Journal of Organometallic Chemistry, 289 (1985) C1—C4
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

HETEROBIMETALLIC (Pd/Pt—Ge/Sn) TRINUCLEAR CLUSTERS CONTAINING A PLANAR $M_3(CO)_3(\mu_2\text{-}M')_3$ CORE: SPECTROSCOPY, CYCLIC VOLTAMMETRY, AND ESR CHARACTERISATION OF ELECTROCHEMICAL REDUCTION PRODUCTS. CRYSTAL STRUCTURES OF $[(M\{\mu_2\text{-}Sn(NR_2)_2\}(CO))_3]$ (M = Pd OR Pt, R = $SiMe_3$)*

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(Received March 25th, 1985)

Summary

The characterisation (IR, NMR, X-ray) is described of a new family of cluster compounds, containing a planar six-membered ring of alternating Pd (or Pt) and Ge (or Sn) atoms, of formula $[(M\{\mu_2\text{-}M'(NR_2)_2\}(CO))_3]$ (M = Pd (II) or Pt (III), M′ = Ge (a) or Sn (b), R = $SiMe_3$); both II and III undergo reversible 1 e^{-1}-reduction in tetrahydrofuran at ca. −1.2 V to yield ESR-characterised reduction products, containing a Pd_nSn_2 or Pt_3Sn_3 core in the case of compounds b. The crystalline complexes IIb or IIIb have a planar $[MSn(CO)]_3$ framework with <M—M> 2.814(16) (Pd) or 2.763(9) (Pt) and <M—Sn> 2.621(5) (Pd) or 2.620(4) (Pt) Å.

Although homonuclear triangulo-clusters are well known for palladium and platinum [1], and a number of them have CO ligands (e.g., $[Pt_3(\mu_2\text{-}CO)_3(PR'_3)_3]$, R′ = C_6H_{11}, <Pt—Pt> 2.654(2) Å [2]), the latter have previously been found to occupy bridging sites, except for $[(Pt\{\mu_2\text{-}Fe(CO)_4\}(CO))_3]^{n-}$ (n = 1, <Pt—Pt> 2.65_6 Å; or n = 2, <Pt—Pt> 2.75_0 Å) [3], and $[\{Pt(\mu\text{-}L)CO\}_3]$ (L = $P(NR^3)(NR^1R^2)$, R^1 = Bu^t = R^3 and R^2 = $SiMe_3$, or R^1 = $SiMe_3$ = R^2 and R^3 = Bu^t or $SiMe_3$) so formulated on the basis of NMR and, in once case, X-ray data, <Pt—Pt> 2.741 Å [Å] [4]. The anion $[Pt_3Sn_8Cl_{10}]^{4-}$ (related to species active in olefin hydrogenation or hydroformylation, and obtained from $K_2[PtCl_4]$, $SnCl_2$, and $[NMe_4]Cl$ in Me_2CO) was assumed to

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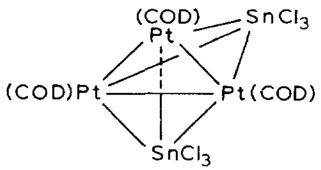

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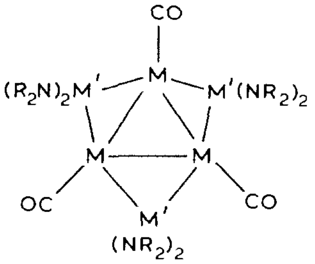

(IIa: M = Pd, M' = Ge;
IIb: M = Pd, M' = Sn;
IIIa: M = Pt, M' = Ge;
IIIb: M = Pt, M' = Sn)

have the structure $[Pt_3(\mu_3\text{-}SnCl)_2(SnCl_3)_6]^{4-}$, because its reaction with cycloocta-1,5-diene (COD) afforded $[SnCl_6]^{2-}$ and the X-ray characterised $[Pt_3(\mu_3\text{-}SnCl_3)_2(COD)_3]$ (<Pt—Pt> 2.58 Å, <Pt—Sn> 2.80 Å) (I) [5]. A μ_2-Sn-ligating triangular noble metal cluster having terminal CO's is represented by $[Os_3SnH_2(CO)_{10}R'_2]$ (R' = $CH(SiMe_3)_2$) [6a], and others, based on an Os_3 core and SnR_2, are reported in ref. 6b.

We now present data on the series $[(M\{\mu_2\text{-}M'(NR_2)_2\}(CO))_3]$ (II) and (III) (R = $SiMe_3$). These compounds are prepared in high yield from $[M\{M'(NR_2)_2\}_3]$ and CO [7]. A quasi-isoleptic complex, $[(Ru\{\mu_2\text{-}GeMe_2\}(CO))_3]$, has long been known [8]; it has the same skeletal geometry as II and III, although it has six electrons fewer than IIa.

The terminal nature of the carbonyl ligands is evident from (i) the position of ν(CO) ("Nujol"): 2040 (IIa), 2038 (IIb), 2025 (IIIa), and 2020 (IIIb) cm^{-1}; and (ii) the ^{13}C NMR CO chemical shift (located only for complex IIIb, at 215.7 ppm). The ^{13}C and ^1H chemical shifts for the $M'(NR_2)_2$ ligands differ somewhat from those in $[M\{M'(NR_2)_3\}_3]$ or $M'(NR_2)_2$, e.g., (^{13}C and ^1H, respectively, in ppm), 7.50 (6.50) and 0.36 (0.20) for IIa (IIIa in parentheses), 6.80 and 0.45 ppm for $[Pd\{Ge(NR_2)_3\}_3]$, and 6.10 and 0.44 ppm for $Ge(NR_2)_2$. Some ^{195}Pt parameters on compounds IIIa and IIIb are summarised in Fig. 1; for data on $[Pt\{M'(NR_2)_2\}_3]$, see ref. 7.

Each of the clusters II and III readily undergoes a single reversible electrochemical reduction ($-E_0$ (V): 1.36 (IIa), 1.16 (IIb), 1.13 (IIIa), 1.04, (IIIb); in tetrahydrofuran (THF) with $[NBu^n{}_4][BF_4]$ (0.5 mol dm^{-3}) as supporting electrolyte, using Pt electrodes), with two further irreversible reductions at more negative potentials. In contrast, each complex $[M\{M'(NR_2)_2\}_3]$ undergoes two irreversible electrochemical reductions in the range 0 to −2.7 V.

Each of the one-electron reduction products II' and III', from II or III, was generated in THF by in situ controlled potential electrolysis (Pt electrode) at −40°C at a potential slightly greater than E_0, in the cavity of a Varian E104A ESR spectrometer. The fluid solution spectra each showed a broad ESR signal with no evidence of satellites. Upon freezing, anisotropic axially symmetrical spectra were obtained (g_{iso}, $g_{\parallel}$, $g_{\perp}$: 2.016, 2.083, 1.985 (IIa'); 2.020, 2.065, 1.969 (IIb'); 2.018, 2.088, 2.008 (IIIa'); 2.015, 2.087, 2.007

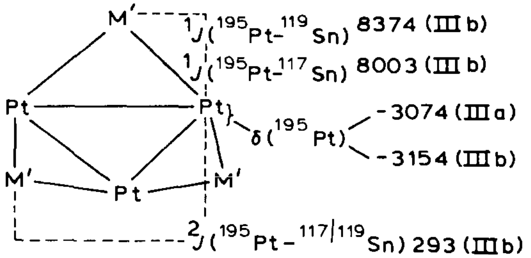

Fig. 1. Some ^{195}Pt NMR chemical shifts (δ in ppm rel. to $K_2[PtCl_4]$) (recorded at 77 MHz) and coupling constants (J in Hz) for complexes IIIa and IIIb in C_6D_6 at 30° C.

(IIIb′); $a_{\parallel}$ (^{195}Pt)/G, $a_{\perp}$ (^{195}Pt) (G): < 10, 69 (IIIa′); 44, 54 (IIIb′); $a_{\parallel}$ ($^{119,117}Sn$) (G), $a_{\perp}$ ($^{119,117}Sn$) (G): 75, 82 (IIb′); no ^{73}Ge or ^{105}Pd satellite lines were observed for (IIa′)). Computer simulations (see ref. 9) indicated that the reduced PdSn cluster IIb′ has two equivalent tin atoms, whilst the Pt analogue IIIb′ has retained its Pt_3Sn_3 cluster integrity; the g value anisotropy, $g_{iso} \gg g_e$, indicates that IIb′ still contains Pd.

As the time scale of the electrolysis experiment is much greater than that of cyclic voltammetry (CV) we conclude that the radical anions are reversibly generated by (CV) and these are the Pt species $[(Pt\{\mu\text{-}M'(NR_2)_2\}(CO))_3]^{\overline{\cdot}}$ (III′), observed by ESR; whereas the Pd-containing radical anions are less stable and undergo decomposition in THF at −40° C to yield in the Pd—Sn

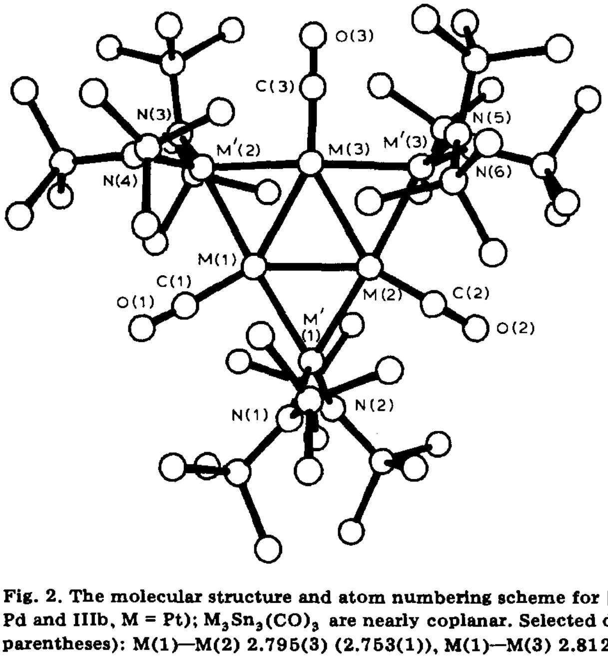

Fig. 2. The molecular structure and atom numbering scheme for $[(M\{\mu_2\text{-}Sn(NR_2)_2\}(CO))_3]$ (IIb, M = Pd and IIIb, M = Pt); $M_3Sn_3(CO)_3$ are nearly coplanar. Selected dimensions (data for the latter in parentheses): M(1)—M(2) 2.795(3) (2.753(1)), M(1)—M(3) 2.812(3) (2.761(1)), M(2)—M(3) 2.834(3) (2.775(1)), M(1)—Sn(1) 2.624(3) (2.619(1)), M(1)—Sn(2) 2.614(3) (2.616(1)), M(2)—Sn(1) 2.628(3) (2.626(1)), M(2)—Sn(3) 2.618(3) (2.614(1)),M(3)—Sn(2) 2.626(3) (2.624(1)), M(3)—Sn(3) 2.618(3) (2.619(1)), <Sn—N> 2.03(8) (2.05(2)) Å; Sn(1)—M(1)—M(2) 57.92(8) (58.48(3)), M(1)—Sn(1)—M(2) 64.32(8) (63.31(3)), M(2)—M(1)—M(3) 60.71(1) (60.43(2)), <NSnN> 105(1) (108(1))°.

case a paramagnetic product (IIb′) which contains two equivalent tin nuclei. The cluster core of IIb′ may be similar to that found in the platinum complex I [5].

Crystal data for complexes IIb and IIIb (in parentheses for the latter): $C_{39}H_{108}N_6O_3Pd_3Si_{12}Sn_3$ ($C_{39}H_{108}N_6O_3Pt_3Si_{12}Sn_3$), M 1721.6 (1987.7), monoclinic (monoclinic), space groups, $P2_1/n$ ($P2_1/n$), a 11.663(2) (11.688(1)), b 23.609(4) (23.582(2)), c 27.432(5) (27.426(2)) Å, β 94.14(2) (94.41(1))°, $Z = 4$ (4), D_c 1.52 (1.75) g cm^{-3}.

The structures of the isomorphous complexes IIb and IIIb are illustrated in Fig. 2. They were solved using 3197 (IIb) or 5034 (IIIb) reflections with $I > \sigma(I)$ (measured on a CAD-4 diffractometer with Mo-K_α radiation) by routine heavy atom methods and refined for non-hydrogen atoms by full-matrix least-squares to $R = 0.098$ (0.067), $R' = 0.119$ (0.086) (data for IIIb in parentheses)[‡].

The <M—Sn> distances in complexes IIb and IIIb are significantly longer than in $[M\{Sn(NR_2)_2\}_3]$ (2.53 (M = Pd) [7] or 2.49 (Pt) [10]), while <Sn—N> distances are ca. 0.04 Å shorter, and <NSnN> angles are similarly approaching tetrahedral values (with Pt > Pd).

Acknowledgements. We thank Johnson, Mathey PLC for loans of Pd and Pt; S.E.R.C. for a postdoctoral assistantship to G.K.C., and [with B.P. Chemicals, Ltd. (Hull)] for a CASE award to M.C.M. We are grateful to Dr. D.J. Gulliver for his interest.

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[‡] The atomic coordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.