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TRIMETHYLPHOSPHITE DERIVATIVES OF THE MIXED COBALT—IRIDIUM TETRANUCLEAR CLUSTER $Co_2Ir_2(CO)_{12}$

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Summary

Up to four carbonyl groups of $Co_2Ir_2(CO)_{12}$ have been replaced by trimethylphosphite to form tetranuclear clusters of formula $Co_2Ir_2(CO)_{12-n}[P(OMe)_3]_n$. The clusters do not exhibit the redistribution of the metal core which is observed in the case of mixed cobalt—rhodium clusters. Attachment of three or four trimethylphosphites to the metal skeleton of the cluster inhibits the scrambling of the carbonyl groups.

Introduction

Carbonyl groups of $Co_4(CO)_{12}$ can be replaced at moderate temperatures by two electron donor phosphorus ligands such as phosphines and phosphites [1]. Depending upon reaction parameters (mainly temperature and ligand to cluster ratio) the products are $Co_4(CO)_{11}L$, $Co_4(CO)_{10}L_2$, $Co_4(CO)_9L_3$ or $Co_4(CO)_8L_4$. The same substitution reactions performed with $Ir_4(CO)_{12}$ require elevated temperature [2,3] and lead mainly to tri- and tetrasubstituted products. Comparison of the substitution reactions in the intermediate cluster $Co_2Ir_2(CO)_{12}$ with those of the related homonuclear clusters is of interest. The behaviour of the cobalt—iridium cluster with respect to the metal core redistribution, as encountered during a similar study on cobalt—rhodium mixed clusters $Co_2Rh_2(CO)_{12}$ and $Co_3Rh(CO)_{12}$ [4], is a further feature of interest.

Results and discussion

Monosubstituted derivative $Co_2Ir_2(CO)_{11}P(OMe)_3$ can be easily prepared at room temperature by adding a stoichiometric amount of the phosphorus ligand to a light petroleum solution of $Co_2Ir_2(CO)_{12}$. This fast reaction is comparable to that of $Co_4(CO)_{12}$ and is quite different from that of $Ir_4(CO)_{12}$. The mono-

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substituted derivative $Ir_4(CO)_{11}P(OMe)_3$ is more conveniently prepared by reduction of the mononuclear complex $Ir(CO)_2$(*p*-toluidine)Cl in the presence of Zn, carbon monoxide and trimethylphosphite [5].

Preparation of the disubstituted derivative of $Co_2Ir_2(CO)_{12}$ is also easily achieved with the appropriate trimethylphosphite/cluster ratio (2/1) at room temperature. Black crystals of $Co_2Ir_2(CO)_{10}[P(OMe)_3]_2$ separate at −20°C from the petroleum ether solution.

In contrast it is very difficult to obtain $Co_2Ir_2(CO)_9[P(OMe)_3]_3$. When the calculated stoichiometry (L/Cluster = 3) was used, only the disubstituted derivative $Co_2Ir_2(CO)_{10}[P(OMe)_3]_2$ was formed, whereas more drastic conditions lead to $Co_2Ir_2(CO)_8[P(OMe)_3]_4$ as major product. Variation the temperature or the ligand/cluster ratio did not result in a satisfactory method. In all cases yields in $Co_2Ir_2(CO)_9[P(OMe)_3]_3$ were below 10%.

Synthesis of the tetrasubstituted $Co_2Ir_2(CO)_8[P(OMe)_3]_4$ requires moderate heating, ca. 60°C, and some excess of ligand (L/Cluster = 6); $Co_2Ir_2(CO)_8$-$[P(OMe)_3]_4$ was the major product. No attempt was made to make more substituted clusters. The ease of reaction of $P(OMe)_3$ with $Co_2Ir_2(CO)_{12}$ clearly indicates that this cluster resembles $Co_4(CO)_{12}$ more than $Ir_4(CO)_{12}$ in respect of substitution reactions. The unexpected difficulty of the trisubstitution step cannot be satisfactory explained in absence of kinetic data, such as those obtained with $Ir_4(CO)_{12}$ [2,6] and $Co_4(CO)_{12}$ [7].

A point of interest when dealing with heteronuclear mixed clusters is the occurrence of redistribution of the metal core. It has been shown that facile redistribution occurs in the synthesis of the series of mixed cobalt—rhodium clusters $Co_3Rh(CO)_{12-n}L_n$ and $Co_2Rh_2(CO)_{12-n}L_n$ ($L = P(OMe)_3$, $n = 0$ to 4). This phenomenon is also evident in the synthesis of the parent cluster carbonyls [8] and when mass spectra are recorded. In contrast, for the mixed cobalt—iridium clusters which we have studied the Co_2Ir_2 core remains unchanged in all cases. The greater stability of this series of clusters $Co_2Ir_2(CO)_{12-n}L$ can be related to the reinforcement of the metal—metal bond when going down a column of the periodic table. Nevertheless we must emphasize that this stability could not be entirely foreseen because Chini et al. [8] have observed redistribution in the Rh_3Ir and Rh_2Ir_2 core. Absence of the redistribution in the Co_2Ir_2-$(CO)_{12-n}L_n$ series seems to be unique for d^9 heteronuclear clusters of $M_4(CO)_{12}$ formula. This could be of significance in considering the catalytic properties of this type of complex, since clusters are often assumed to fragment into mononuclear species.

Infrared spectra

Infrared spectra of substituted clusters $Co_2Ir_2(CO)_{12-n}L_n$ are very similar to those of $Co_4(CO)_{12-n}L_n$ (Table 1) indicating similarity in their structures [1]. In all cases the IR spectra in the $\nu(CO)$ region are easily interpreted in term of terminal and bridging CO groups (see Table 1). Three CO bridging groups are bound to the base of the C_{3v} structure while the remaining CO groups are terminal. The substitution ($n = 1$ to 4) occurs only at terminal positions and probably results in successive bonding of one $P(OMe)_3$ group to each metal atom.

With homometallic clusters, isomeric forms of the complexes are possible as

TABLE 1

INFRARED SPECTRA OF THE DERIVATIVES $Co_2Ir_2(CO)_{12-n}L_n$ (spectra in dichloromethane)

	Terminal CO	CO bridge
$Co_2Ir_2(CO)_{11}P(OMe)_3$	2088.5m, 2085m 2051.5s 2045s 2024s 2014.5w 2005w	1888w 1854.5m 1834m
$Co_2Ir_2(CO)_{10}[P(OMe)_3]_2$	2070sh 2065.2m 2033s 2011s 2001sh	1833m 1810m
$Co_2Ir_2(CO)_9[P(OMe)_3]_3$	2050.5m 2047sh 2018.5s 1994s 1988sh 1975sh	1853w 1823m 1792.5sh
$Co_2Ir_2(CO)_8[P(OMe)_3]_4$	2026m 1995sh 1970s	1830sh 1793s 1725sh

three positions for substitution are available. Two of them are on the base of the tetrahedron (axial or equatorial) and one in apical position. Moreover when the four metals are no longer equivalent, the number of possible isomers grows rapidly. Examination of the IR spectra shows that mono-, di- and tri-substituted derivatives exhibit a splitting of the characteristic ν_1CO-band (about 3 cm^{-1}). This is indicative of the presence of a mixture of isomers. Broadening of the bands in the IR spectra of $Co_2Ir_2(CO)_8[P(OMe)_3]_4$ preclude any conclusions on this topic.

NMR spectra

^{13}C NMR spectra studies on $Rh_4(CO)_{12}$ [9], $Co_4(CO)_{12}$ [10—12], $Ir_4(CO)_{12-n}$-L_n [13—14] and $Co_3Rh(CO)_{12}$ [15] have shown that scrambling of the CO groups is a general phenomenon for tetrahedral carbonyl clusters. A simple way of revealing this scrambling of CO on phosphite substituted carbonyl clusters (when $n > 1$) is provided by the proton NMR spectra.

^{1}H NMR data for the $Co_2Ir_2(CO)_{12-n}L_n$ series are listed in Table 2. Coupling and chemical shift are in the same range as in the $Co_4(CO)_{12-n}L_n$, $Co_3Rh(CO)_{12-n}L_n$, and $Co_2Rh_2(CO)_{12-n}L_n$ series. When there is scrambling of CO, the different [P(OMe)$_3$] ligands give only one doublet; this is the case for $Co_2Ir_2(CO)_{10}[P(OMe)_3]_2$. In contrast, signals arising from $Co_2Ir_2(CO)_9[P(OMe)_3]_3$ and $Co_2Ir_2(CO)_8[P(OMe)_3]_4$ indicate the absence of CO scrambling. Heating the

TABLE 2

COUPLING CONSTANTS AND CHEMICAL SHIFTS IN $CDCl_3$

	δ (ppm)	J(P—H) (Hz)
$Co_2Ir_2(CO)_{11}[P(OMe)_3]$ [a]	3.72	12.1 (doublet)
$Co_2Ir_2(CO)_{10}[P(OMe)_3]_2$ [a]	3.70	12.2 (doublet)
$Co_2Ir_2(CO)_9[P(OMe)_3]_9$ [a]	3.70	— unresolved set
$Co_2Ir_2(CO)_8[P(OMe)_3]_4$ [b]	3.75	11.1
	3.66	11.0 (3 doublets)
	3.56	10.8

[a] 60 MHz spectra. [b] 250 MHz spectrum.

most stable derivative $Co_2Ir_2(CO)_8[P(OMe)_3]_4$ to 40°C does not affect the rigid nature of the molecule.

Steric hindrance upon increasing the number of $P(OMe)_3$ attached to the metal core of the cluster is the dominating factor in the $Co_2Ir_2(CO)_{12-n}L_n$ series. The behaviour is comparable to that of the $Co_3Rh(CO)_{12-n}L_n$ series, and contrast [4] with that of the $Co_2Rh_2(CO)_{12-n}L_n$ series, in which scrambling remains upon substitution up to $n = 4$.

Experimental

General comments

All reactions were carried out under nitrogen, using deaerated solvents. $Co_2Ir_2(CO)_{12}$ was prepared by a new procedure from $(C_8H_{12}IrCl)_2$ and $Co_2(CO)_8$. Infrared spectra were recorded on Perkin—Elmer 225 spectrometer. NMR spectra were recorded on Varian A 60 and Cameca 250 spectrometers. Mass spectra were obtained by electron impact on Varian MAT 311.

Preparation of $Co_2Ir_2(CO)_{12}$

A hexane solution of $Co_2(CO)_8$ and $(C_8H_{12}IrCl)_2$ was stirred for 24 h. The white precipitate of $CoCl_2$ was filtered off and the solution was cooled to —20°C. Black crystals of $Co_2Ir_2(CO)_{12}$ were collected (yield 60% calculated from 200 mg of $(C_8H_{12}IrCl)_2$).

Preparation of $Co_2Ir_2(CO)_{11}P(OMe)_3$

Freshly distilled trimethylphosphite (1.67×10^{-4} mol) was added to a petroleum ether solution of $Co_2Ir_2(CO)_{12}$ (1.67×10^{-4} mol) and the mixture was kept at room temperature for two hours. Upon cooling to 0°C, yellow crystals (unidentified) separated from the solution. The solution was concentrated and cooled to —20°C affording black crystals of $Co_2Ir_2(CO)_{11}P(OMe)_3$, which was characterized by its IR spectrum and elemental analysis (Found: C, 18.41; H, 1.03. $C_{14}H_9Co_2Ir_2O_{14}P$ calcd.: C, 17.94; H, 0.96%) and mass spectrum (parent molecular ion and stepwise loss of all the carbonyls).

Preparation of $Co_2Ir_2(CO)_{10}[P(OMe)_3]_2$

Trimethylphosphite (6.8×10^{-4} mol) was added dropwise to a stirred solution of $Co_2Ir_2(CO)_{12}$ (3.4×10^{-4} mol). The infrared spectra showed that the disubstituted derivative was formed within two hours. Crystallization afforded black crystals of the desired product. (Found: C, 18.89; H, 1.82. $C_{16}H_{18}Co_2Ir_2O_{16}P_2$ calcd.: C, 18.60; H, 1.74%). Mass spectra: ($Co_2Ir_2(CO)_nL_2^+$ n = 10 to 0).

Preparation of $Co_2Ir_2(CO)_9[P(OMe)_3]_3$

As previously mentioned, no satisfactory route to this complex was found. In a typical experiment we used 200 mg of $Co_2Ir_2(CO)_{12}$ dissolved in 30 ml of toluene and added $P(OMe)_3$ dropwise ($P(OMe)_3$/Cluster = 3.6). The mixture was maintained at 40°C and was stirred for 16 h. The products were separated on a silica gel column using hexane/CH_2Cl_2 as eluent; the fractions were collected in the order of increasing degree of substitution, i.e. $Co_2Ir_2(CO)_{10}L_2$ then $Co_2Ir_2(CO)_9L_3$ and finally $Co_2Ir_2(CO)_8L_4$. The trisubstituted derivative was characterized by its IR spectrum and mass spectra ($Co_2Ir_2(CO)_nL_3^+$; n = 9 to 0).

Preparation of $Co_2Ir_2(CO)_8[P(OMe)_3]_4$

Trimethylphosphite (1.33×10^{-4} mol) was added dropwise to a solution of $Co_2Ir_2(CO)_{12}$ (4.4×10^{-4} mol). After a few minutes $Co_2Ir_2(CO)_{10}L_2$ was formed and no further evolution of gas occurred even when the solution was kept at 60° C. An excess of $P(OMe)_3$ (4.4×10^{-4} mole) (L/Cluster = 8) was added, and the solution was maintained at 60° C for four hours. Separation of the product mixture on a silica gel column afforded some $Co_2Ir_2(CO)_9L_3$, the desired $Co_2Ir_2(CO)_8[P(OMe)_3]_4$ (Found: C, 19.39; H, 3.09. $C_{20}H_{36}Co_2Ir_2O_{20}P_4$ calcd.: C, 19.60; H, 2.94%) and some unidentified products. Satisfactory mass spectral data could not be obtained for this compound under electron impact.

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