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TRIMETHYLPHOSPHITE DERIVATIVES OF MIXED COBALT-RHODIUM TETRANUCLEAR CLUSTERS

D. LABROUE, R. QUEAU and R. POILBLANC

Laboratoire de Chimie de Coordination du CNRS associé à l'Université Paul Sabatier, 205 route de Narbonne, 31400 Toulouse (France)

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Summary

$[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ and $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ react with trimethylphosphite to give mixtures of substitution products. Pure $[\text{Co}_3\text{Rh}(\text{CO})_{12-n}[\text{P}(\text{OMe})_3]_n]$ and $[\text{Co}_2\text{Rh}_2(\text{CO})_{12-n}[\text{P}(\text{OMe})_3]_n]$ ($n = 1-3$) can be separated and isomeric species can be recognized by use of IR and NMR spectra. Redistribution of metal atoms of the parent carbonyl cluster occurs during the synthesis and in the mass spectrometer. Not all the substituted clusters show scrambling of carbonyls; because the bulk of the phosphite ligands, $[\text{Co}_3\text{Rh}(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$ and $[\text{Co}_3\text{Rh}(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$ are rigid.

Introduction

Part of the interest in the chemistry of clusters lies in their potential use as homogeneous catalysts: It is possible that the metallic core of a cluster may promote specific catalytic activity as a result of interaction between neighbouring metal atoms. In this connection, studies of series of isostructural heteronuclear carbonyl clusters with varying metal ratios may provide information on the reactivity of individual metal centres.

Mixed tetranuclear carbonyl clusters of d^9 metals were first synthesized and studied by Chini et al. [1]. We have now investigated the replacement of carbonyl ligands in $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ and $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ by phosphorus donors. This series of clusters can be considered as derivatives of $\text{Co}_4(\text{CO})_{12}$ obtained by ligand and metal substitutions.

Results and discussion

$[\text{Co}_4(\text{CO})_{12}]$ is known to react with monodentate phosphorus ligands to give the complexes $[\text{Co}_4(\text{CO})_{12-n}\text{L}_n]$ ($n = 1-4$) [2-4] on addition of PR_3 or

TABLE 1
 REACTIONS OF $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ AND $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ WITH $\text{P}(\text{OMe})_3$

Starting material	Mole ratio Phosphite to cluster	Identified products	Yields ^a
$\text{Co}_3\text{Rh}(\text{CO})_{12}$	1/1	$\text{Co}_3\text{Rh}(\text{CO})_{11}\text{L}$	70
$\text{Co}_3\text{Rh}(\text{CO})_{12}$	3/1	$\text{Co}_3\text{Rh}(\text{CO})_{11}\text{L}$	30
		$\text{Co}_3\text{Rh}(\text{CO})_{10}\text{L}_2$	40
		$\text{Co}_2(\text{CO})_6\text{L}_2$	10
$\text{Co}_3\text{Rh}(\text{CO})_{12}$	3/1	$\text{Co}_3\text{Rh}(\text{CO})_{10}\text{L}_2$	20
		$\text{Co}_3\text{Rh}(\text{CO})_9\text{L}_3$	30
		$\text{Co}_2\text{Rh}_2(\text{CO})_{10}\text{L}_2$	20
		$\text{Co}(\text{CO})_2\text{L}_3^+$	10
$\text{Co}_3\text{Rh}(\text{CO})_{10}\text{L}_2$	2/1	$\text{Co}_2(\text{CO})_6\text{L}_2$	10
		$\text{Co}_3\text{Rh}(\text{CO})_{10}\text{L}_2$	20
		$\text{Co}_3\text{Rh}(\text{CO})_9\text{L}_3$	60
$\text{Co}_2\text{Rh}_2(\text{CO})_{12}$	1/1	$\text{Co}_2\text{Rh}_2(\text{CO})_{11}\text{L}$	70
$\text{Co}_2\text{Rh}_2(\text{CO})_{12}$	2/1	$\text{Co}_2\text{Rh}_2(\text{CO})_{11}\text{L}$	20
		$\text{Co}_2\text{Rh}_2(\text{CO})_{10}\text{L}_2$	40
		$\text{Co}(\text{CO})_2\text{L}_3^+$	10
$\text{Co}_2\text{Rh}_2(\text{CO})_{12}$	3/1	$\text{Co}_2(\text{CO})_6\text{L}_2$	10
		$\text{Co}_3\text{Rh}(\text{CO})_{10}\text{L}_2$	20
		$\text{Co}_2\text{Rh}_2(\text{CO})_9\text{L}_3$	30
		$\text{Co}_4(\text{CO})_{10}\text{L}_2$	10

^a Yields were not evaluated in terms of starting material, and only indicate the relative proportions of species eluted from a silica gel column.

$\text{P}(\text{OR})_3$ to a solution of the unsubstituted cluster at moderate temperatures. For heteronuclear clusters Cooke and May [5] have shown that the reaction of $[\text{HFeCo}_3(\text{CO})_{12}]$ with the same class of phosphorus ligands leads to complex mixtures of products, from which they isolated $[\text{HFeCo}_3(\text{CO})_{12-n}\text{L}_n]$ ($n = 1-3$). We have now carried out substitution reactions on $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ and $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ using $\text{P}(\text{OMe})_3$. In both cases it is possible to isolate dark brown crystal of mono-, di- or tri-substituted complexes of general formula $[\text{Co}_3\text{Rh}(\text{CO})_{12-n}\text{L}_n]$ and $[\text{Co}_2\text{Rh}_2(\text{CO})_{12-n}\text{L}_n]$ (Table 1) ($\text{L} = \text{P}(\text{OMe})_3$).

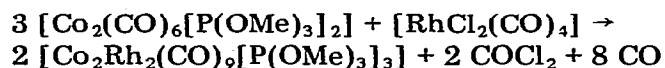
The yields of the various products isolated after purification are very dependent on the reaction conditions employed but it appears that the selectivity decreases with an increase of the proportion of added phosphite. As noticed first by Chini et al., facile redistribution of the metal atoms occur during substitution, leading to unexpected ratios of the metals in the cluster cores. This marked difference from the substitution reactions of the clusters $[\text{HFeCo}_3(\text{CO})_{12}]$, on which no redistribution of metal occurs, is associated with the different electronic structures of the metals. Facile, random, redistribution processes can be expected in isoelectronic mixed clusters, such as the series we have investigated in which both metals have a formal d^9 configuration, but redistributions are not favoured in mixed clusters of metals of different periodic groups where the separate metals have different ligand requirements. It seems probable that redistribution processes also easily occur during the reactions of homogeneous carbonyl clusters such as $[\text{Co}_4(\text{CO})_{12}]$, $[\text{Rh}_4(\text{CO})_{12}]$ or clusters of higher nuclearity. This fact has been widely ignored up to now in homogeneous cluster chemistry but it may well strongly affect the reactivity

TABLE 2
ANALYTICAL DATA (%)

Compound	Found (calcd.) (%)		
	C	H	P
$[\text{Co}_3\text{Rh}(\text{CO})_{11}\text{P}(\text{OMe})_3]$	23.59 (23.30)	1.26 (1.29)	4.35 (4.57)
$[\text{Co}_3\text{Rh}(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$	23.76 (23.40)	2.23 (2.20)	7.67 (7.87)
$[\text{Co}_3\text{Rh}(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$	23.89 (23.94)	2.98 (3.10)	10.28 (10.09)
$[\text{Co}_2\text{Rh}_2(\text{CO})_{11}\text{P}(\text{OMe})_3]$	22.20 (22.39)	1.19 (1.26)	4.10 (4.15)
$[\text{Co}_2\text{Rh}_2(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$	22.53 (22.53)	2.11 (2.11)	7.27 (7.44)
$[\text{Co}_2\text{Rh}_2(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$	22.78 (22.72)	2.84 (2.74)	9.81 (9.40)

pattern in such clusters*.

As selectivity in the synthesis of trisubstituted clusters is very poor, we tried a route similar to that described by Nixon and Hosseini [6] for the synthesis of $[\text{Co}_2\text{Rh}_2(\text{CO})_8(\text{PF}_3)_4]$.



This route did not lead to a higher yield of $[\text{Co}_2\text{Rh}_2(\text{CO})_9\text{L}_3]$, the major product after two days at room temperature being $\text{Co}_2\text{Rh}_2(\text{CO})_{10}\text{L}_2$, together with unreacted $[\text{Co}_2(\text{CO})_6\text{L}_2]$.

All the complexes are dark-brown and air-stable for only very short time. The crystals are best stored under nitrogen. They dissolve in all common organic solvents to give deep red brown solutions. Satisfactory elemental analytical data were obtained as listed in Table 2.

Mass spectra

In the mass spectra, the parent molecular ions $[\text{Co}_2\text{Rh}_2(\text{CO})_{12-n}\text{L}_n]^+$ or $[\text{Co}_3\text{Rh}(\text{CO})_{12-n}\text{L}_n]^+$ and peaks corresponding to stepwise loss of all the carbonyl groups giving $[\text{Co}_2\text{Rh}_2\text{L}_n]^+$ or $[\text{Co}_3\text{RhL}_n]^+$ are readily identifiable ($n = 1-3$). With this series of mixed cobalt-rhodium clusters the mass spectra are complicated by the redistribution phenomena producing tetranuclear ions containing metal ratios different from those present in the original cluster.

NMR spectra

The ^1H NMR data of the phosphite substituted mixed clusters are shown in Table 3. In the case of the $\text{Co}_2\text{Rh}_2(\text{CO})_{12-n}\text{L}_n$ series, the ^1H NMR spectra at room temperature are very similar to those of the homonuclear analogous

* A very recent work by Darensbourg and Incorvia [16] based on kinetics measurements shows that in the substitution reaction of $\text{Co}_3(\text{CO})_{12}$ by $\text{P}(\text{OMe})_3$ intermediates involving metal-metal bond cleavage must be considered.

TABLE 3

¹H NMR SPECTRA OF THE SUBSTITUTED CLUSTERS Co₃Rh(CO)_{12-n}L_n AND Co₂Rh₂(CO)_{12-n}L_n (CDCl₃ solution)

<i>n</i>	Compound	δ (ppm)	<i>J</i> (Hz)	
1	[Co ₃ Rh(CO) ₁₁ P(OMe) ₃]	3.75	11.7	doublet
	[Co ₂ Rh ₂ (CO) ₁₁ P(OMe) ₃]	3.73	12.3	doublet
2	[Co ₃ Rh(CO) ₁₀ [P(OMe) ₃] ₂]	3.72		multiplet
	[Co ₂ Rh ₂ (CO) ₁₀ [P(OMe) ₃] ₂]	3.78	12.2	doublet
3	[Co ₃ Rh(CO) ₉ [P(OMe) ₃] ₃]	3.74	11.2	3 doublets
		3.71	11.4	
	[Co ₂ Rh ₂ (CO) ₉ [P(OMe) ₃] ₃]	3.68	11.0	
	[Co ₂ Rh ₂ (CO) ₉ [P(OMe) ₃] ₃]	3.73	12.0	

[Co₄(CO)_{12-n}L_n] [3], so we assume that scrambling of CO is occurring as it is commonly observed in carbonyl clusters [7–9].

In contrast, the spectra of [Co₃Rh(CO)₁₀L₂] and [Co₃Rh(CO)₉L₃] indicate that the phosphorus atoms do not become equivalent through fluxional processes. Nevertheless, the unsubstituted parent molecule [Co₃Rh(CO)₁₂] is non rigid at room temperature. Johnson et al. have demonstrated [10] that scrambling of all the carbonyl groups of the cluster occurs down to -30°C. The ³¹P NMR spectra of [Co₃Rh(CO)₉L₃] after accumulation of 15000 spectra exhibit only two doublets, at 132.7 ppm and 129.1 ppm (ref. H₃PO₄) with coupling constants |*J*(Rh–P)| 230 and 223 Hz. No signals from phosphorus attached to cobalt atoms are visible. This indicates that the unique rhodium atom of the cluster is bonded to a phosphite ligand in two different ways. As the IR spectra also show (see below), Co₃Rh(CO)₉L₃ has been isolated as a mixture of isomers; therefore, one of the isomers has a phosphorus in an equatorial position (Fig. 1a) while the other has it in an axial position (Fig. 1b).

It is commonly assumed that scrambling is favoured by replacement of carbonyl groups by more electron-donating substituents [11,12], but at the same time an opposing steric effect results from the relatively non-mobile phosphorus ligand. In most cases the gross effect is rather unpredictable, and it would be of interest to know more about the mechanism of carbonyl scrambling

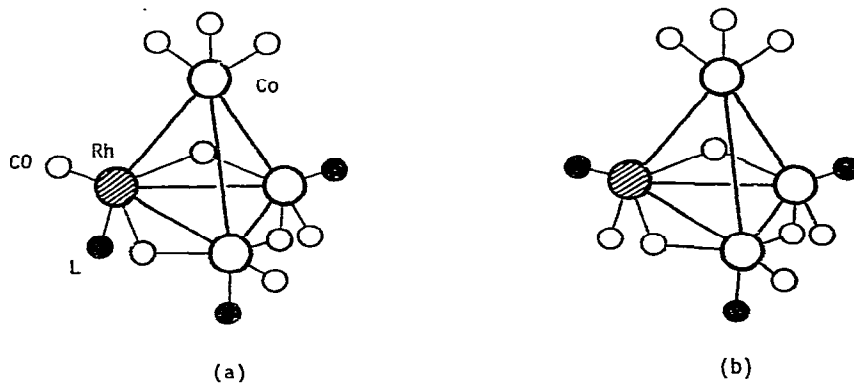


Fig. 1. Suggested structures for both isomers [Co₃Rh(CO)₉L₃]. Phosphorus ligands bound to cobalt atoms have been placed in arbitrary but plausible positions.

in order to interpret the different behaviour of $[\text{Co}_2\text{Rh}_2(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$ and $[\text{Co}_3\text{Rh}(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$. This is a matter of more than academic interest, because carbonyl scrambling may be related to catalytic activity of the cluster through the occurrence of a "dynamic vacant site" [13].

Infrared spectra

The crystallographic structures of $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ and $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ are not available, but Chini et al. have shown [1], on the basis of the infrared spectra that these complexes adopt the C_{3v} structure of $[\text{Co}_4(\text{CO})_{12}]$ or $[\text{Rh}_4(\text{CO})_{12}]$, with the rhodium lying in the basal plane defined by the three bridging carbonyl groups [14,15].

In the $\nu(\text{CO})$ region, the IR spectra of $[\text{Co}_3\text{Rh}(\text{CO})_{12-n}\text{L}_n]$ and $[\text{Co}_2\text{Rh}_2(\text{CO})_{12-n}\text{L}_n]$ are very similar to those of $[\text{Co}_4(\text{CO})_{12-n}\text{L}_n]$ (see Table 4). As we noticed first in the case of the substitution derivatives of $[\text{Co}_4(\text{CO})_{12}]$ [3], the $\nu_1(\text{CO})$ frequency is a reliable indicator of the degree of substitution (n) whatever the metal ratio Co/Rh in the cluster. With $\text{P}(\text{OMe})_3$, monosubstituted clusters have $\nu_1(\text{CO})$ lying in the range 2084–2087 cm^{-1} , for a disubstituted complex the frequency is lowered by ca. 14 cm^{-1} : 2065–2070 cm^{-1} , and for a trisubstituted cluster $\nu_1(\text{CO})$ is in the range 2052–2056 cm^{-1} .

With phosphorus ligands other than $\text{P}(\text{OMe})_3$ the $\nu_1(\text{CO})$ frequencies may change a little but in no case by as much as 14 cm^{-1} . This observation makes it easy to determine the degree of substitution for all the clusters we have studied, and can be extended with a small adjustment of numerical values to the $\nu_1(\text{CO})$ frequencies of other related tetrahedral series such as $[\text{Rh}_4(\text{CO})_{12-n}\text{L}_n]$, $[\text{Ir}_4(\text{CO})_{12-n}\text{L}_n]$ or even heteronuclear $[\text{HFeCo}_3(\text{CO})_{12-n}\text{L}_n]$. Splitting of this typical band provides good evidence of the existence of a mixture of isomers, and such splitting is found for the complexes $[\text{Co}_3\text{Rh}(\text{CO})_{10}\text{P}(\text{OMe})_3]_2$, $[\text{Co}_3\text{Rh}(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$ and $[\text{Co}_2\text{Rh}_2(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$.

Experimental

General comments

All reactions were carried out under nitrogen, using deaerated solvent. The carbonyl clusters $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ and $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ were prepared as previously described [1]. Infrared spectra were recorded on a Perkin–Elmer 225 spectrophotometer and mass spectra were recorded with a Varian MAT 311 spectrometer. NMR spectra were recorded on Varian A60, Cameca 250 or Bruker WH 90 (^{31}P) spectrometers.

All reactions were carried out in ~50 ml of petroleum ether (50–60°C).

Preparation of $[\text{Co}_3\text{Rh}(\text{CO})_{11}\text{P}(\text{OMe})_3]$

Addition of trimethylphosphite (7×10^{-4} mol) to a petroleum ether solution of $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ (7×10^{-4} mol) led within an hour at room temperature to the substitution of one carbonyl group of the initial cluster. Cooling to -20°C afforded black crystals of the desired complex.

Preparation of $[\text{Co}_3\text{Rh}(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$

Trimethylphosphite (4×10^{-4} mol) was added dropwise to a stirred solution

TABLE 4
 INFRARED SPECTRA OF THE CLUSTERS $[\text{Co}_{4-x}\text{M}_x(\text{CO})_{12-n}\text{L}_n]$ IN THE $\nu(\text{CO})$ REGION (cm^{-1}) (hexadecane solution).

Compound	Terminal CO					Bridged CO				
	ν	ν	ν	ν	ν	ν	ν	ν	ν	ν
$[\text{Co}_4(\text{CO})_{11}\text{P}(\text{OMe})_3]$	2086.5m	2047.5vs	2042vs	2028s	2010w	1998w	1879w	1849m	1834m	
$[\text{Co}_3\text{Rh}(\text{CO})_{11}\text{P}(\text{OMe})_3]$	2084.3m	2043.8s	2024.3s	2017.5m	1996m	1890w	1860.3s	1848s		
$[\text{Co}_2\text{Rh}_2(\text{CO})_{11}\text{P}(\text{OMe})_3]$	2084m	2052s	2043s	2026m	2015(hs)	1900w	1868m	1848m		
$[\text{Co}_4(\text{CO})_{10}\text{P}(\text{OMe})_3]_2$	2070m	2036s	2016s	2000m	1984m	1828.5m	1814.5m			
$[\text{Co}_3\text{Rh}(\text{CO})_{10}\text{P}(\text{OMe})_3]_2$	2070m	2067s	2031.7s	2012m	2000w	1874w	1842m	1823m		
$[\text{Co}_2\text{Rh}_2(\text{CO})_{10}\text{P}(\text{OMe})_3]_2$	2065m	2032s	2012.5s	2003(sh)		1841m				
$[\text{Co}_4(\text{CO})_9\text{P}(\text{OMe})_3]_3$	2052s	2010vs	2003s	1998(sh)	1983(sh)	1974m	1820m	1805m		
$[\text{Co}_3\text{Rh}(\text{CO})_9\text{P}(\text{OMe})_3]_3$	2054m	2050m	2021s	1998s	1983m	1863w	1819m			
$[\text{Co}_2\text{Rh}_2(\text{CO})_9\text{P}(\text{OMe})_3]_3$	2053w	2043m	2010(sh)	2004s	1985m	1830(sh)	1824s			

of $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ (2×10^{-4} mol) at room temperature. The reaction was followed by infrared spectroscopy. The major product was $[\text{Co}_3\text{Rh}(\text{CO})_{11}\text{P}(\text{OMe})_3]$. Further addition of 2×10^{-4} mol of $\text{P}(\text{OMe})_3$ produces a higher degree of substitution. Most of the $[\text{Co}_2(\text{CO})_6[\text{P}(\text{OMe})_3]_2]$ formed was removed by fractional crystallization and the remaining products were separated by chromatography on silica gel (See Table 1).

Preparation of $[\text{Co}_3\text{Rh}(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$

Trimethylphosphite (11.2×10^{-4} mol) was added dropwise to a stirred solution of $[\text{Co}_3\text{Rh}(\text{CO})_{12}]$ (3.7×10^{-4} mol) at 30°C . The pale yellow precipitate of $[\text{Co}(\text{CO})_2[\text{P}(\text{OMe})_3]_3]^+$, $[\text{Co}(\text{CO})_4]^-$ was filtered off.

The infrared spectra of the solutions were very complex, so we arbitrarily stopped the reaction after 24 h. Chromatographic separation was necessary to isolate pure complexes. At least five fractions can be separated. The two first, eluted with hexane and hexane/toluene 1/1 have not been fully identified, but their yellowish colour as well as their elution characteristics suggest that they are dinuclear species. Elution with toluene/methylene chloride afforded three brown fractions identified as $[\text{Co}_3\text{Rh}(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$, $[\text{Co}_2\text{Rh}_2(\text{CO})_{10}\text{P}(\text{OMe})_3]_2]$ and $[\text{Co}_3\text{Rh}(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$.

Preparation of $[\text{Co}_2\text{Rh}_2(\text{CO})_{11}\text{P}(\text{OMe})_3]$

An equivalent amount of trimethylphosphite was added to an ether petroleum solution of $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ (5.1×10^{-4} mol). After 1 h the mixture was cooled to -20°C to give black crystals of $[\text{Co}_2\text{Rh}_2(\text{CO})_{11}\text{P}(\text{OMe})_3]$.

Preparation of $[\text{Co}_2\text{Rh}_2(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$

$\text{P}(\text{OMe})_3$ (6.6×10^{-4} mol) was added dropwise to a stirred solution of $\text{Co}_2\text{Rh}_2(\text{CO})_{12}$ (3.3×10^{-4} mol). Within a few minutes a pale yellow precipitate of $[\text{Co}(\text{CO})_2[\text{P}(\text{OMe})_3]_3]^+$ $[\text{Co}(\text{CO})_4]^-$ separated out. This was filtered off and 0.8×10^{-4} mol of $\text{P}(\text{OMe})_3$ was added to the filtrate. After removal of the solvent in vacuo, the oily residue was dissolved in toluene and chromatographed on a column of silica gel. Elution with hexane/toluene 1/1 gave a brown fraction of $[\text{Co}_2\text{Rh}_2(\text{CO})_{11}\text{P}(\text{OMe})_3]$. Pure toluene gave a second brown fraction of $[\text{Co}_2\text{Rh}_2(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$. A third fraction of identical colour, eluted with methylene chloride, was not fully identified.

Preparation of $[\text{Co}_2\text{Rh}_2(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$

Trimethylphosphite (14×10^{-4} mol) was added dropwise to a stirred solution of $[\text{Co}_2\text{Rh}_2(\text{CO})_{12}]$ (4.7×10^{-4} mol). The mixture was kept for 24 h at 40°C . The solvent was evaporated and the oily residue dissolved in toluene and chromatographed on silica gel. Elution with hexane/toluene 1/1 gave $[\text{Co}_2(\text{CO})_6[\text{P}(\text{OMe})_3]_2]$. Pure toluene then gave a brown fraction of $[\text{Co}_3\text{Rh}(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$. $[\text{Co}_2\text{Rh}_2(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$ and $[\text{Co}_3\text{Rh}(\text{CO})_9[\text{P}(\text{OMe})_3]_3]$ were eluted as third and fourth fractions with toluene/methylene chloride 2/1. Finally, $[\text{Co}_4(\text{CO})_{10}[\text{P}(\text{OMe})_3]_2]$ was eluted with pure methylene chloride.

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