until cloudy. Cooling in an ice bath for 1 h gave small needle-like dark orange crystals; 49% yield. Only 16% yield was obtained when the experiment was performed without the catalyst, [PPN] [CN]. Melting point 155 °C (dec.). IR in cyclohexane: 1988(m), 1975(sh), 1971(vs). NMR in $CDCl_3$: ^1H, 1.83 [d, $^2J(PH) = 8$ Hz, MeP]; 1.93 [d, $^2J(PH) = 8$ Hz, MeP]; 3.04 [t, $^2J(PH) =$ 10 Hz, $C\underline{H}_2P_2$]; ^{31}P, −8.7 [m, $^2J(P^aP^b) = 44$, $^3J(P^aP^b) = 4.8$]; −12.9 [m]. MS: Envelope centered at m/e 802. Calc. for $^{102}Ru_3(CO)_8(dmpm)_2$, 802. *Anal.* Calc. for $C_{18}H_{28}O_8P_4Ru_3$: C, 27.0; H, 3.5. Found: C, 26.7; H, 3.4%.

In similar experiments with reaction times of 4.5 and 6 h yields of 81 and 95% respectively have been obtained. Monitoring by IR indicated that the reaction of 1 with dmpm to give 2 was very slow in the absence of catalyst.

Acknowledgement

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