

BIS(DIPHENYLPHOSPHINO)METHANE-SUBSTITUTED PRODUCTS FROM $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_9$

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Summary

The reaction between the alkylidyne cluster $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_9$ and bis(diphenylphosphino)methane (dppm) gives two disubstituted stereoisomers of formula $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_7(\mu\text{-PPh}_2\text{CH}_2\text{PPh}_2)$ (I and II) and one monosubstituted product containing an uncoordinated phosphoryl group, $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_8[\text{PPh}_2\text{-CH}_2\text{P}(\text{O})\text{Ph}_2]$ (III). On heating in toluene under reflux, the kinetically favoured isomer I is transformed into the thermodynamically stable isomer II. Further reaction with a second molecule of dppm gives rise to two derivatives, $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_5(\mu\text{-dppm})_2$ (IV) and $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_6(\mu\text{-dppm})(\text{dppm})$ (V). All the products have been characterized by IR and ^{13}C and ^{31}P NMR spectroscopy.

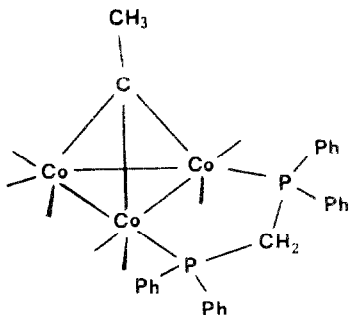
Introduction

In recent years interest in the use of transition metal carbonyl clusters (TMCC's) as catalysts has increased, and several examples of homogeneous catalytic processes have been identified [1]. With the objective of preserving the cluster integrity by avoiding irreversible fragmentations, attention has been focussed on ancillary ligands, able to hold together the metallic centres. Among them diphosphines are the subject of much study [2] since they prefer to bridge metal-metal edges rather than to chelate to a single metal atom. Two reports from Balavoine and coworkers have recently described the characterization of a product formed in the reactions of the $(\mu_3\text{-CCH}_3)\text{Co}_3(\text{CO})_9$ cluster, a typical hydroformylation catalyst, with $\text{PPh}_2\text{CH}_2\text{PPh}_2$ [3] and $\text{PPh}_2\text{CH}_2\text{PMe}_2$ [4], and during the preparation of this manuscript, a paper appeared from Downard, Robinson and Simpson dealing with the reactions of $\text{RCO}_3(\text{CO})_9$ ($\text{R} = \text{Me}, \text{Ph}$) with polydentate ligands [5]. Although the main features of their work are confirmed by our results as far as dppm ligand is concerned, we have obtained a larger collection of spectral data (mainly NMR) which, in turn, allows a better characterization of the structural and dynamic properties of the derivatives. In addition, we have been able to isolate and characterize a novel product containing an uncoordinated phosphoryl group.

Results and discussion

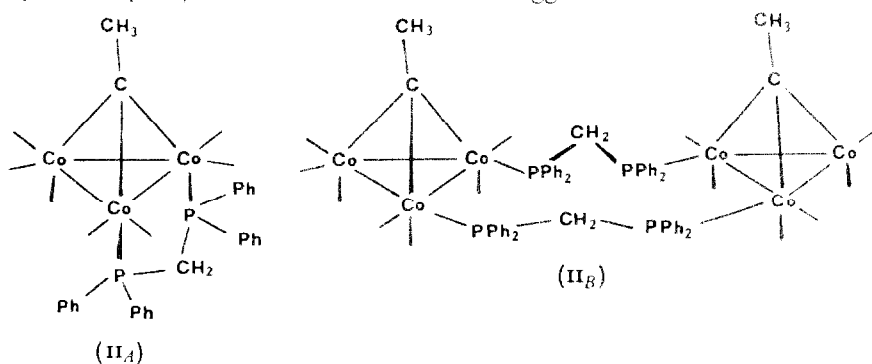
The thermal reaction between $(CCH_3)Co_3(CO)_9$ and dppm afforded three products I, II, and III, in 70, 20 and 5% yield respectively. The most abundant compound, I, corresponds to the derivative previously characterized by X-ray diffraction [3.5] although there are some discrepancies between the published spectral data and ours (see Table I).

The ^{13}C NMR spectrum of I at -70° shows three absorptions at 209.4, 204.0 and 203.4 ppm in the intensity ratio of 2/2/3, and these coalesce at room temperature into a single resonance (205.7 ppm). The ^{31}P NMR spectrum exhibits a single peak at 36.1 ppm, as expected for an equatorially-disubstituted derivative.



(I)

Compound II shows an IR pattern very similar to that for I and the elemental analyses for the two compounds are also very similar, the molecular ion was not observable by the available electron impact technique, and crystals suitable for X-ray diffraction could not be obtained. The ^{13}C NMR spectrum of II shows three carbonyl absorptions, at $-60^\circ C$ (208.2, 203.7, and 203.4 ppm) in the intensity ratio of 2/2/3 (Fig. 1). As the temperature is increased all the resonances broaden then collapse into a single peak at room temperature, indicating that a delocalized CO exchange process over the entire metallic frame is taking place. Only a single ^{31}P NMR resonance is observed from -60 to $+25^\circ C$, suggesting that the two phosphorus coordination sites are equivalent; significantly, the chemical shift is ca. 50 ppm downfield from that for I. The possibility of a species involving chelation to a single metal atom must be discarded since it should give a 1/3/3 intensity pattern in the ^{13}C NMR low temperature limiting spectrum. Two structures containing equivalent phosphorus donor atoms can be suggested for II:



(IIB)

(IIA)

TABLE I
 SPECTROSCOPIC DATA FOR COMPOUNDS I-V

Compound	IR ^a $\nu(\text{CO})(\text{cm}^{-1})$	¹³ C NMR ^b , δ (ppm)	³¹ P NMR ^c , δ (ppm)
(CCH ₃)Co ₃ (CO) ₇ (μ -dppm)	(I) 2061 vs. 2009 vs. 2005 vs. 1993 w, 1971 w br	289.1(C ap.); 205.7(CO); 136.2–128.3(Ph); 45.8(CH ₃); 45.1(CH ₂ , t, J 21.7 Hz)	36.1
(CCH ₃)Co ₃ (CO) ₇ (μ -dppm)	(II) 2061 vs. 2009 vs br, 1994 w, 1971 w	288.9(C ap.); 204.9(CO); 140.5–128.5(Ph) 45.3(CH ₃)	89.2
(CCH ₃)Co ₃ (CO) ₈ [PPh ₂ CH ₂ P(O)Ph ₂]	(III) 2075 m, 2031 vs., 2017 vs., 2009 s, 1991 w, 1982 w	270.2(C ap.); 206.5(CO); 134.7–127.9(Ph) 42.9(CH ₃); 32.3(CH ₂ , m)	{ 22.8(d, J 18.3 Hz, 1) 35.5(d, J 18.3 Hz, 1)
(CCH ₃)Co ₃ (CO) ₅ (μ -dppm) ₂	(IV) 2014 vs. 2004 m, 1968 s br, 1928 w, 1908 w	290.8(C ap.); 217.1, 212.4, 204.4(CO); 136.5–127.3(Ph); 48.4(CH ₃); 45.3(CH ₂ , m)	34.6(m, 1), 31.7(m, 1)
(CCH ₃)Co ₃ (CO) ₆ (μ -dppm)(dppm)	(V) 2045 vs. 2014 s, 1990 m, 1966 w, 1948 w	289.7(C ap.); 213.1, 212.8(CO); 141.3– 126.7(Ph); 34.8(CH ₃); 29; 4(CH ₂ , m)	{ -30.6(d, J 52.8 Hz, 1) 26.3(s, 2) 31.2(d, J 52.8 Hz, 1)

^a Compounds I, II, III were examined in n-hexane, and compounds IV, V in CCl₄. ^b In CDCl₃ at ambient temperature; all the spectra in the carbonyl region were recorded with derivatives obtained from ¹³CO enriched (CCH₃)Co₃(CO)₉ (ca 15%). ^c In CDCl₃; chemical shifts are relative to 85% H₃PO₄.

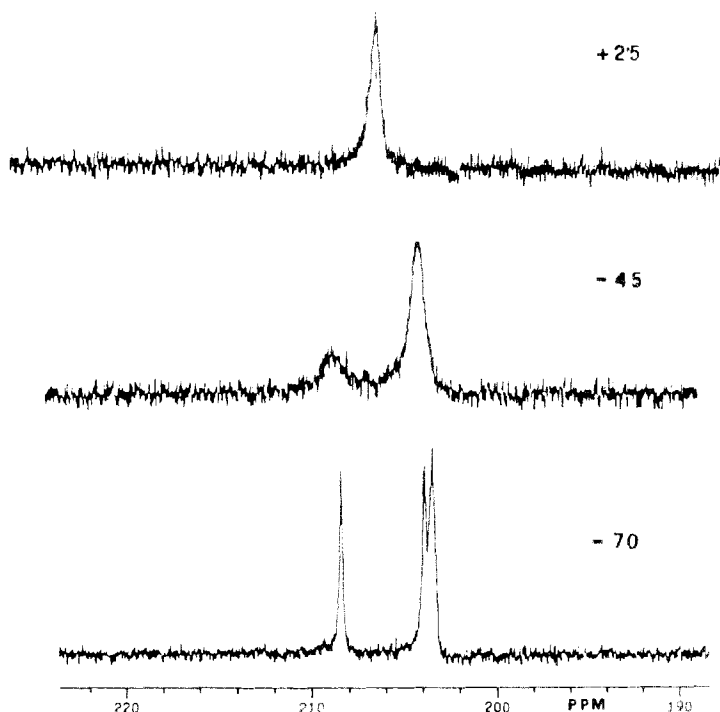


Fig. 1. Variable-temperature ^{13}C NMR spectra of $(\text{CCH}_3)_3\text{Co}_3(\text{CO})_7(\mu\text{-dppm})$ (II) recorded at 67.9 MHz in CDCl_3 .

Structure IIa seems to be more likely from the following observations:

- (i) The ^{31}P and ^{13}C NMR resonances for I and II show very similar linewidths, suggesting similar T_1 values, similar correlation times, τ_c , for molecular tumbling and hence similar molecular dimensions.
- (ii) The ^{13}C NMR spectral pattern and dynamic behaviour of II are very close to those of I (vide infra).
- (iii) Among the reaction products, no monosubstituted dimeric species $\{(\text{CCH}_3)_3\text{Co}_3(\text{CO})_8\}_2(\mu\text{-dppm})$, analogous to the hypothetical disubstituted dimeric structure IIb was found. Furthermore IIb would be subjected to steric strain arising from two adjacent dppm moieties, which have tight "bites".

The isolation of two stereoisomers $(\text{CCH}_3)_3\text{Co}_3(\text{CO})_7(\mu\text{-dppm})$ implies that the phosphorus atoms are rigid at room temperature whereas intramolecular CO exchange occurs readily for both derivatives. This behaviour is related to the low flexibility of dppm ligand; thus $\text{Co}_4(\text{CO})_{10}(\text{dppm})$ [7] exists in two isomeric forms whereas the analogous reactions of $\text{Co}_3(\text{CO})_6(\mu_3\text{-CCl})$ [7] and $\text{Co}_4(\text{CO})_{12}$ [8] with bis(diphenylphosphino)ethane (dppe) afford single disubstituted derivatives, furthermore for $\text{Co}_4(\text{CO})_{10}(\text{dppe})$ variable temperature ^{13}C NMR spectroscopy shows that there is a rapid axial-equatorial exchange at room temperature between the phosphorus atoms of the flexible dppe ligand [8].

On heating in toluene under reflux, isomer I is slowly converted into isomer II, probably by equatorial-axial interchange of the coordinated phosphorus atoms; this

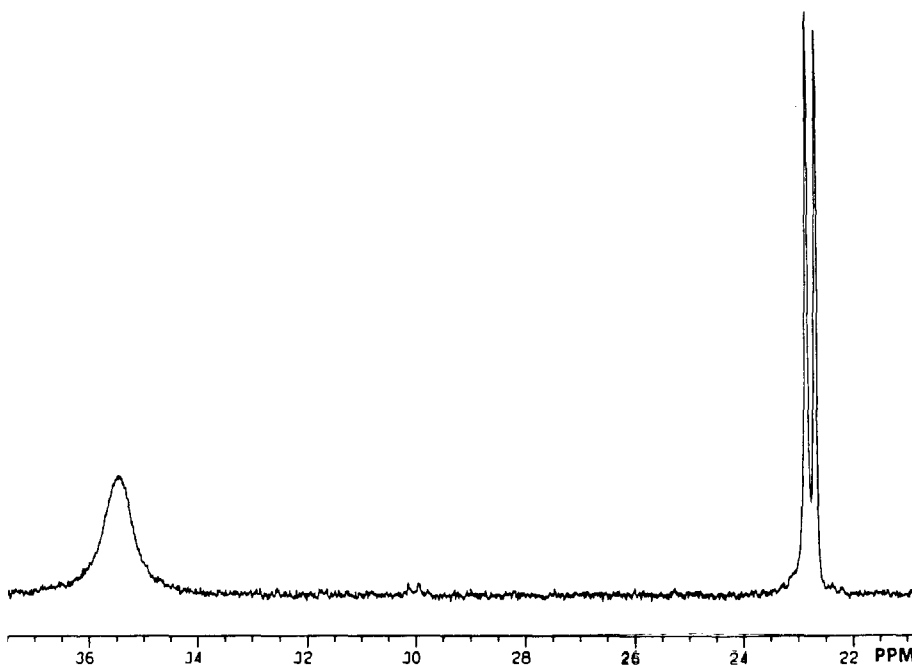


Fig. 2. Ambient temperature ^{31}P NMR spectrum of $(\text{CCH}_3)\text{Co}_3(\text{CO})_8[\text{PPh}_2\text{CH}_2\text{P}(\text{O})\text{Ph}_2]$ (III) recorded at 106.9 MHz in CDCl_3 .

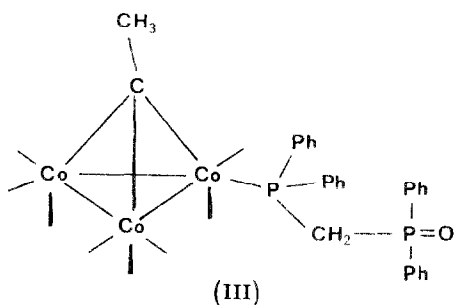
transformation (although not quantitative because of extensive decomposition at the high temperature required) indicates that I is the kinetically favoured isomer and II the more thermodynamically stable.

The CO scrambling processes in I and II are very similar. A mechanism proposed for intramolecular carbonyl exchange in the axially disubstituted stereoisomer II involves a merry-go-round process [9] in the Co_3 plane, coupled with axial-equatorial scrambling localized at the unique $\text{Co}(\text{CO})_3$ moiety, which is already evident in the low temperature limiting spectrum and gives rise to the high-field resonance of integrated intensity 3. A similar, but conical, merry-go-round process may operate in the equatorially disubstituted isomer I, as proposed for the $\text{Ru}_3(\text{CO})_{10}(\text{PPh}_2\text{CH}_2\text{PPh}_2)$ derivative [10].

The IR spectrum and elemental analysis of III unambiguously indicate that it is a monosubstituted derivative [11]. The high fluxionality of the CO frame (single absorption in the ^{13}C NMR spectrum down to -100°C) is also consistent with this formulation. The ^{31}P NMR spectrum exhibits two peaks: one is in the expected region for cobalt-bonded phosphines and the other is surprisingly far from the range for the free ligand, and the chemical shift suggests the presence of a phosphoryl group ($\text{Ph}_2\text{P}=\text{O}$). This suggestion is supported by the observation of an intense IR absorption at 1262 cm^{-1} in CCl_4 solution, in the region of the $\text{P}=\text{O}$ stretching mode [12].

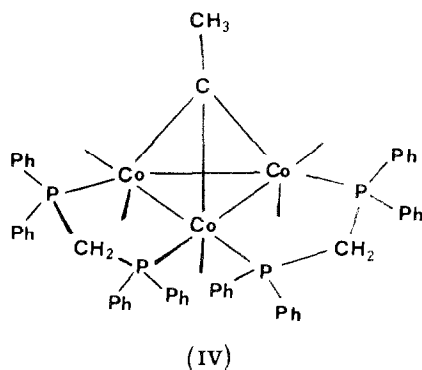
At room temperature (Fig. 2) the resonance assigned to ^{31}P atom coordinated to the cluster is very broad, and only the signal assigned to $\text{Ph}_2\text{P}=\text{O}$ group appears as a doublet; at -40°C the increased quadrupolar relaxation of the ^{59}Co nuclei causes a

sharpening of the resonance at 35.5 ppm and allows observation of the complete P-P coupling pattern [13].



We can exclude the possibility that III comes from a phosphine oxide impurity in the dppm employed, and so we believe that it arises from an oxidation process [14] of the pendant phosphorus atom in the elusive $(\text{CCH}_3)_3\text{Co}_3(\text{CO})_5(\text{dppm})$ intermediate. The high polarity of III makes its separation from the decomposition products that are invariably formed on TLC plates rather difficult and we suspect that such products derived from oxidation of diphosphines may be more frequent than one would expect.

We next treated preformed I with an equivalent amount of dppm in refluxing toluene for 45 min. The main product was a green compound whose spectral data suggest the formulation $(\mu\text{-CCH}_3)_3\text{Co}_3(\text{CO})_5(\mu\text{-dppm})_2$ (IV). The ^{13}C NMR spectrum at -50°C shows three resonances, at 217.3(s,1), 212.4(s,2), and 204.5(d, $^2J(\text{P-C})$ 24 Hz,2) and these do not change as the temperature is increased to $+25^\circ\text{C}$ except for some broadening induced by the quadrupolar ^{59}Co nuclei. On the other hand, the ^{31}P spectrum at low temperature shows a reasonably well resolved AA'BB' spin system (Fig. 3). Both the ^{13}C and ^{31}P data fit well with a structure characterized by two dppm moieties equatorially bridging adjacent edges of the Co_3 triangle. A structure of this derivative has been already suggested in ref. 5, and the observation of the above coupling pattern in the ^{31}P NMR spectrum provides strong support for that structure.



A second product obtained from the reaction of I with dppm is a brown complex, whose IR spectrum clearly suggests there is an increased substitution with respect to I. Its ^{31}P NMR spectrum (see Fig. 4) is very revealing, showing three resonances in

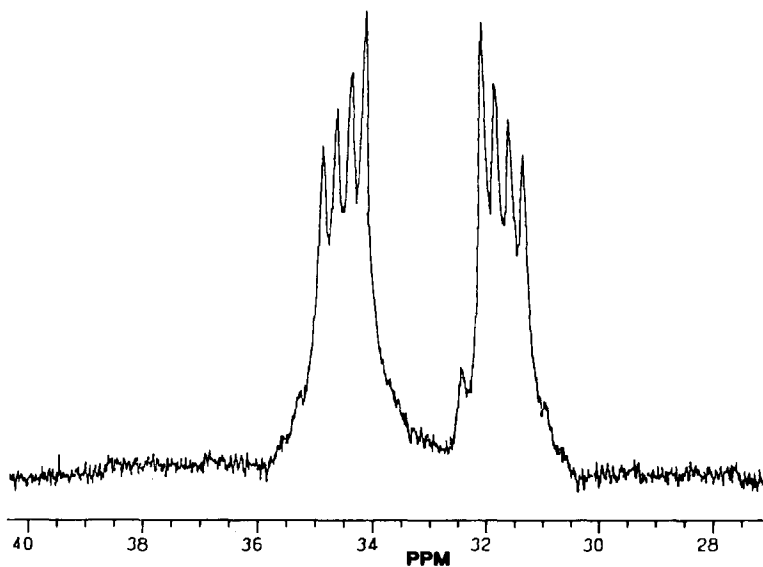


Fig. 3. Low temperature ^{31}P NMR limiting spectrum (-50°C) of $(\text{CCH}_3)_3\text{Co}_3(\text{CO})_5(\mu\text{-dppm})_2$ (IV) recorded at 106.9 MHz in CDCl_3 .

the relative intensity ratio 1/2/1. The highest field absorption falls in the region typical of uncoordinated phosphorus donor atoms and furthermore exhibits a coupling $J(\text{P-P})$ of ca. 49 Hz with the other resonance of intensity 1. On the basis

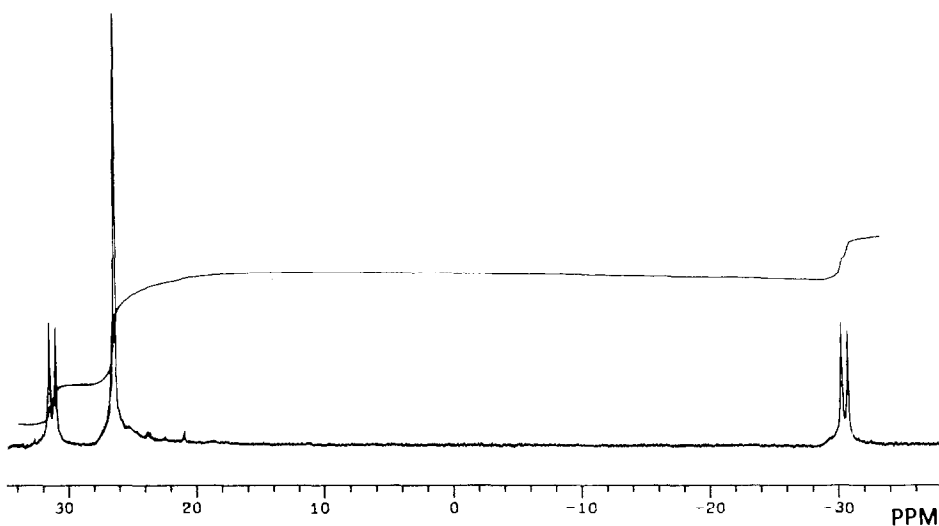
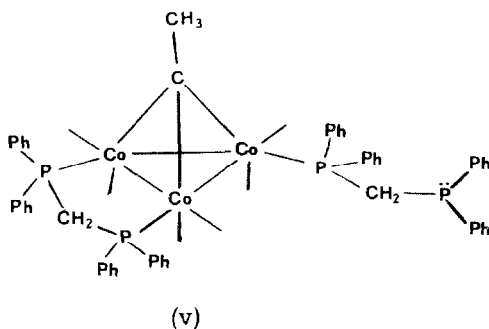


Fig. 4. -30°C ^{31}P spectrum of $(\text{CCH}_3)_3\text{Co}_3(\text{CO})_6(\mu\text{-dppm})(\text{dppm})$ (V) recorded at 106.9 MHz in CDCl_3 .

of this pattern, V is suggested to be a trisubstituted derivative bearing a dangling phosphorus atom.



Experimental

The cluster $(CCH_3)Co_3(CO)_9$ was prepared by the published procedure [15]. Bis(diphenylphosphino)methane (dppm) was purchased from Strem and used without purification. Solvents were dried over molecular sieves and saturated with nitrogen prior to use. TLC separation was performed by using extra-long (60 cm) preparative silica gel plates with 1/3 diethyl ether/hexane as eluant.

The IR spectra were recorded on a Perkin-Elmer 580 B instrument with matched 0.5 mm NaCl cells, and NMR spectra on a JEOL GX 270/89 spectrometer operating at 67.9 MHz (¹³C) or 106.9 MHz (³¹P). Elemental analyses were obtained by use of a F&M 185 C,H,N Analyzer and a Perkin-Elmer 303 Atomic Absorption Spectrophotometer.

Enrichment of $(CCH_3)Co_3(CO)_9$ at ca 15% level was achieved by stirring a sample of cluster (0.200 g) in 30 ml of cyclohexane overnight at room temperature under < 1 atm. ¹³CO (Monsanto Corp.) in a Schlenk tube (overall volume, 100 ml).

Reaction of $(CCH_3)Co_3(CO)_9$ with dppm

A mixture of $(CCH_3)Co_3(CO)_9$ (0.200 g, 0.44 mmol) dppm (0.170 g, 0.44 mmol), and 50 ml of benzene was stirred for 3 h at 45°C (external thermostatic bath) under N₂. The solution was cooled, filtered, and concentrated under reduced pressure; subsequent TLC workup gave three products I, II, and III in ca. 70, 20, and 5% yield, respectively.

$(CCH_3)Co_3(CO)_7(dppm)$ (I), brown. Anal. Found: C, 52.8; H, 3.0; Co, 22.4. C₃₄H₂₅O₇Co₃P₂ calc: C, 52.06; H, 3.19; Co, 22.58%.

$(CCH_3)Co_3(CO)_7(dppm)$ (II), purple. Anal. Found: C, 52.5; H, 2.9; Co, 22.8%.

$(CCH_3)Co_3(CO)_8[PPPh_2CH_2P(O)Ph_2]$ (III), dark brown. Anal. Found: C, 50.6; H, 2.8; Co, 21.6. C₃₅H₂₅O₉Co₃P₂ calc: C, 50.72; H, 3.02; Co, 21.38%.

Thermal transformation of isomer I into isomer II

A solution of $(CCH_3)Co_3(CO)_7(dppm)$, isomer I, (0.100 g, 0.13 mmol) in toluene was refluxed under N₂. The progress of the reaction was monitored by analytical TLC (precoated silica gel plates Merck). After 2 h transformation of isomer I into II was virtually complete, but this process was accompanied by extensive decomposition into an intractable brown residue (up to 35%).

Reaction of preformed (CCH₃)Co₃(CO)₇(dppm), (isomer I) with dppm

A mixture of (CCH₃)Co₃(CO)₇(dppm) (I) (0.100 g, 0.13 mmol), dppm (0.050 g, 0.13 mmol) and toluene was refluxed for 45 min under N₂. TLC separation gave the thermodynamically favoured isomer II in 5% yield, along with IV and V in 25 and 20% yield, respectively.

(CCH₃)Co₃(CO)₅(dppm)₂ (IV), dark green. Anal. Found: C, 61.4; H, 4.1; Co, 15.9. C₅₇H₄₇O₅Co₃P₄ calc: C, 61.51; H, 4.27; Co, 15.92%.

(CCH₃)Co₃(CO)₆(dppm)₂ (V), brown. Anal. Found: C, 61.3; H, 4.0; Co, 15.8. C₅₈H₄₇O₆Co₃P₄ calc: C, 61.05; H, 4.12; Co, 15.53%.

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