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# Cobalt-platinum carbonyl complexes with carbido ligands. Crystal structure of the hexanuclear mixed-metal cluster $[Co_3Pt_3(\mu\text{-H})(\mu_6\text{-C})(\mu\text{-CO})_4(CO)_5(PPr^i_3)_3]$ *

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## Abstract

Reactions between the $\mu_3$-methylidyne tricobalt complex $[Co_3(\mu_3\text{-CH})(CO)_9]$ and the platinum reagents $[Pt(C_2H_4)_2(PR_3)]$ (R = cyclo-$C_6H_{11}$ or $Pr^i$) in light petroleum at room temperature afford the mixed-metal carbido-carbonyl clusters $[Co_3Pt_2(\mu\text{-H})(\mu_5\text{-C})(\mu\text{-CO})_2(CO)_7(PR_3)_2]$ (R = cyclo-$C_6H_{11}$ or $Pr^i$) and $[Co_3Pt_3(\mu\text{-H})(\mu_6\text{-C})(\mu\text{-CO})_4(CO)_5(PPr^i_3)_3]$. The structure of the latter has been established by an X-ray diffraction study. The carbido-carbon atom is located inside the $Co_3Pt_3$ core, with the metal atoms occupying essentially octahedral sites and with meridional arrangements of the $Co_3$ and $Pt_3$ groups. However, the core is open, since one Pt $\cdots$ Pt separation (3.260(1) Å) is too long for a direct metal–metal connectivity. The other Pt–Pt distance (2.868(1) Å) is such as to suggest that this vector is bridged by the hydrido ligand; a feature confirmed by the $^1H$ NMR data. The three platinum atoms are ligated by $PPr^i_3$ groups. Four of the Co–Pt vectors (2.599(2)–2.661(2) Å) are bridged by CO ligands, and a fifth (2.842(2) Å) is semi-bridged. The three non-bridged Co–Pt connectivities are longer (2.937(2)–3.060(2) Å). One cobalt atom carries two terminal CO groups and the other two cobalts are each coordinated by one such group. The NMR spectra ($^1H$, $^{13}C\text{-}\{^1H\}$, and $^{31}P\text{-}\{^1H\}$) of the new cluster compounds are reported and discussed.

## Introduction

Following the discovery of the complexes $[Pt(C_2H_4)_3]$ and $[Pt(C_2H_4)_2(PR_3)]$ (R = alkyl or aryl) [1], these species have become versatile reagents for preparing 'mixed-metal' compounds containing platinum [2]. Reactions with metal carbonyl complexes generally proceed under very mild conditions with addition of Pt atoms

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* Dedicated to Professor Günther Wilke on the occasion of his 65th birthday.

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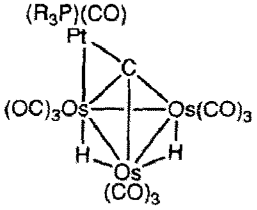

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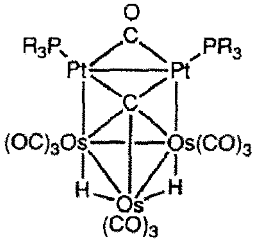

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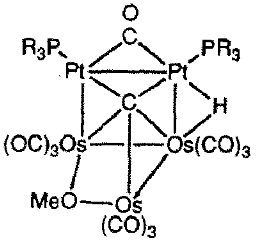
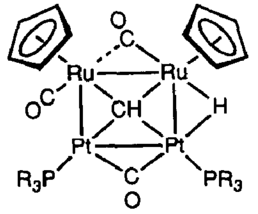


III

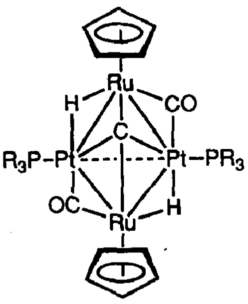
R = cyclo-$C_6H_{11}$

or $Pt(PR_3)$ fragments, derived from $[Pt(C_2H_4)_3]$ or $[Pt(C_2H_4)_2(PR_3)]$, respectively. In the majority of reactions the integrity of the ligands in the precursors are preserved in the resulting cluster, apart from their migration to the platinum atoms or to sites bridging metal–metal bonds. Recently, however, we have observed a different reactivity pattern leading to the synthesis of carbido-carbonyl clusters. These products are formed by degradation of bridging $CH_2$, CH, CCO, or COMe ligands present in suitable precursors. Thus treatment of the triosmium compound $[Os_3(\mu\text{-}H)(\mu_3\text{-}CH)(CO)_{10}]$ with $[Pt(C_2H_4)_2\{P(\text{cyclo-}C_6H_{11})_3\}]$ affords the tetra- and penta-nuclear metal carbido-carbonyl clusters $[Os_3Pt(\mu\text{-}H)_2(\mu_4\text{-}C)(CO)_{10}\{P(\text{cyclo-}C_6H_{11})_3\}]$ (I) and $[Os_3Pt_2(\mu\text{-}H)_2(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(\text{cyclo-}C_6H_{11})_3\}_2]$ (II). Moreover, the reaction between the platinum reagent and the methoxyalkylidyne compound $[Os_3(\mu\text{-}H)(\mu_3\text{-}COMe)(CO)_{10}]$ yields the pentanuclear metal cluster $[Os_3Pt_2(\mu\text{-}H)(\mu\text{-}OMe)(\mu_5\text{-}C)(\mu\text{-}CO)(CO)_9\{P(\text{cyclo-}C_6H_{11})_3\}_2]$ (III) [3]. We have also characterised the diruthenium-diplatinum compounds $[Ru_2Pt_2(\mu\text{-}H)(\mu_4\text{-}CH)(\mu\text{-}CO)(CO)_2(PR_3)_2(\eta\text{-}C_5H_5)_2]$ (IV) and $[Ru_2Pt_2(\mu\text{-}H)_2(\mu_4\text{-}C)(\mu\text{-}CO)_2(PR_3)_2(\eta\text{-}C_5H_5)_2]$ (V), obtaining these products from reactions between the $\mu$-methylene complexes $[Ru_2(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)(L)(\eta\text{-}C_5H_5)_2]$ (L = CO or NCMe) and the species $[Pt(C_2H_4)_2(PR_3)]$ (R = cyclo-$C_6H_{11}$ or $Pr^i$) [4]. The $\mu_4$-carbido clusters V form via the $\mu_4$-methylidyne complexes IV, which are in turn produced via the complexes $[Ru_2Pt(\mu\text{-}CH_2)(\mu\text{-}CO)(CO)_2(PR_3)(\eta\text{-}C_5H_5)_2]$ (VI).

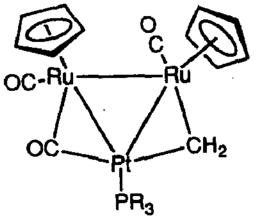
The preparation of the platinum-containing mixed-metal carbido-carbonyl clusters I–V, in the manner described, prompted us to study reactions between the reagents $[Pt(C_2H_4)_2(PR_3)]$ and $[Co_3(\mu_3\text{-}CH)(CO)_9]$ to establish whether carbido



**IVa** R = cyclo-$C_6H_{11}$
**IVb** R = $Pr^i$



**Va** R = cyclo-$C_6H_{11}$
**Vb** R = $Pr^i$



**VIa** R = cyclo-$C_6H_{11}$
**VIb** R = $Pr^i$

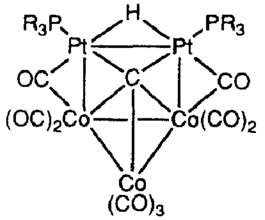
clusters containing cobalt and platinum could be obtained by this route. The results of this investigation are described in this paper.

## Results and discussion

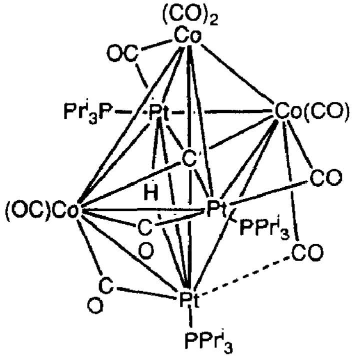
At room temperature, in light petroleum, the compounds $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ and $[Co_3(\mu_3\text{-}CH)(CO)_9]$ react to give the green crystalline carbido-cluster $[Co_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_7\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ (VIIa) in ca. 60% yield. The spectroscopic properties are fully consistent with the formulation shown, with the arrangement of the metal atom core and $\mu_5$-C atom similar to that of II.

In the IR spectrum in the carbonyl region, compound VIIa shows bands at 2062, 2024, 2004, and 1816 $cm^{-1}$. The latter may be assigned to the bridging CO groups which are related by a mirror plane of symmetry. In the $^1H$ NMR spectrum the presence of the $\mu$-H group is revealed by a triplet signal ($J$(PH) 11 Hz) at $\delta$ $-6.18$. This resonance displays $^{195}Pt$ satellite peaks, the magnitude of the $^{195}Pt$–$^1H$ coupling (817 Hz) being diagnostic for the presence of a Pt($\mu$-H)Pt group [5,6]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum showed a singlet resonance at $\delta$ 30.5 ppm with a $^{195}Pt$–$^{31}P$ coupling pattern consistent with the existence of a P–Pt–Pt–P unit with chemically equivalent $^{31}P$ nuclei ($J$(PtP) 3779 and 115 Hz) [3,7]. The spectrum was not of sufficient quality to calculate the magnitude of $J$(PtPt) or $J$(PP).

A similar reaction between $[Pt(C_2H_4)_2(PPr^i_3)]$ and $[Co_3(\mu_3\text{-}CH)(CO)_9]$ afforded a mixture of two carbido clusters $[Co_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_7(PPr^i_3)_2]$ (VIIb)



| | R |
|---|---|
| **VIIa** | cyclo-$C_6H_{11}$ |
| **VIIb** | $Pr^i$ |



**VIII**

and $[Co_3Pt_3(\mu\text{-}H)(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_5(PPr^i_3)_3]$ (VIII), readily separated by column chromatography on alumina. The microanalytical and spectroscopic data for VIIb showed it to be an analogue of VIIa. The nature of VIII was established by an X-ray diffraction study which is described below, together with the spectroscopic properties.

Compound VIIb was more soluble than VIIa, and hence better NMR spectra were observed for the former. In particular, the $^{13}C\text{-}\{^1H\}$ NMR spectrum of VIIb, measured at $-80\,°C$, revealed a diagnostic resonance for the carbido carbon atom at $\delta$ 434.5 ppm [9,10]. This signal was broad, as were the peaks due to the two equivalent $Co(CO)_2$ fragments and the $Co(CO)_3$ group at $\delta$ 206.7 and 202.0 ppm, respectively. The broadness of the resonances is typical for a cobalt complex, being due to the $^{59}Co$ quadrupolar effect. A signal at $\delta$ 239.5 with $^{195}Pt\text{-}^{13}C$ satellite peaks ($J$(PtC) 1147 Hz) is attributable to the two equivalent bridging carbonyl groups. The $^1H$ NMR spectrum has a triplet resonance ($J$(PH) 12 Hz) at $\delta$ $-6.12$ ppm with $^{195}Pt$ satellites ($J$(PtH) 802 Hz) and thus may be ascribed to the $Pt(\mu\text{-}H)Pt$ moiety. The $^{31}P\text{-}\{^1H\}$ NMR spectrum had a singlet signal at $\delta$ 41.3 ppm, and as in the corresponding spectrum of VIIa, the observation of two distinct $^{195}Pt\text{-}^{31}P$ couplings ($J$(PtP) 3799 and 117 Hz) is in agreement with a P–Pt–Pt–P arrangement [3,7,8].

It was observed that VIII could also be obtained by treating VIIb with one equivalent of $[Pt(C_2H_4)_2(PPr^i_3)]$, suggesting that the latter was a hexanuclear metal species with a $Co_3Pt_3$ core. This was confirmed by the X-ray diffraction study. The molecular parameters obtained are listed in Table 1, and the structure is shown in Fig. 1.

The metal atoms adopt a somewhat distorted octahedral arrangement, since one of the platinum–platinum distances (Pt(1) $\cdots$ Pt(3) 3.260(1) Å) is too long for a metal–metal connectivity. Although the $\mu$-H ligand was not found in the electron density maps, it very probably bridges the Pt(2)–Pt(3) vector since the distance (2.868(1) Å) between these two atoms is similar to those found in other compounds with $Pt(\mu\text{-}H)Pt$ units [6]. Moreover, the $^1H$ NMR data, discussed below, supports this conclusion. The two Co–Co separations are virtually identical (Co(1)–Co(3) 2.692(3), Co(2)–Co(3) 2.693(3) Å). Interest centres on the carbido-carbon atom which lies within the metal framework but is closer to the cobalt atoms (Co(1)–C

Table 1

Selected internuclear distances (Å) and angles (°) for $[Co_3Pt_3(\mu\text{-}H)(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_5(PPr^i_3)_3]$ (VIII), with estimated standard deviations in parentheses

| | | | |
|---|---|---|---|
| Pt(1)...Pt(3) | 3.260(1) | Pt(1)–Co(1) | 2.649(2) |
| Pt(1)–Co(2) | 2.652(2) | Pt(1)–Co(3) | 2.937(2) |
| Pt(1)–P(1) | 2.314(4) | Pt(1)–C | 2.16(1) |
| Pt(1)–C(1) | 2.12(2) | Pt(1)–C(2) | 2.06(2) |
| Pt(2)–Pt(3) | 2.868(1) | Pt(2)–Co(1) | 2.959(2) |
| Pt(2)–Co(2) | 3.060(2) | Pt(2)–Co(3) | 2.599(2) |
| Pt(2)–P(2) | 2.262(4) | Pt(2)–C | 2.14(1) |
| Pt(2)–C(3) | 2.03(2) | Pt(3)–Co(1) | 2.842(2) |
| Pt(3)–Co(2) | 2.661(2) | Pt(3)–P(3) | 2.307(5) |
| Pt(3)–C | 2.04(2) | Pt(3)–C(4) | 2.16(2) |
| Pt(3)–C(6) | 2.62(3) | Co(1)–Co(3) | 2.692(3) |
| Co(1)–C | 1.83(2) | Co(1)–C(2) | 1.85(1) |
| Co(1)–C(6) | 1.85(2) | Co(1)–C(9) | 1.76(2) |
| Co(2)–Co(3) | 2.693(3) | Co(2)–C | 1.86(2) |
| Co(2)–C(1) | 1.87(2) | Co(2)–C(4) | 1.83(2) |
| Co(2)–C(5) | 1.78(2) | Co(3)–C | 1.90(2) |
| Co(3)–C(3) | 1.94(2) | Co(3)–C(7) | 1.73(2) |
| Co(3)–C(8) | 1.78(2) | C(1)–O(1) | 1.17(2) |
| C(2)–O(2) | 1.19(2) | C(3)–O(3) | 1.14(3) |
| C(4)–O(4) | 1.18(3) | C(5)–O(5) | 1.12(2) |
| C(6)–O(6) | 1.12(3) | C(7)–O(7) | 1.14(3) |
| C(8)–O(8) | 1.13(3) | C(9)–O(9) | 1.15(3) |
| Pt(3)–Pt(1)–Co(1) | 56.4(1) | Pt(3)–Pt(1)–Co(2) | 52.3(1) |
| Co(1)–Pt(1)–Co(2) | 87.2(1) | Pt(3)–Pt(1)–Co(3) | 78.1(1) |
| Co(1)–Pt(1)–Co(3) | 57.3(1) | Co(2)–Pt(1)–Co(3) | 57.3(1) |
| Pt(3)–Pt(1)–P(1) | 147.4(1) | Co(1)–Pt(1)–P(1) | 137.1(1) |
| Co(2)–Pt(1)–P(1) | 135.4(1) | Co(3)–Pt(1)–P(1) | 134.3(1) |
| Pt(3)–Pt(1)–C | 37.8(4) | Co(1)–Pt(1)–C | 43.3(4) |
| Co(2)–Pt(1)–C | 44.0(4) | Co(3)–Pt(1)–C | 40.4(4) |
| P(1)–Pt(1)–C | 91.6(5) | Pt(3)–Pt(2)–Co(1) | 58.4(1) |
| Pt(3)–Pt(2)–Co(2) | 53.2(1) | Co(1)–Pt(2)–Co(2) | 74.8(1) |
| Pt(3)–Pt(2)–Co(3) | 91.3(1) | Co(1)–Pt(2)–Co(3) | 57.5(1) |
| Co(2)–Pt(2)–Co(3) | 56.1(1) | Pt(3)–Pt(2)–P(2) | 125.5(1) |
| Co(1)–Pt(2)–P(2) | 141.2(1) | Co(2)–Pt(2)–P(2) | 141.9(1) |
| Co(3)–Pt(2)–P(2) | 143.1(1) | Pt(3)–Pt(2)–C | 45.3(4) |
| Co(1)–Pt(2)–C | 38.0(4) | Co(2)–Pt(2)–C | 36.9(4) |
| Co(3)–Pt(2)–C | 46.1(4) | P(2)–Pt(2)–C | 170.7(4) |
| Pt(1)–Pt(3)–Pt(2) | 88.7(1) | Pt(1)–Pt(3)–Co(1) | 50.9(1) |
| Pt(2)–Pt(3)–Co(1) | 62.4(1) | Pt(1)–Pt(3)–Co(2) | 52.0(1) |
| Pt(2)–Pt(3)–Co(2) | 67.1(1) | Co(1)–Pt(3)–Co(2) | 83.2(1) |
| Pt(1)–Pt(3)–P(3) | 129.5(1) | Pt(2)–Pt(3)–P(3) | 140.8(1) |
| Co(1)–Pt(3)–P(3) | 131.3(1) | Co(2)–Pt(3)–P(3) | 140.1(2) |
| Pt(1)–Pt(3)–C | 40.6(4) | Pt(2)–Pt(3)–C | 48.2(4) |
| Co(1)–Pt(3)–C | 39.9(4) | Co(2)–Pt(3)–C | 44.2(4) |
| P(3)–Pt(3)–C | 168.1(4) | Pt(1)–Co(1)–Pt(2) | 99.8(1) |
| Pt(1)–Co(1)–Pt(3) | 72.7(1) | Pt(2)–Co(1)–Pt(3) | 59.2(1) |
| Pt(1)–Co(1)–Co(3) | 66.7(1) | Pt(2)–Co(1)–Co(3) | 54.5(1) |
| Pt(3)–Co(1)–Co(3) | 90.0(1) | Pt(1)–Co(1)–C | 54.1(4) |
| Pt(2)–Co(1)–C | 46.0(4) | Pt(3)–Co(1)–C | 45.7(5) |
| Co(3)–Co(1)–C | 45.0(5) | Pt(1)–Co(2)–Pt(2) | 97.2(1) |
| Pt(1)–Co(2)–Pt(3) | 75.7(1) | Pt(2)–Co(2)–Pt(3) | 59.7(1) |
| Pt(1)–Co(2)–Co(3) | 66.7(1) | Pt(2)–Co(2)–Co(3) | 53.2(1) |
| Pt(3)–Co(2)–Co(3) | 93.9(1) | Pt(1)–Co(2)–C | 53.9(4) |
| Pt(2)–Co(2)–C | 43.6(4) | Pt(3)–Co(2)–C | 49.9(5) |

*(continued)*

Table 1 (continued)

| | | | |
|---|---|---|---|
| Co(3)–Co(2)–C | 45.0(5) | Pt(1)–Co(3)–Pt(2) | 101.5(1) |
| Pt(1)–Co(3)–Co(1) | 55.9(1) | Pt(2)–Co(3)–Co(1) | 68.0(1) |
| Pt(1)–Co(3)–Co(2) | 56.0(1) | Pt(3)–Co(3)–Co(2) | 70.6(1) |
| Co(1)–Co(3)–Co(2) | 85.5(1) | Pt(1)–Co(3)–C | 47.4(4) |
| Pt(2)–Co(3)–C | 54.1(4) | Co(1)–Co(3)–C | 42.8(5) |
| Co(2)–Co(3)–C | 43.7(5) | Pt(1)–C–Pt(2) | 171.8(8) |
| Pt(1)–C–Pt(3) | 101.6(6) | Pt(2)–C–Pt(3) | 86.6(5) |
| Pt(1)–C–Co(1) | 82.6(5) | Pt(2)–C–Co(1) | 96.1(6) |
| Pt(3)–C–Co(1) | 94.3(6) | Pt(1)–C–Co(2) | 82.1(5) |
| Pt(2)–C–Co(2) | 99.5(6) | Pt(3)–C–Co(2) | 85.9(6) |
| Co(1)–C–Co(2) | 164.4(8) | Pt(1)–C–Co(3) | 92.2(6) |
| Pt(2)–C–Co(3) | 79.7(5) | Pt(3)–C–Co(3) | 165.45(8) |
| Co(1)–C–Co(3) | 92.2(7) | Co(2)–C–Co(3) | 91.3(6) |
| Pt(1)–C(1)–O(1) | 137(1) | Co(2)–C(1)–O(1) | 139(1) |
| Pt(1)–C(2)–O(2) | 139(1) | Co(1)–C(2)–O(2) | 136(1) |
| Pt(2)–C(3)–O(3) | 145(2) | Co(3)–C(3)–O(3) | 134(2) |
| Pt(3)–C(4)–O(4) | 133(2) | Co(2)–C(4)–O(4) | 144(2) |
| Co(2)–C(5)–O(5) | 178(2) | Pt(3)–C(6)–O(6) | 129(2) |
| Co(1)–C(6)–O(6) | 154(3) | Co(3)–C(7)–O(7) | 173(2) |
| Co(3)–C(8)–O(8) | 171(2) | Co(1)–C(9)–O(9) | 177(2) |

1.83(2), Co(2)–C 1.86(2), Co(3)–C 1.90(2), Pt(1)–C 2.16(1), Pt(2)–C 2.14(1), and Pt(3)–C 2.04(2) Å). Although the encapsulation of a carbido ligand within a metal atom cage is well established for homonuclear metal species [9], this structural feature is as yet rare for mixed metal clusters. One recently reported example is the compound $[N(PPh_3)_2][Fe_3Rh_3(\mu_6\text{-}C)(CO)_{15}]$, prepared by treating $[N(PPh_3)_2]_2$-$[Fe_3(\mu_3\text{-}CCO)(CO)_9]$ with $[Rh_2(\mu\text{-}Cl)_2(CO)_4]$ in tetrahydrofuran [11]. However, this $\mu_6$-C triirontrirhodium cluster has a trigonal-antiprismatic metal skeleton enclosing the carbido-carbon atom, in contrast with the metal atom arrangement in VIII.

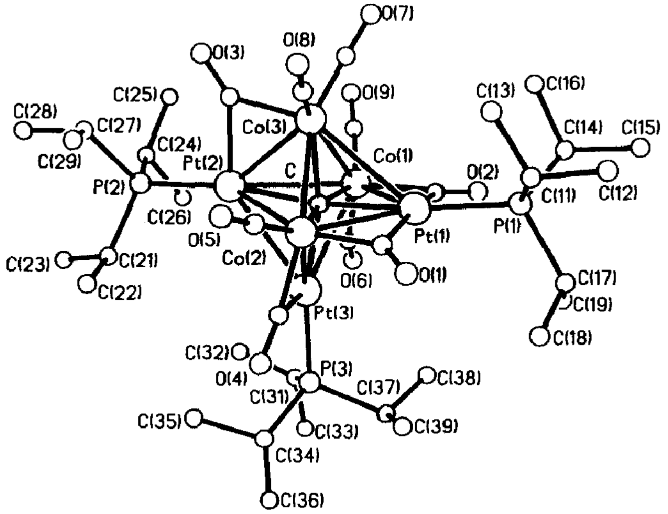


Fig. 1. The molecular structure of $[Co_3Pt_3(\mu\text{-}H)(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_5(PPr^i_3)_3]$ (VIII) showing the crystallographic numbering scheme.

Four of the Pt–Co vectors in VIII are bridged by carbonyl ligands and these separations (2.599(2)–2.661(2) Å) are shorter than the non-bridged Pt–Co bonds (2.937(2)–3.060(2) Å), as expected. However, it is noteworthy that the Pt(3)–Co(1) distance (2.842(2) Å) lies between these two ranges as a consequence of the C(6)O(6) ligand semi-bridging this vector (Co(1)–C(6)–O(6) 154(3), Pt(3)–C(6)–O(6) 129(2)°). The cobalt atoms Co(1) and Co(2) each carry a terminal CO group, while Co(3) is coordinated by two such groups. As expected, the platinum atoms are each ligated by a $PPr^i_3$ group (mean Pt–P 2.294 Å).

Having established the structure of VIII the spectroscopic data were readily interpretable. In the IR spectrum bands in both the terminal and the bridging CO region were observed (see Experimental). The $^{31}P$-$\{^1H\}$ NMR spectrum exhibits three resonances. A singlet at $\delta$ 47.8 ppm ($J$(PtP) 4883 and 78 Hz) is assigned to P(1) (Fig. 1) since it does not show $^{31}P$–$^{31}P$ coupling. A doublet signal at $\delta$ 46.2 ppm ($J$(PP) 17 Hz) is tentatively assigned to P(2), since it shows coupling to three $^{195}Pt$ nuclei ($J$(PtP) 4619, 142 and 75 Hz). The remaining doublet resonance at $\delta$ 39.8 ppm ($J$(PP) 17 Hz) is assigned to P(3), and has $J$(PtP) couplings of 4900 and 56 Hz. In the $^1H$ NMR spectrum the resonance at $\delta$ −9.30 ppm is diagnostic for a hydrido ligand bridging a Pt–Pt bond [5,6]. The appearance of this resonance as a doublet-of-doublets ($J$(PH) 13 and 2 Hz) with two sets of $^{195}Pt$ satellite peaks ($J$(PtH) 700 and 663 Hz) establishes that the $\mu$-H ligand bridges between two non-equivalent PtP groups. The chemical shift contrasts with that observed at $\delta$ −1.31 ppm for the 'agostic' $\mu_4$-CH group in $[Fe_4(\mu\text{-}H)(\mu_4\text{-}CH)(CO)_{12}]$ [12]. Hence interaction between the carbido and hydrido ligands in VIII is unlikely. Moreover, for any C–H interaction to occur the H atom must lie inside the cluster framework, a feature which would be expected to lead to a chemical shift different from that observed.

The $^{13}C$-$\{^1H\}$ NMR spectrum failed to show a resonance for the $\mu_6$-C nucleus even when measured at −40 °C, the lowest temperature possible due to solubility limitations. Signals for carbonyl ligands were observed at $\delta$ 243.7, 238.8 and 210.9 ppm. The sharp peak at 243.7 ppm is attributed to the $\mu$-C(3)O(3) group (Fig. 1), and the broad resonance at 238.8 ppm to the semi-bridging and three bridging carbonyl ligands which surround the open Pt(1)Co(1)Pt(3)Co(2) face. The third resonance (210.9 ppm) is ascribed to the terminal CO units.

Compound VIII is an 86 electron cluster, and the polyhedral skeletal electron pair theory would predict a closo-octahedral metal framework [13,14]. However, the presence of the three platinum atoms with their preference for 16 rather than 18 electron shells is obviously critical, and in VIII, as in other clusters containing platinum, an alternative method of relating the observed metal core structures to the number of cluster valence electrons is required [15].

The results described in this paper, and earlier [3,4], demonstrate that a range of mixed-metal carbido-carbonyl cluster compounds containing platinum are accessible via reactions between the reagents $[Pt(C_2H_4)_2(PR_3)]$ and homonuclear metal carbonyl complexes containing $\mu_3$-CH or $\mu$-$CH_2$ ligands. These reactions probably proceed via a pathway involving addition of a $Pt(PR_3)$ fragment to the homo-, di- or -tri-nuclear metal carbonyl species to afford an intermediate with one or more metal centres coordinatively unsaturated. The latter situation would promote C–H bond activation, leading to formation of a carbido ligand and migration of a hydrogen atom to a bridging site.

## Experimental

All experiments were carried out under nitrogen, using Schlenk tube techniques. Light petroleum refers to that fraction of b.p. 40–60 °C. The compounds $[Pt(C_2H_4)_2(PR_3)]$ (R = cyclo-$C_6H_{11}$ or $Pr^i$), $[Pt(cod)_2]$ (cod = cycloocta-1,5-diene) [16] and $[Co_3(\mu_3\text{-}CH)(CO)_9]$ [17] were prepared as previously described. Products were separated by column chromatography on alumina (Brockman activity II). The instrumentation used for the spectroscopic measurements has been described earlier [3]. IR spectra were recorded on $CH_2Cl_2$ solutions. For the NMR studies measurements were made in $CDCl_3$ ($^1H$ or $^{31}P\text{-}\{^1H\}$) or $CD_2Cl_2\text{-}CH_2Cl_2$ ($^{13}C\text{-}\{^1H\}$) solutions at room temperature unless otherwise stated. All chemical shifts ($\delta$) are in ppm, and coupling constants are in Hz. The $^{31}P\text{-}\{^1H\}$ chemical shifts are positive to high frequency of 85% $H_3PO_4$ (external).

### *Synthesis of the cobalt-platinum compounds*

(i) A mixture of the compounds $[Co_3(\mu_3\text{-}CH)(CO)_9]$ (0.06 g, 0.14 mmol) and $[Pt(C_2H_4)_2\{P(cyclo\text{-}C_6H_{11})_3\}]$ (0.14 g, 0.27 mmol) was stirred in light petroleum (20 $cm^3$) at room temperature for ca. 15 h. The green precipitate which formed was allowed to settle, and the supernatant liquid was removed with a syringe. The precipitate was dissolved in $CH_2Cl_2$/light petroleum (5 $cm^3$, 1/1) and chromatographed (2 × 15 cm column). Elution with the same solvent mixture removed a trace of $[Co_3(\mu_3\text{-}CH)(CO)_9]$, followed by a green fraction. Removal of solvent in vacuo from the latter, followed by washing with light petroleum (2 × 15 $cm^3$) afforded green microcrystals of $[Co_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_7\{P(cyclo\text{-}C_6H_{11})_3\}_2]$ (VIIa) (0.11 g, 59%) (Found: C, 38.7; H, 5.0. $C_{46}H_{67}Co_3O_9P_2Pt_2$ calcd.: C, 39.7; H, 4.9%); $\nu_{max}(CO)$ at 2062s, 2024vs, 2004vs, and 1816m $cm^{-1}$. NMR: $^1H$, $\delta$ −6.18 (t, 1 H, $\mu$-H, $J(PH)$ 11, $J(PtH)$ 817), and 0.77–1.85 (m, 66 H, $C_6H_{11}$); $^{13}C\text{-}\{^1H\}$, $\delta$ 242.6 ($\mu$-CO), 210.5 (br, CoCO), and 36.4–20.4 ($C_6H_{11}$); $^{31}P\text{-}\{^1H\}$, $\delta$ 30.5 (s, $J(PtP)$ 3779 and 115).

(ii) The complex $[Pt(C_2H_4)_2(PPr^i_3)]$ (0.56 mmol) was prepared in situ by adding $[Pt(cod)_2]$ (0.23 g, 0.56 mmol) in small portions to cold (0 °C) ethylene-saturated light petroleum (20 $cm^3$). A solution of $PPr^i_3$ (0.56 $cm^3$ of a 1.0 mmol $dm^{-3}$ solution in light petroleum) was then added. The mixture, containing $[Pt(C_2H_4)_2(PPr^i_3)]$, which forms quantitatively, was treated with solid $[Co_3(\mu_3\text{-}CH)(CO)_9]$ (0.12 g, 0.27 mmol). After stirring for 1 h at room temperature, solvent was removed in vacuo. The residue was dissolved in $CH_2Cl_2$/light petroleum (5 $cm^3$, 1/4), and chromatographed (3 × 20 cm column). Elution with the same solvent mixture afforded two green eluates. The first, upon removal of solvent in vacuo, gave green microcrystals of $[Co_3Pt_2(\mu\text{-}H)(\mu_5\text{-}C)(\mu\text{-}CO)_2(CO)_7(PPr^i_3)_2]$ (VIIb) (0.20 g, 64%). The second, after removal of solvent in vacuo gave green microcrystals of $[Co_3Pt_3(\mu\text{-}H)(\mu_6\text{-}C)(\mu\text{-}CO)_4(CO)_5(PPr^i_3)_3]$ (VIII) (0.09 g, 22%).

For VIIb (Found: C, 29.0; H, 3.9. $C_{28}H_{43}Co_3O_9P_2Pt_2$ calcd.: C, 29.2; H, 3.8%); $\nu_{max}(CO)$ at 2063s, 2025vs, 2005vs, and 1817m $cm^{-1}$. NMR: $^1H$, $\delta$ −6.12 (t, 1 H, $\mu$-H, $J(PH)$ 12, $J(PtH)$ 802), 1.24 (d of d, 36 H, Me, $J(HH)$ 7, $J(PH)$ 14), and 2.70 (m, 6 H, CH); $^{13}C\text{-}\{^1H\}$ (at −80 °C), $\delta$ 434.5 (br, $\mu_5$-C), 239.5 ($\mu$-CO, $J(PtC)$ 1147), 206.7, 202.0 (br, CoCO), 22.8 (br, CH), and 19.6 (br, Me); $^{31}P\text{-}\{^1H\}$, $\delta$ 41.3 (s, $J(PtP)$ 3799 and 117). For VIII (Found: C, 29.6; H, 4.3. $C_{37}H_{64}Co_3O_9P_3Pt_3$ calcd.: C, 29.5; H, 4.3%); $\nu_{max}(CO)$ at 2032m, 2000s, 1824m, and 1807sh $cm^{-1}$.

Table 2. Atomic positional parameters (fractional coordinates $\times 10^4$) for compound VIII with estimated standard deviations in parentheses

| Atom | *x* | *y* | *z* |
|---|---|---|---|
| Pt(1) | 1456(1) | 1397(1) | 8901(1) |
| Pt(2) | 1062(1) | 1553(1) | 6319(1) |
| Pt(3) | 2600(1) | 942(1) | 7282(1) |
| Co(1) | 2168(2) | 2054(1) | 7749(1) |
| Co(2) | 604(2) | 771(1) | 7728(1) |
| Co(3) | 59(2) | 1851(1) | 7603(1) |
| P(1) | 1419(3) | 1400(2) | 10301(2) |
| P(2) | 1000(3) | 1596(2) | 4949(2) |
| P(3) | 4187(4) | 467(3) | 7167(3) |
| C | 1347(12) | 1432(6) | 7591(8) |
| C(1) | 648(14) | 622(7) | 8839(10) |
| O(1) | 481(13) | 252(6) | 9274(7) |
| C(2) | 2493(12) | 2058(7) | 8852(8) |
| O(2) | 3063(12) | 2317(7) | 9299(8) |
| C(3) | −284(16) | 2006(10) | 6474(11) |
| O(3) | −957(14) | 2243(8) | 6148(8) |
| C(4) | 1547(17) | 239(10) | 7407(13) |
| O(4) | 1662(14) | −241(6) | 7304(12) |
| C(5) | −559(14) | 365(7) | 7517(11) |
| O(5) | −1308(12) | 122(8) | 7376(12) |
| C(6) | 3530(17) | 1915(13) | 7406(14) |
| O(6) | 4365(12) | 2034(7) | 7261(12) |
| C(7) | −156(18) | 2522(8) | 7927(13) |
| O(7) | −382(18) | 2944(8) | 8175(13) |
| C(8) | −1186(17) | 1554(10) | 7864(12) |
| O(8) | −2021(11) | 1434(9) | 8027(12) |
| C(9) | 2130(23) | 2768(9) | 7511(17) |
| O(9) | 2077(22) | 3226(8) | 7325(17) |
| C(11) | 148(14) | 1115(8) | 10665(9) |
| C(12) | 37(17) | 1092(10) | 11560(11) |
| C(13) | −853(15) | 1355(12) | 10269(15) |
| C(14) | 1592(14) | 2096(8) | 10727(9) |
| C(15) | 1726(18) | 2155(10) | 11676(11) |
| C(16) | 795(22) | 2508(10) | 10367(17) |
| C(17) | 2504(15) | 977(9) | 10825(11) |
| C(18) | 2390(19) | 362(8) | 10632(15) |
| C(19) | 3610(15) | 1234(12) | 10637(14) |
| C(21) | 1751(16) | 1032(11) | 4479(12) |
| C(22) | 1196(21) | 461(9) | 4646(17) |
| C(23) | 2088(20) | 1123(12) | 3605(11) |
| C(24) | 1591(20) | 2236(10) | 4571(13) |
| C(25) | 1041(26) | 2737(11) | 4869(19) |
| C(26) | 2799(22) | 2251(14) | 4815(18) |
| C(27) | −407(15) | 1603(10) | 4525(11) |
| C(28) | −463(21) | 1632(13) | 3589(12) |
| C(29) | −1124(16) | 1155(12) | 4817(17) |
| C(31) | 5197(14) | 853(10) | 6583(14) |
| C(32) | 4789(22) | 1012(13) | 5751(15) |
| C(33) | 6319(18) | 643(20) | 6591(25) |
| C(34) | 4077(17) | −216(9) | 6766(16) |
| C(35) | 3460(20) | −221(10) | 5890(17) |
| C(36) | 5040(25) | −567(14) | 6747(29) |
| C(37) | 4912(19) | 372(13) | 8152(15) |
| C(38) | 5228(25) | 906(15) | 8572(17) |
| C(39) | 4108(30) | −15(18) | 8690(18) |

NMR: $^1$H, $\delta$ $-9.30$ (d of d, 1 H, $\mu$-H, $J$(PH) 13 and 2, $J$(PtH) 700 and 663), 1.09–1.22 (m, 54 H, Me), and 2.35–2.87 (m, 9 H, CH); $^{13}$C-{$^1$H} (at $-40\,^\circ$C), $\delta$ 243.7, 238.8 ($\mu$-CO), 210.9 (CoCO), and 32.1–14.6 (Pr$^i$); $^{31}$P-{$^1$H}, $\delta$ 47.8 (s, $J$(PtP) 4883 and 78), 46.2 (d, $J$(PP) 17, $J$(PtP) 4619, 142 and 75), and 39.8 (d, $J$(PP) 17, $J$(PtP) 4900 and 56).

*Crystal structure determination*

Crystals of VIII were grown from $CH_2Cl_2$/light petroleum. Diffracted intensities were collected at 293 K from a crystal of dimensions ca. $0.51 \times 0.50 \times 0.60$ mm on a Nicolet R3m/$\mu$ diffractometer. Of the 7412 data collected ($\theta$–$2\theta$ scans, $2\theta \leq 45\,^\circ$), 4292 unique data had $F \geq 5\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by an empirical method based upon azimuthal scan data [18].

*Crystal data.* $C_{37}H_{64}Co_3O_9P_3Pt_3$, $M = 1507.9$, monoclinic, space group $P2_1/n$, $a$ 12.536(2), $b$ 24.068(4), $c$ 16.512(3) Å, $\beta$ 91.72(1)°, $U$ 4980(2) Å$^3$, $Z = 4$, $D_c$ 2.01 g cm$^{-3}$, $F(000) = 2872$, Mo-$K_\alpha$ X-radiation (graphite monochromator), $\bar{\lambda}$ 0.71069 Å, $\mu$(Mo-$K_\alpha$) 96.0 cm$^{-1}$.

The structure was solved by direct methods, and successive difference Fourier syntheses were used to locate all non-hydrogen atoms. Hydrogen atoms were included in calculated positions (C–H 0.96 Å) with either fixed isotropic thermal parameters ca. $1.2 \times U_{\text{equiv.}}$ of the parent carbon atoms (C*H*Me$_2$), or a common refined isotropic thermal parameter (CH*Me*$_2$). The $\mu$-H hydrogen atom was not located. Refinement by blocked-cascade least squares led to $R = 0.045$ ($R' = 0.043$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0007\,|F|^2]$ giving a satisfactory analysis of variance. The final electron density difference synthesis showed no peaks $> 1.1$ or $< -1.4$ e Å$^{-3}$. Initial calculations were performed on a Digital $\mu$-Vax computer with the SHELXPLUS crystallographic package, and final refinement was performed on a Data General 'Eclipse' computer with the SHELXTL system of programs [18]. Scattering factors, with corrections for anomalous dispersion, were taken from reference [19]. Atom coordinates for VIII are given in Table 2. Full listings of bond distances and angles, and thermal parameters have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Structure factors are available from the authors.

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