Synthesis and spectroscopic characterization of the heteronuclear diphosphine linked cluster $Os_3(CO)_{11}(Ph_2PCH_2PPh_2)Rh_6(CO)_{15}$

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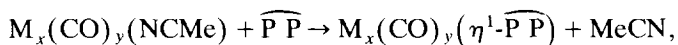
(Received July 10, 1991)

Abstract

The synthesis of the heteronuclear diphosphine linked cluster $Os_3(CO)_{11}(Ph_2PCH_2PPh_2)Rh_6(CO)_{15}$ is reported. The structure of this compound is discussed on the basis of its IR and ^{31}P NMR spectra.
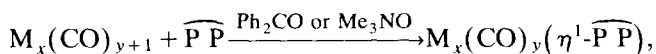
Introduction of labile ligands, e.g. acetonitrile [1,2], in the coordination sphere of carbonyl clusters enables us to carry out selective substitution with the various ligands under mild conditions. Such an approach seems particularly effective in the synthesis of heteronuclear clusters, where two different cluster fragments are linked by bidentate ligands, diphosphines for example [DPPM ($Ph_2PCH_2PPh_2$), DPPE ($Ph_2P(CH_2)_2PPh_2$), DPPA ($Ph_2PC\equiv CPPh_2$)].

When two identical clusters are to be linked, the activation of the starting carbonyl complexes by Ph_2CO^- in the presence of diphosphine affords double clusters in good yields ($[Ru_3(CO)_{11}]_2DPPE$, 43% [3]; $[Ru_3(CO)_{11}]_2DPPA$, 70% [4]; $[RCCo_3(CO)_8]_2DPPE$, 40–80% [5]). However, the yield of other similar reactions is not usually so high because of the possible variety of diphosphine coordination modes on a cluster framework including polymeric compound formation [6]. In the case of the different clusters interlinking, the yield should be considerably lower by statistical distribution of the products among possible pairs of linked cluster fragments.

The optimal synthetic strategy for generation of heteronuclear double clusters linked by a bidentate ligand consists of (1) coordination of an appropriate ligand in η^1-mode on one cluster core, for example
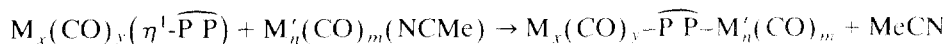
$$M_x(CO)_y(NCMe) + \widehat{P\,P} \rightarrow M_x(CO)_y\left(\eta^1\text{-}\widehat{P\,P}\right) + MeCN,$$

or

$$M_x(CO)_{y+1} + \widehat{P\,P} \xrightarrow{\text{Ph}_2\text{CO or Me}_3\text{NO}} M_x(CO)_y\left(\eta^1\text{-}\widehat{P\,P}\right),$$
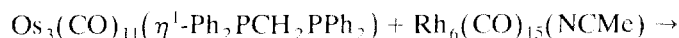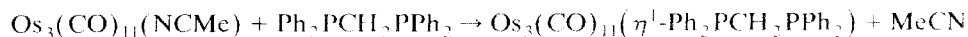
where $\widehat{P\,P} \equiv$ diphosphine,

under mild conditions, thus avoiding side reactions in which the second phosphorus atom of the diphosphine becomes coordinated; (2) binding of a "dangling" phosphorus atom of η^1-diphosphine with another cluster fragment

$$M_x(CO)_y(\eta^1\text{-}\overparen{P\ P}) + M'_n(CO)_m(NCMe) \rightarrow M_x(CO)_y\text{-}\overparen{P\ P}\text{-}M'_n(CO)_m + MeCN$$

The application of a preliminary activated cluster $M'_n(CO)_m(NCMe)$ is particularly important to avoid statistical distribution of the products at this stage.

The proposed synthetic route was used in the synthesis of the heteronuclear double cluster $Os_3(CO)_{11}Ph_2PCH_2PPh_2Rh_6(CO)_{15}$ (I)

$$Os_3(CO)_{11}(NCMe) + Ph_2PCH_2PPh_2 \rightarrow Os_3(CO)_{11}(\eta^1\text{-}Ph_2PCH_2PPh_2) + MeCN$$

$$Os_3(CO)_{11}(\eta^1\text{-}Ph_2PCH_2PPh_2) + Rh_6(CO)_{15}(NCMe) \rightarrow$$

$$Os_3(CO)_{11}Ph_2PCH_2PPh_2Rh_6(CO)_{15}$$

This reaction sequence seems the optimum one because $Os_3(CO)_{11}(\eta^1\text{-}Ph_2PCH_2PPh_2)$ remains η^1-coordination for a long time without any side reactions [6]. On the contrary, reaction of $Rh_6(CO)_{15}(NCMe)$ with DPPM leads to $Rh_6(CO)_{14}(\mu_2\text{-}Ph_2PCH_2PPh_2)$, formation of η^1-intermediate not being detected by IR spectroscopy or TLC.

The yield of heteronuclear double cluster achieved in such a way is high enough with the use of DPPM. An attempt at different clusters interlinking by DPPA under similar conditions gave double clusters in a very low yield (0.5–3.0%) [7].

Results of elemental analysis and spectral characteristics of 1 are given in Table 1. ^{31}P NMR spectrum displays two signals of equal intensity. The high field doublet readily assigns to the phosphorus atom bound to the Os_3 core. The low

Table 1

Spectral (IR, ^{31}P NMR) and analytical data of $Os_3(CO)_{11}Ph_2PCH_2PPh_2Rh_6(CO)_{15}$ (I) and some related compounds

^{31}P NMR spectrum of I

Chemical shifts (ppm)
vs. ext. 85% H_3PO_4; -7.53 (d) {$J(P-P) = 44.6$}
positive values deshielded   22.04 (dd) {$J(P-P) = 44.6$, $J(Rh-P) = 135.4$}
{Coupling constants J (Hz)}

IR data

Compound	ν_{CO}, CHCl$_3$ (cm^{-1})								
(I)	2108w	2100m	2067vs	2057msh	2035m	2020s	1990w	1976w	1796mbr
$Rh_6(CO)_{15}PPh_3$ (II)	2100m		2064vs		2036m				1788mbr
Differential									
spectrum (I)–(II)	2108w			2056m		2019s	1990w	1976w	
$Os_3(CO)_{11}PPh_3$	2109w			2054m	2034sh	2019s	1987w	1974w	

Elemental analysis of $Os_3(CO)_{11}PPh_2CH_2PPh_2Rh_6(CO)_{15}$

	Calculated	Found
%C	26.58	26.35
%H	0.96	1.17

field pattern, doublet of doublets, has the typical ^{103}Rh–^{31}P coupling constant 135.4 Hz and corresponding coupling with the nonequivalent Os_3 bound phosphorus atom. This resonance was assigned to Rh_6 bound phosphorus.

According to the proposed structure, cluster fragments $Os_3(CO)_{11}$ and $Rh_6(CO)_{15}$ are considerably independent. Therefore, the vibrational spectrum of 1 should be a superposition of the spectra of the corresponding phosphine derivatives, e.g. $Rh_6(CO)_{15}PPh_3$ and $Os_3(CO)_{11}PPh_3$. In fact, the difference in the $Rh_6(CO)_{15}PPh_3$ IR spectrum in the carbonyl region from that of I, using standard software of a Specord M-80 IR instrument, gives a $\nu(CO)$ pattern which closely matches that of $Os_3(CO)_{11}PPh_3$ with respect to band position and their relative intensities.

Experimental

$Os_3(CO)_{11}(MeCN)$, $Rh_6(CO)_{15}(MeCN)$ and $Rh_6(CO)_{15}PPh_3$ were prepared by published methods [1,2]. $Os_3(CO)_{11}PPh_3$ for IR measurements was obtained by reaction of $Os_3(CO)_{11}(MeCN)$ with PPh_3 and purified by column chromatography.

Solution of DPPM (51.5 mg, 0.134 mmol) in 40 cm^3 $CHCl_3$ was added dropwise to a $CHCl_3$ solution of $Os_3(CO)_{11}(MeCN)$ (123.2 mg, 0.134 mmol). Immediately after ligand addition, a solution of $Rh_6(CO)_{15}(MeCN)$ (144.2 mg, 0.134 mmol) in 40 cm^3 $CHCl_3$ was added to the reaction mixture. Column chromatography (SiO_2, column 4×12 cm, eluants hexane/$CHCl_3$ 4:3 and 1:1) gave the following compounds (in the order of elution): $Os_3(CO)_{12}$, $Rh_6(CO)_{16}$, $Os_3(CO)_{11}Ph_2PCH_2$ $PPh_2Rh_6(CO)_{15}$ (61.2 mg, 20%), $Rh_6(CO)_{14}(\mu\text{-DPPM})$ (40 mg, 21%).

Further study of this approach for synthesis of heteronuclear double diphosphine linked clusters is in progress.

Acknowledgement

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