93. The *Lewis* Basicity of the $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ Clusters and the X-Ray Crystal Structure of $[\{ZnI_2\}\{Pt_3(\mu\text{-}CO)_3(PPh(i\text{-}Pr)_2)_3\}]$

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Dedicated to Prof. *Hans-Georg von Schnering* on the occasion of his 60th birthday

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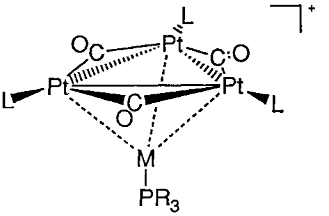
The cluster compounds $[Pt_3(\mu\text{-}CO)_3(PR_3)_3]$ act as *Lewis* bases towards the metal halides of Group XI, MX, Group XII, MX_2, and Group XIII, MX_3, to form cluster compounds of the composition $[\{MX_n\}\{Pt_3(\mu\text{-}CO)_3(PR_3)_3\}]$. The X-ray crystal structure, NMR and IR data are given for the compound $[\{ZnI\}\{Pt_3(\mu\text{-}CO)_3(PPh(i\text{-}Pr)_2)_3\}]$.

The $[Pt_3(\mu\text{-}CO)_3L_3]$ moiety (L = CO, PR_3), {3:3:3}, is a recurrent structural element in a wide variety of homo- and heteronuclear clusters [1]. Furthermore, in recent years compounds of this composition, which can be isolated, when L is a bulky tertiary phosphine, have received particular attention, as it has become apparent that they readily form 'addition compounds' with the cationic fragments $[M(PR_3)]^+$ [2] [3], **1**, and with the cations M^+ [4], **2**, (M = Cu, Ag, and Au). In compounds of type **1**, the {3:3:3} moiety is capped by the $[M(PR_3)]^+$ fragment, while in compounds of type **2** the M^+ cation is placed between the two Pt_3-triangular units.

Furthermore, compounds in which the $[ML]^+$ unit of compounds of type **1** has been replaced by Tl^+ have been recently described [5], while clusters are known in which the M^+



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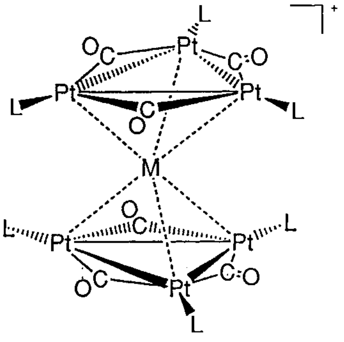

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cation in compounds of type **2** is replaced by Hg [6] or Hg_2 [7]. Finally, pentametallic clusters in which the {3:3:3} triangle is capped on both sides by HgX fragments (X = Cl, Br, and I) are also known [3] [8].

The interaction between the {3:3:3} unit and a metal cation can be conveniently described in terms of a *Lewis* base/*Lewis* acid interaction, as it has been shown that the HOMO- and LUMO-molecular orbitals of the Pt_3 moiety can be considered as corresponding to those of a conventional σ-donor and weak π-acceptor ligands, *e.g.*, a tertiary phosphine [9–11].

We now find that the formation of 'coordination compounds' containing these {3:3:3} clusters as '*Lewis* bases' is not restricted to the *Lewis* acids such as M^+ and $[ML]^+$ (M = Cu, Ag, and Au), but it extends also to the halides of these metal centers, MX, as well as those of Group XII (MX_2) and Group XIII (MX_3). Thus, we have recently isolated and characterized clusters of composition $[\{MX_n\}\{3:3:3\}]$ where MX_n = CuCl (**3a**), CuBr (**3b**), CuI (**3c**), $ZnBr_2$ (**4a**), ZnI_2 (**4b**), $CdBr_2$ (**5a**), CdI_2 (**5b**), and $InBr_3$ (**6**) (L = bulky tertiary phosphine, *e.g.*, $P(i\text{-}Pr)_3$ or $PPh(i\text{-}Pr)_2$ [12]. In agreement with the *Lewis* base/*Lewis* acid analogy developed earlier, and on the basis of their IR and MNR spectra, one can formulate the above clusters as containing the basic trimetallic structure present in compounds of type **1**. We report here the detailed preparation, NMR and IR data and the X-ray crystal structure of air-stable dark-red $[\{ZnI_2\}\{Pt_3(\mu\text{-}CO)_3(PPh(i\text{-}Pr)_2)_3\}]$, **4b**.

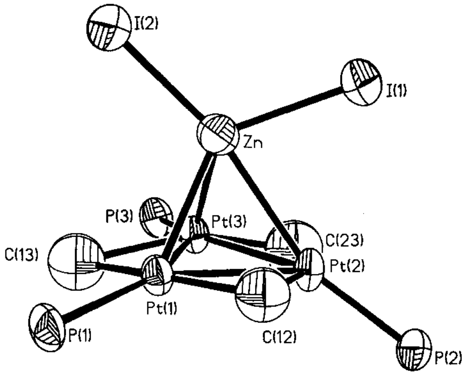

Figure. *ORTEP view of the four metal atoms of compound* $[\{ZnI_2\}\{Pt_3(\mu\text{-}CO)_3(PPh(i\text{-}Pr)_2)_3\}]$ (**4b**), *as well as the C, P, and I donors*

Table 1. *The Skeletal Atoms in the Molecular Structure of* $[\{ZnI_2\}\{Pt_3(\mu\text{-}CO)_3(PPh(i\text{-}Pr)_2)_3\}]$ (**4b**) *in the Crystalline State.* Selected Interatomic Distances [Å] and Angles [°].

Zn–Pt(1)	2.650(5)	Pt(1)–Pt(2)	2.679(2)
Zn–Pt(2)	2.755(5)	Pt(2)–Pt(3)	2.686(2)
Zn–Pt(3)	2.624(5)	Pt(1)–Pt(3)	2.683(2)
av. Pt–P	2.29(1)	Zn–I(1)	2.575(7)
av. Pt–C	2.06(9)	Zn–I(2)	2.535(5)
Pt(1)–Pt(2)–Pt(3)	60.00(6)	Pt(1)–Zn–Pt(3)	61.1(1)
Pt(2)–Pt(3)–Pt(1)	59.87(4)	Pt(2)–Zn–Pt(3)	59.8(1)
Pt(3)–Pt(1)–Pt(2)	60.13(5)	I(1)–Zn–I(2)	114.2(2)
Pt(1)–Zn–Pt(2)	59.3(1)		

The basic structure of **4b** consists of a Pt_3-triangle capped by a Zn-atom. An ORTEP view of the four metal atoms, as well as the C, P, and I donors, is shown in the *Figure*. Selected bond lengths and angles are given in *Table 1*. The $ZnPt_3$ tetrahedron is distorted having two Zn–Pt distances at 2.650(5) Å and one at 2.755(5) Å. There are also slight differences in the Pt–Pt distances. While two of the P-atoms are slightly below the Pt_3 plane (10°), the third, P(2), shows a stronger distortion (38°) because of its interaction with I(1) of the ZnI_2 moiety. As found in complexes of types **1** and **2**, the CO ligands in **4b** are slightly bent towards the ZnI_2 moiety. Such distortions have been previously found in $[Ag\{Pt_3(\mu\text{-}CO)_3(P(i\text{-}Pr)_3)_3\}](CF_3SO_3)$ [4a] and $[\{(P(i\text{-}Pr)_3)Cu\}\{Pt_3(\mu_2\text{-}CO)_3(P(i\text{-}Pr)_3)_3\}][PF_6]$ [3], **1a**. The Zn–Pt distances are comparable with the Cu–Pt distances in **1a** (2.601(4) Å, average) while the Zn–I distances (2.558(7) Å, average) are comparable with those found in complexes of the type $[ZnI_2L_2]$ (2.55–2.60 Å) [13] where the zinc ion has tetrahedral coordination. The Zn-atom is placed approximately above the center of the Pt_3 triangle and the plane defined by ZnI_2 goes through P(2) and bisects the Pt(1)–Pt(3) edge. The I–ZN–I angle is 114.2(2)°, the atom I(1) defines an angle of 66.1° with the axis going through the center of the Pt_3 triangle and Zn. The corresponding angle for I(2) is 48.1°. Therefore, this molecule is unsymmetrically placed above the Pt_3 triangle, presumably because of the *van der Waals* interaction between the I-atoms and the phosphines.

As the other compounds of the types **4**, as well as those of the types **3**, **5**, and **6** were prepared and characterized in analogy to **4b** and show IR and NMR data comparable with those of **4b**, it is deduced that the compounds of types **4** and **5** have structures similar to **4b**, those of type **3** are related to **1**, while those of type **6** have structures in which the In-atom is octahedrally surrounded by three Pt- and three Br-atoms. Thus, it can be stated that the Pt_3 clusters of {3:3:3}-type can be truly considered as 'monodentate ligands', albeit of 'non-classical' type.

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Experimental Part

General. Manipulations and measurements were carried out as described in [14].

$[\{ZnI_2\}\{Pt_3(\mu\text{-}CO)_3(PPh(i\text{-}Pr)_2)_3\}]$ (**4b**). It was obtained in *ca.* 60% yield by adding solid ZnI_2 (1.2 equiv.) to a THF soln. of $[Pt_3(\mu\text{-}CO)_3(PPh(i\text{-}Pr)_2)_3]$ (1 equiv.). The soln. was evaporated to dryness. The residue dissolved in CH_2Cl_2, the soln. filtered over *Celite*, and a layer of Et_2O floated on top of it and placed in a refrigerator at –25°. The crystals thus obtained gave satisfactory microanalytical data and were suitable for X-ray diffraction. IR: v = 1880*w*, 1817*vs*, 1786*s*. $^{31}P\{^1H\}$-NMR (104.25 MHz, H_3PO_4 ext., $CDCl_3$, *ca.* 300 K): 62 (^1J(Pt,P) = 5030, ^2J(Pt,P) = 361, ^3J(P,P) = 27.0).

The other complexes were similarly prepared and characterized. Full experimental data will be published at a later date.

Collection and Reduction of X-Ray Intensity Data. Red single crystals of **4b** were grown from CH_2Cl_2/Et_2O soln. A summary of crystal data together with various details concerning intensity measurements is given in *Table 2*. No significant deviation in the intensity of three standard reflections throughout the data collection were observed. The data were corrected for *Lorentz* and polarization effects, whereas no absorption correction was applied. Atomic scattering factors were taken from International Tables of X-Ray Crystallography [15].

Table 2. *Crystal Data for* $[\{ZnI_2\}\{Pt_3(\mu\text{-}CO)_3(PPh(i\text{-}Pr)_2)_3\}]$ (**4b**)

Formula	$C_{39}H_{57}I_2O_3P_3PtZn$	Crystal dimension [mm]	0.1 × 0.1 × 0.1
F_w	1571.2	Radiation	Mo$K\alpha$
a [Å]	16.80(1)	Diffractometer	*Picker-Stoe-Diff-4*
b [Å]	13.97(1)	Scan mode	ω/θ
c [Å]	24.13(1)	Scan width	1.05
α [°]	90.0	Background time (s)	5
β [°]	107.00(4)	2θ limits [°]	3–50
γ [°]	90.0	Reflect. collected No.	4735
V [Å^3]	5420.47	No. unique data	3155 ($I \geq 6\sigma(I)$)
Z	4	Final No. of variables	248
Space group	*Cc* (9)	Final R, R_w	0.052, 0.076

Solution and Refinement of the Structure. The structure was solved using *Patterson* and difference *Fourier* methods. A full matrix least-squares refinement was used and the function that was minimized was $\Sigma w(|F_o|\text{-}|F_c|)$. Anisotropic displacement parameters were used only for Pt, P, Zn, and I, all other atoms were refined isotropically. The Ph and i-Pr groups are strongly disordered and, therefore, their bond lengths and angles have been kept fixed (Ph d(C–C) = 1.4 Å, angle (C–C–C) = 120°; i-Pr d(C–C) = 1.54 Å, angle 109°). The calculations were carried out on a Micro-VAX II using the SHELXTL-Plus and the XTAL 2.0 programs. Final positional and displacement parameters and tables of observed and calculated structure factors are available upon request.

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