The Reaction of Bis(isopropylphosphino)methane with Ruthenium Carbonyl

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Abstract

Reaction of $^{i}PrHPCH_2PH^{i}Pr$ with $[Ru_3(CO)_{12}]$ in the presence of $[(Ph_3P)_2N]CN$ catalyst gave sequentially $[Ru_3(CO)_{10}(\mu\text{-}^{i}PrHPCH_2PH^{i}Pr)]$ and $[Ru_3(CO)_9(\mu\text{-H})(\mu_3\text{-}^{i}PrHPCH_2P^{i}Pr)]$. The former complex exists in two isomeric forms. The structures were determined by ^1H and ^{31}P NMR spectroscopy.

Introduction

There has been much recent interest in stabilizing cluster complexes against fragmentation by the use of strongly bound bridging ligands such as bis(diphenylphosphino)methane or bis(dimethylphosphino)methane [1–8]. Pyrolysis under hydrogen of derivatives of these ligands with ruthenium carbonyl has yielded trinuclear complexes with the unusual triply bridging $[R_2PCH_2PR]^-$ ligand, including $[Ru_3(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}R_2PCH_2PR)]$, R = Me or Ph [1, 2, 8, 9]. This triply bridging ligand has great potential for stabilizing clusters against fragmentation, and such stabilization is essential in developing cluster catalysis. The above syntheses require forcing conditions, and a milder synthetic method was therefore considered desirable. The secondary diphosphines of general formula R_2PCH_2PHR or $RHPCH_2PHR$ offer a milder route to the phosphido-phosphine ligands, as a result of the much greater lability of PH compared to PC bonds [10, 11]. Some examples of their use include the formation of $[Fe_3(CO)_9(\mu\text{-H})(\mu_3\text{-}\eta^2\text{-}R_2PCH_2PR)]$ and $[Fe_3(CO)_9(\mu_3\text{-}\eta^2\text{-}RHPCH_2PR)]$ along with other interesting products by reaction of R_2PCH_2PHR or $RHPCH_2PHR$ respectively with $[Fe_2(CO)_9]$ [10]. This paper reports similar ruthenium complexes formed from $RHPCH_2PHR$ (R = ^{i}Pr) and the isolation of a precursor in which the diphosphine precursor is intact.

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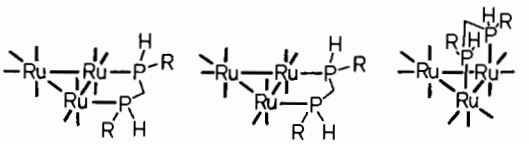
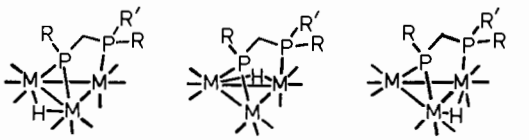
Results and Discussion

In order to effect substitution of $^{i}PrHPCH_2PH^{i}Pr$ onto $[Ru_3(CO)_{12}]$ under as mild conditions as possible, the catalyst $[(Ph_3P)_2N]CN$ was used [12]. Substitution occurred at room temperature to give a mixture which was shown by ^{31}P NMR spectroscopy to contain three species. This mixture was separated into two components, one of them a mixture of two species, by preparative thin layer chromatography. The components were then identified by elemental analysis, mass spectrometry, IR and NMR spectroscopy.



1a **1b** **1c**



M	R	R′			
Ru	^{i}Pr	H	**2a**	**2b**	**2c**
Ru	Ph	Ph	**3a**	**3b**	**3c**
Ru	Me	Me	**4a**	**4b**	**4c**
Fe	^{i}Pr	^{i}Pr	**5a**	**5b**	**5c**

The first component, complex **1**, was identified as the expected substitution product $[Ru_3(CO)_{10}(\mu\text{-}^{i}PrHPCH_2PH^{i}Pr)]$ which was present in two isomeric forms. It gave a parent ion in the mass spectrum and, as expected, only terminal carbonyl stretching frequencies in the IR. The major isomer gave a singlet in the $^{31}P\{^1H\}$ NMR at $\delta - 5.7$ ppm and this split further to a doublet in the ^{31}P NMR due to $^1J(PH) = 350$ Hz (Fig. 1). The PH resonance in the ^1H NMR was at $\delta = 4.73$, $^1J(PH) = 350$ Hz. This complex is assigned structure **1a**, since the equatorial substitution on $[Ru_3(CO)_{12}]$ is favoured and the conforma-

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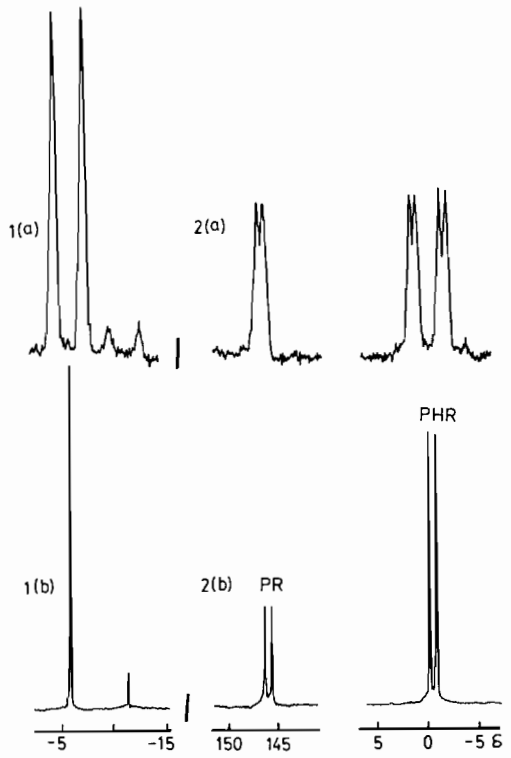

Fig. 1. ^{31}P NMR spectra (121.5 MHz) of $[Ru_3(CO)_{10}(\mu\text{-}^iPrHPCH_2PH^iPr)]$ (1) and $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}^iPrPCH_2\text{-}PH^iPr)]$ (2). In each case spectrum (a) is ^1H coupled and (b) is ^1H decoupled.

tion of the diphosphine with *anti* isopropyl substituents, **1a**, will be less sterically hindered than with *syn* isopropyl substituents, **1b**. The second minor isomer is identified only by the ^{31}P and $^{31}P\{^1H\}$ NMR spectra, having $\delta(^{31}P) = -11.2$, $^1J(PH) = 350$ Hz. These data preclude any structures involving rearrangement of the ligand but do not distinguish between possible structures **1b** and **1c**. The structure **1b** is tentatively suggested based on previous experience that the meso and racemic forms of this ligand can each form complexes and that they do not readily interconvert [11], and that equatorial rather than axial substitution on $[Ru_3(CO)_{10}]$ is preferred [1–3, 8, 12]. The complexes **1a** and **1b** appear to be the first cluster complexes in which the $RHPCH_2PHR$ ligand remains intact, and the successful synthesis in this case is clearly a result of the mild conditions of reaction.

The second component isolated by chromatography, complex **2**, was identified as $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}^iPrHPCH_2P^iPr)]$. Complex **2** gave a parent ion in the mass spectrum and only terminal carbonyl bands in the IR spectrum. There are three possible isomers **2a**, **2b** and **2c**. The analogous complex $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}Ph_2PCH_2PPh)]$ (**3**) exists as a mixture of the isomers **3a** and **3b**≡**3c** (since R = R′), with **3b** predominant, $[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}Me_2PCH_2PMe)]$ (**4**) exists only as **4a** and $[Fe_3(CO)_9\text{-}(\mu\text{-}H)(\mu\text{-}^iPr_2PCH_2P^iPr)]$ (**5**) exists only as **5b**≡**5c**. In all complexes **2**–**5**, the phosphido phosphorus atom occurs in the region δ 97–190 ppm and the phosphine atom in the region δ −13–55 ppm (Table I) [1, 10]. The downfield shift is characteristic of a phosphido group bridging a metal–metal bond. The presence of one hydrogen atom on P^b but not on P^a for **2** was confirmed by recording the ^1H coupled ^{31}P NMR spectrum (Fig. 1). The best criterion for structure determination in this system appears to be based on the hydride signal, $Ru_2(\mu\text{-}H)$ in the ^1H NMR spectrum. For the complexes **2**–**5** whose structures are known with confidence, isomers **a** give two $^2J(PH)$ couplings whose ratio falls in the region $^2J(P^aH)/^3J(P^bH) = 3.4–4.4$ whereas isomers **b** or **c** give $^2J(P^aH)/^2J(P^bH) = 1.3–1.6$ (Table I). These ranges are reasonable since $J(P^bH)$ should be smaller for isomer **a** than for **b** or **c**. On this basis, the isomer from the present reaction is assigned structure **2a**. It is clear that the energies of the possible isomers are very similar and the factors which influence their relative stabilities are obscure.

Complex **2** is clearly formed from **1** by loss of a carbonyl ligand followed by intramolecular oxidative addition of a P–H group to the cluster. Consistent with this, when complex **1** was heated in benzene solution it was converted in high yield to **2**. A similar mechanism has been proposed for formation of the R_2PCH_2PR ligand in related systems [1, 2, 10], but this appears to be the best defined reaction yet observed since the cluster precursor can be isolated.

TABLE I. Selected NMR Data for some Complexes $[M_3(CO)_9(\mu\text{-}H)(\mu\text{-}RP^aCH_2P^bRR')]$ in Isomeric Forms Analogous to **2a** or **2b**

Complex			Isomer	δ(P^a) (ppm)	δ(P^b) (ppm)	$^2J(P^aP^b)$ (Hz)	δ(H) (ppm)	$J(P^aH)$ (Hz)	$J(P^bH)$ (Hz)	Reference
M	R	R′								
Ru	Ph	Ph	**a**	122.4	18.9	100	−16.07	27	6	1
Ru	Ph	Ph	**b**	134.6	20.4	100	−16.72	16	12	1
Ru	Me	Me	**a**	97.1	−12.9	96	−16.39	26	7	13
Ru	^{i}Pr	H	**a**	145.9	−0.5	79	−16.48	24	7	this work
Fe	^{i}Pr	^{i}Pr	**b**	189.5	55.2	79.2	−22.5	28	17.5	10

The work confirms the utility of the secondary phosphine in facilitating conversion to phosphido derivatives [10].

Experimental

^1H and ^{31}P NMR spectra were recorded using Varian XL200 or XL300 spectrometers using Me_4Si or H_3PO_4 references.

$[Ru_3(CO)_{10}(\mu\text{-}^iPrHPCH_2PH^iPr)]$ and $[Ru_3(CO)_9(\mu\text{-}H)(\mu\text{-}^iPrHPCH_2P^iPr)]$

To a solution of $[Ru_3(CO)_{12}]$ (0.20 g, 0.31 mmol) in dry tetrahydrofuran (40 ml) was added $^iPrHPCH_2PH^iPr$ (0.051 g, 0.31 mmol) and then $[(Ph_3P)_2N]CN$ (9 mg) as catalyst. The colour changed from orange–red to burgundy red. After 4 h stirring at room temperature, the volume of solvent was reduced under vacuum and pentane was added to precipitate the product mixture (200 mg), characterized by ^{31}P NMR as a mixture of **1** and **2**. The product was separated by preparative thin layer chromatography on silica using CH_2Cl_2–pentane (3:7) as eluent.

$[Ru_3(CO)_{10}(\mu\text{-}^iPrHPCH_2PH^iPr)]$: *Anal.* Calc. for $C_{17}H_{18}O_{10}P_2Ru_3$: C, 27.3; H, 2.4. Found: C, 27.9; H, 2.8%. MS: $m/z = 747$ (M^+). Melting point (m.p.) 125 °C. IR: ν(CO), CH_2Cl_2 solution, 2070, 2050, 2040, 2020, 1990, 1970 cm^{-1}. NMR(CD_2Cl_2): ^1H, 1.2–1.6 [m, 12H, *Me*]; 2.08 [m, 4H, $^3J(HH) = 8$, Me_2CH]; 3.5 [m, 2H, CH_2P_2]; 4.73 [m, 2H, $^1J(PH) = 350$, *PH*]; ^{31}P, –5.7 [s, $^1J(PH)$ 350 in coupled spectrum, ^{31}P]. These peaks are due to **1a**. The second isomer, **1b**, present in 7% abundance, gave $\delta = -11.2$ [s, $^1J(PH) = 350$], but the ^1H resonances were not resolved.

$[Ru_3(CO)_9(\mu\text{-}H)(\mu_3\text{-}\eta^2\text{-}^iPrHPCH_2P^iPr)]$: *Anal.* Calc. for $C_{16}H_{18}O_9P_2Ru_3$: C, 26.7; H, 2.5. Found: C, 26.4; H, 2.4%. MS: $m/z = 720(M^+)$. m.p. 110 °C. IR: ν(CO), CH_2Cl_2 solution, 2070, 2040, 2020, 1990 cm^{-1}. NMR(CD_2Cl_2), isomer **2a**: ^1H, 1.1–1.6 [m, 12H, *Me*]; 2.00 [m, $^3J(HH) = 8$, Me_2CH]; 3.22 (m, $^3J(HH) = 8$, $^2J(HH) = 15$, $^2J(PH) = 13$, 6.4, $CH^aH^bP_2$]; 3.94 [m, $^3J(HH) = 8$, $^2J(HH) = 15$, $^2J(PH) = 15$, 8, $CH^aH^bP_2$]; 4.73 [m, $^1J(PH) = 360$, $^3J(HH) = 8$, *PH*]; –16.48 [dd, $^2J(PH) = 24.4$, $^3J(PH) = 7.2$, $Ru_2(\mu\text{-}H)$; ^{31}P, –0.5 [d, $^2J(PP) = 79$, $^1J(PH) = 350$, P^b]; 145.9 [d, $^2J(PP) = 79$, P^a].

Heating a solution of complex **1** in benzene under reflux for 2 h gave conversion to **2**, identified by its ^{31}P NMR spectrum, in high yield. No complex **1** remained, and pure **2** was recovered by preparative tlc, as described above.

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