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ORGANOMETALLIC COMPOUNDS WITH METAL—METAL BONDS

V*. NEW HETERONUCLEAR TETRAMETALLIC CLUSTERS OF PLATINUM WITH COBALT OR MOLYBDENUM AND A NEW HOMOTRIMETALLIC PLATINUM CLUSTER**

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Summary

Two new heteronuclear tetrametallic complexes $(CO)_5Co_2(CO)_2Pt_2(CO)(PPh_3)_2$ (I), $(\eta\text{-}C_5H_5)_2(CO)_2Mo_2(CO)_4Pt_2(PPh_3)_2$ (II) and a new homonuclear trimetallic complex $Pt_3(CO)_2(PPh_3)_4$ (III) have been synthesised by reaction between carbonylmetallate anions $Na[(Co(CO)_4]$ or $Na[(\eta\text{-}C_5H_5)Mo(CO)_3]$ and *cis*- or *trans*-$PtCl_2(PPh_3)_2$.

The compounds were characterised by analysis and IR spectroscopy. On the basis of preliminary X-ray results, I and II appear to have a tetrahedral arrangement of the metallic atoms in a "butterfly"-type structure.

Introduction

Considerable interest has recently been devoted to homo- or heteronuclear polymetallic compounds, especially when they contain three or more metallic atoms.

However, relatively little work has been reported on metal—metal bonds between platinum or palladium, M^1, and transition metals, M^2, in these compounds. Such trimetallic complexes are linear $M^2—M^1—M^2$ [1], or triangular [2-4]. A number of these triangular clusters containing platinum—iron [3], platinum—ruthenium and platinum—osmium bonds [4] have been reported. Recently [5], we described the preparation and characterisation of two heteronuclear clusters,

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Pt(diphos)[$Co_2(CO)_7$] and Pt(diars)[$Co_2(CO)_7$], by a different route from that used previously for the preparation of the other compounds.

Amongst the tetrametallic clusters, many heteronuclear compounds of transition metals have been reported. These are of the type $M^1{}_1\ M^2{}_3$ or $M^1{}_2\ M^2{}_2$ (M^1, M^2 are transition metals).

The various methods of synthesis can be classified under three headings:

(i) Reactions of a carbonylmetallate anion with a metal carbonyl, as in the case of the $Fe_2W_2(\eta\text{-}C_5H_5)_2(CO)_{10}{}^{2-}$ and $Fe_2Mo_2(\eta\text{-}C_5H_5)_2(CO)_{10}{}^{2-}$ clusters [6].

(ii) Condensation reactions of two metal carbonyls for the preparation of $(\eta\text{-}C_5H_5)_2Ni_2(PhC{\equiv}CC{\equiv}CPh)Fe_2(CO)_6$ [7], $H_2Ru_2Re_2(CO)_{16}$ [8] and $(\eta\text{-}C_5H_5)_2\text{-}Rh_2Fe_2(CO)_8$ [9] clusters.

(iii) Halide abstraction, leading to tetrametallic $Co_2Rh_2(CO)_{12}$, $Co_2Ir_2(CO)_{12}$ and $Rh_2Ir_2(CO)_{12}$ clusters [10].

It is noteworthy that in most of these complexes only carbonyl or cyclopentadienyl groups are linked to the different metal atoms. Only one platinum—osmium compound of presumed tetrametallic heteronuclear cluster type has been reported, viz. [$PtOsH(CO)_4(PPh_3)$]$_2$ [4]. In this paper, we describe a new route for the preparation of such clusters. Details of the synthesis and characterisation of two complexes in which the four metallic atoms form a tetrahedral arrangement are given.

Results and discussion

In order to study the influence of the ligand coordinated to the platinum atom, reactions between *cis* or *trans* square planar complexes, e.g. $PtCl_2(PPh_3)_2$, and a carbonylmetallate anion, such as Na[$Co(CO)_4$] or Na[$(\eta\text{-}C_5H_5)Mo(CO)_3$], were carried out. The use of *monodendate* triphenylphosphine instead of *bidendate* ligands [5] did not lead to the expected triangular trimetallic compounds. On the other hand, a tetrametallic heteronuclear and a trimetallic homonuclear platinum cluster are formed in addition to cobalt(0) and molybdenum(0) carbonyls. The mechanism of the reaction appears complicated since we are dealing with not only a nucleophilic substitution but also a redox reaction. One triphenylphosphine ligand remains coordinated to the Pt center, but there is evidence that the other ligand is labile in the course of the reaction.

Reaction of Na[$Co(CO)_4$] with cis- or trans-$PtCl_2(PPh_3)_2$

This reaction, carried out in tetrahydrofuran (THF) yields the same three compounds starting with the *cis*- or the *trans*-$PtCl_2(PPh_3)_2$ isomers. They were separated by chromatography on silica gel (see experimental part). As shown by analytical data and infrared spectra (Table 1), two of the reaction products consist of the well-known phosphine-substituted cobalt carbonyls $Co_2(CO)_6(PPh_3)_2$ and $Co_2(CO)_7(PPh_3)$. The other product of the reaction is a new tetrametallic cluster $(CO)_5Co_2(CO)_2Pt_2(CO)(PPh_3)_2$ (I). The reaction is therefore:

$$2PtCl_2(PPh_3)_2 + 4Na[Co(CO)_4] \rightarrow 4NaCl + (CO)_5Co_2(CO)_2Pt_2(CO)(PPh_3)_2 + Co_2(CO)_8 + 2PPh_3$$

TABLE 1

INFRARED FREQUENCIES (cm^{-1})

Compound	CO stretching	Other vibrations[a]
$Co_2(CO)_6(PPh_3)_2$	[a] 2048 m, 1994 m(sh), 1972 vs, 1950 vs 1897 w, 1812 vw	*1483* s, 1434 vs, 1096vs 748 s, 709 m, 692 vs, 547 s 514 vs, 501 s, 425 m
	[b] 2030 m, 2020 vs, 2001 vs, 1986 vs	
$Co_2(CO)_7(PPh_3)$	[a] 2079 vs, 2030 vs, 2012 s(sh), 1975 vs 1953 vs	*1484* s, 1435 vs, 1094 vs 746 s, 707 m, 693 vs, 540 s 517 vs, 466 m
	[c] 2085 vs, 2048 s, 2034 s, 1998 vs 1964 s	
	[d] 2080 vs, 2075 m, 2043 vs, 2028 vs 2012 (sh), 1995 vs, 1960 s	
	[e] 2079 s, 2026 s, 2010 (sh), 1996 vs 1964 s	
$Co_2Pt_2(PPh_3)_2(CO)_8$	[a] 2058 s, 2031 s, 2009 s, 1990 s 1983 s, 1891 m, 1841 s, 1804 vs	*1482* s, 1436 vs, 1098 s 746 s, 695 vs, 528 vs, 512 vs 499 s, 459 m, 426 m
	[c] 2061 s, 2034 vs, 2018 (sh), 1992 s 1937 m, 1871 m, 1825 s, 1820 s	
$Mo_2Pt_2(PPh_3)_2(CO)_6(\eta\text{-}C_5H_5)_2$	[a] 1831 vs, 1805 w(sh), 1741 vs	*1483* m, 1438 s, 1095 s 1068 m[f], 813 m[f], 746 s 695 s, 575 m, 525 s, 514 s 494 m, 469 m
$Pt_3(CO)_3(PPh_3)_4$	[a] 1830 vs	*1483* s, 1435 s, 1099 s 747 s, 693 vs, 546 m, 523 s 503 (sh), 475 m
	[c] 1816 s	

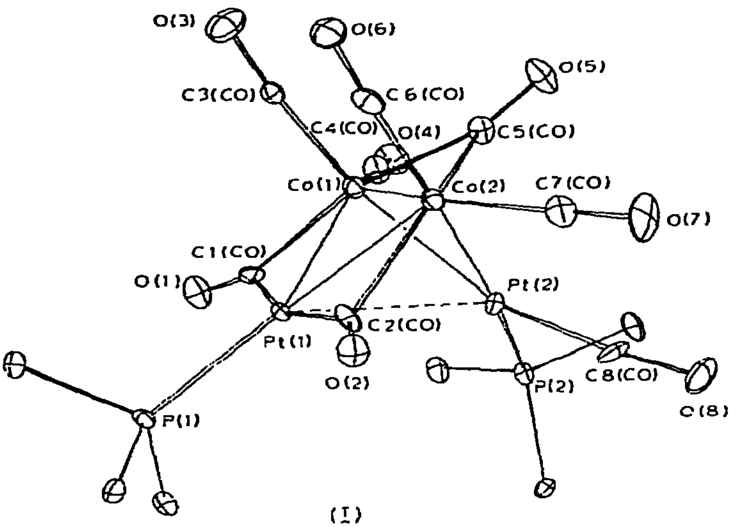
[a] KBr pellet. [b] CS_2 solution (ref. 15). [c] Toluene solution. [d] Cyclohexane solution. [e] Hexane solution (ref. 15). [f] η-C_5H_5 vibrations.

with simultaneously:

$$2Co_2(CO)_8 + 3(PPh_3) \rightarrow Co_2(CO)_6(PPh_3)_2 + Co_2(CO)_7(PPh_3) + n\ CO$$

The infrared spectra recorded in the range 2100-1500 cm^{-1} during the reaction suggest that reoxidation of the carbonylmetallate anion (vide infra) occurs together with elimination of the phosphine moiety from platinum and formation of the heteronuclear complex.

The heteronuclear tetrametallic cluster. Compound I is fairly stable in air in the solid state but not in solution. All of its solutions decompose slowly, even under nitrogen, with loss of carbonyl and formation of other heteronuclear species which were not further studied. Infrared spectra of the compound in both the solid state and in solution, reveal five terminal carbonyl absorptions between 2060 and 1950 cm^{-1} and three bridged carbonyl stretching absorptions between 1890 and 1800 cm^{-1}. The number of CO absorption bands (equal to the number of carbonyl groups) is consistent with the asymmetric structure confirmed by the results of the X-ray determinations [11].



(I)

Fig. 1. The molecular structure of $(CO)_5Co_2(CO)_2Pt_2(CO)(PPh_3)_2$ (I). Distances in the cluster Co(1)—Co(2) = 2.498(3), Co(1)—Pt(1) = 2.540(2), Co(2)—Pt(1) = 2.579(2), Co(1)—Pt(2) = 2.554(3), Co(2)—Pt(2) = 2.528(3) and Pt(1)—Pt(2) = 2.987(4) Å.

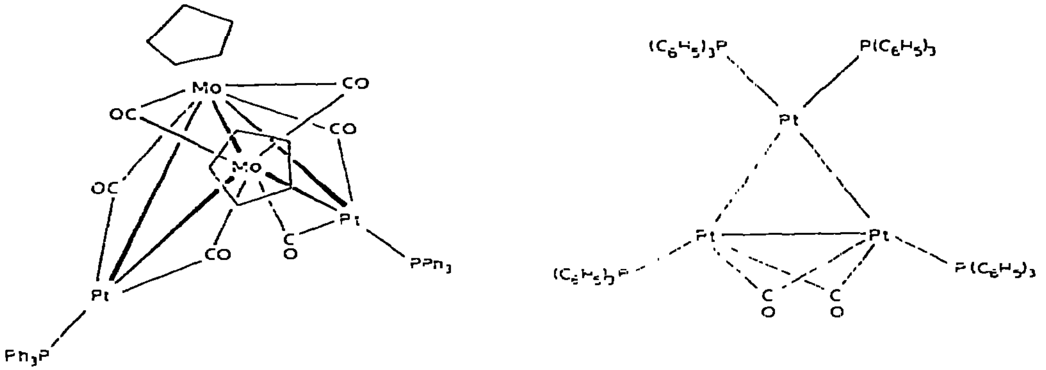
The structure (Fig. 1) shows clearly that the four metallic atoms form an open tetrahedron of the "butterfly" type, the two $PtCo_2$ triangles sharing a "hinge" Co(1)—Co(2), bridged by one of the carbonyl groups. The first Pt(1)Co(1)-Co(2) triangle has sides bridged by carbonyl; a triphenylphosphine is bonded to the Pt(1) atom. The second triangle has no carbonyl bridge, but the Pt(2) atom remains in a square planar arrangement with two platinum—cobalt bonds, a terminal carbonyl group and a triphenylphosphine.

Reaction of $PtCl_2(PPh_3)_2$ with $Na[(\eta\text{-}C_5H_5)Mo(CO)_3]$

The reaction is carried out in THF and furnishes compounds which confirm the preceding results. Chromatography on silica gel (see experimental part) reveals four species. The dimer $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ and free triphenylphosphine are eluted first; two products could then be separated and characterised as heteronuclear polymetallic $(\eta\text{-}C_5H_5)_2(CO)_2Mo_2(CO)_4Pt_2(PPh_3)_2$ and homonuclear $Pt_3(CO)_3(PPh_3)_4$ clusters.

It is noteworthy that, in contrast to the case of the cobalt carbonyl derivatives described above, no phosphine-substituted molybdenum carbonyl is formed. Indeed, this was expected from the results previously reported by Nyholm et al. [12], who studied the substitution reaction of the carbonyl groups in $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ using tertiary phosphines; far ultraviolet irradiation was used to form such compounds. On the other hand, the presence of $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ supports the observed reoxidation of the carbonylmetallate anions during our reactions. Martinengo et al. [10] observed such a reoxidation stage in the preparation of the $Co_2Ir_2(CO)_{12}$ cluster.

The heteronuclear tetrametallic cluster. The last compound eluted is a platinum—molybdenum complex which corresponds to the analytical formula



(II) (III)

Fig. 2. The molecular structure of $(\eta\text{-}C_5H_5)_2(CO)_2Mo_2(CO)_4Pt_2(PPh_3)_2$ (II) and $Pt_3(CO)_2(PPh_3)_4$ (III).

$(\eta\text{-}C_5H_5)_2(CO)_2Mo_2(CO)_4Pt_2(PPh_3)_2$ (II). The infrared spectra, both in the solid state and in solution, show only two bridged carbonyl stretching frequencies (see Table 1). Infrared data also indicate that the phosphine ligand is still coordinated to platinum and the cyclopentadienyl π-bonded to the molybdenum.

In accordance with both the 16-18 electron rule for each metallic atom and the presence of the two observed bands, we suggest the structure shown in Fig. 2. The bridged carbonyl groups are located between Pt—Mo as well as between the two molybdenum atoms. Owing to the complexity of the molecular frames in this or other heterometallic clusters, no bands could be assigned in the far infrared spectra to the metal—metal stretching frequencies. NMR measurements were unsuccessful because the complex decomposed extensively in $CDCl_3$ solution.

The homonuclear trimetallic compound $Pt_3(CO)_2(PPh_3)_4$ (III). This homonuclear trimetallic cluster seems to have a structure different from that previously reported for analogous species by Booth et al. [13]. IR spectra both in the solid state and in solution (Table 1) show only one absorption in the carbonyl stretching region. The band observed at 1830 cm^{-1} in KBr suggests that bridged carbonyl groups are present. We propose a structure such as that shown in Fig. 2 since it is the only one which obeys the 16-18 electron rule. This complex was also isolated in reactions between $PtCl_2(PPh_3)_2$ and $Na[Mn(CO)_5]$ [14], but surprisingly it was not observed in the preceding reaction between $PtCl_2(PPh_3)_2$ and $Na[Co(CO)_4]$.

Experimental

All reactions and chromatographic separations were carried out under nitrogen. Solvents were distilled under nitrogen before use.

Infrared spectra of the different complexes were recorded on a Beckman IR 12 spectrophotometer in the range 4000-400 cm^{-1}.

All starting materials were prepared by published methods. Microanalyses for C and H were performed in our Institute. Platinum was determined by the stannous chloride colorimetric method [16], cobalt by atomic absorption spectrometry [17]. Molecular weights were determined osmometrically or cryoscopically.

Reaction of cis-$PtCl_2(PPh_3)_2$ with $Na[Co(CO)_4]$

A solution of $Na[Co(CO)_4]$, prepared from $Co_2(CO)_8$ (2.20 g, 6.43 mmol) by reduction with sodium amalgam in 100 ml of freshly distilled THF, was filtered and added to a suspension of *cis*-$PtCl_2(PPh_3)_2$ (5.00 g, 6.33 mmol) in THF (50 ml) at approximately 0°C. This mixture was stirred at room temperature for 4 h. The heavy precipitate formed was filtered off, washed with water and dried in vacuum. The product was $Co_2(CO)_6(PPh_3)_2$ (2.1 g, 2.6 mmol). The THF solution was evaporated to dryness. The black residue was chromatographed with pentane and gave $Co_2(CO)_7(PPh_3)_2$ (0.55 g, 0.96 mmol). Elution with diethyl ether—pentane (1/5 v/v) gave a red solution which on evaporation yielded red needles of compound I (1.8 g, 1.42 mmol). Further elution with diethyl ether gave only decomposition products. The red product was slowly recrystallised from toluene solution in the presence of pentane vapour to give red plates. (Found: C, 42.14; H, 2.46; Co, 9.35; Pt, 30.08. Mol. wt., 1210. $C_{44}H_{30}Co_2O_8P_2Pt_2$ calcd.: C, 42.06; H, 2.38; Co, 9.38; Pt, 31.08%. Mol. wt., 1256.)

Reaction of trans-$PtCl_2(PPh_3)_2$ with $Na[Co(CO)_4]$

The reaction was carried out in a manner analogous to that described above and afforded the same products with approximately the same yields.

Reaction of cis-$PtCl_2(PPh_3)_2$ with $Na[(\eta\text{-}C_5H_5)Mo(CO)_3]$

A solution of $Na[(\eta\text{-}C_5H_5)Mo(CO)_3]$, prepared from $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ (0.76 g, 1.5 mmol) by reduction with sodium amalgam in 40 ml of THF, was added with stirring to a suspension of *cis*-$PtCl_2(PPh_3)_2$ (1.1 g, 1.3 mmol) in 20 ml of THF. The temperature was increased from 0 to 45°C and maintained constant for 3 hours. After filtration, the red solution was evaporated to dryness in vacuum and the dark red residue chromatographed on silica gel, using pentane as solvent. Free phosphine was obtained by evaporation of the first fraction. Further elution with pentane gave a red band which, following evaporation, was shown to consist of $[(\eta\text{-}C_5H_5)Mo(CO)_3]_2$ (0.30 g, 0.6 mmol). Elution with diethyl ether—pentane (1/5 v/v) gave the yellow compound III which was recrystallised from benzene (0.20 g, 0.12 mmol). (Found: C, 52.52; H, 3.55; Pt, 31.90; m.p., 200-205°C (dec.). $C_{74}H_{60}O_2P_4Pt_3$ calcd.: C, 52.28; H, 3.52; Pt, 35.02%.) Continued elution of the dark brown band with pure diethyl ether yielded a black compound II which was recrystallised from CH_2Cl_2 solution (0.30 g, 0.22 mmol). (Found: C, 44.51; H, 3.18. Mol. wt., 1350; m.p., 226-228°C (dec.). $C_{52}H_{40}Mo_2O_6P_2Pt_2$ calcd.: C, 44.46; H, 2.85%. Mol. wt., 1405.)

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