Journal of Organometallic Chemistry, 352 (1988) C29–C33
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Preliminary communication

Synthesis of Pt–Cu, Pt–Ag and Pt–Au clusters and crystal structure of the copper(I)–platinum(0) cluster $[CuPt_3(\mu\text{-}CO)_3(PPh_3)_5]BF_4$

Pierre Braunstein, Sylvie Freyburger

Laboratoire de Chimie de Coordination, UA 416 du CNRS, Université Louis Pasteur, Institut Le Bel, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex (France)

and Odile Bars

Laboratoire de Cristallochimie, UA 254 du CNRS, Université de Rennes I, Avenue du Général Leclerc, F-35042 Rennes Cédex (France)

(Received June 1st, 1988)

Abstract

The mixed-metal cluster compounds $[MPt_3(\mu\text{-}CO)_3(PPh_3)_5]X$ (M = Cu, X = BF_4; M = Ag, X = NO_3; M = Au, X = PF_6) have been synthesized in high yields from $[Pt(PPh_3)_2(C_2H_4)]$ and group 11 reagents. The copper–platinum cluster $[CuPt_3(\mu\text{-}CO)_3(PPh_3)_5]BF_4$ has been characterized by X-ray diffraction. It adopts a distorted tetrahedral geometry with the $Cu(PPh_3)$ group capping the Pt_3 face, one Pt atom of which is bonded to two PPh_3 ligands.

Mixed-metal clusters containing Pt–Au [1–7], Pt–Ag [8–11] or Pt–Cu [6] bonds are attracting increasing interest. This is largely because of (i) the wish to create new molecular systems and make synthetic and structural comparisons between closely related or isolobal fragments [12] and (ii) the possibility of using such clusters as molecular precursors of heterogeneous catalytic materials containing bimetallic combinations of particular interest [13].

Complexes of the type $[AuPt_3(\mu\text{-}CO)_3(PR_3)_n]X$ ($n = 4$ or 5, X = NO_3 or PF_6) were synthesized previously through the reactions of eq. 1, 2:

$$AuCl(PCy_3) + Pt_3(\mu\text{-}CO)_3(PCy_3)_3 \xrightarrow[Tl[PF_6]]{C_6H_6} [AuPt_3(\mu\text{-}CO)_3(PCy_3)_4]PF_6 + TlCl \quad (1)$$

$$6\,Au(PPh_3)(NO_3) + 3\,Pt(PPh_3)_3 + CO \xrightarrow{\text{acetone}} [AuPt_3(\mu\text{-}CO)_3(PPh_3)_5]NO_3 + 5[Au(PPh_3)_2]NO_3 \quad (2)$$

0022-328X/88/$03.50

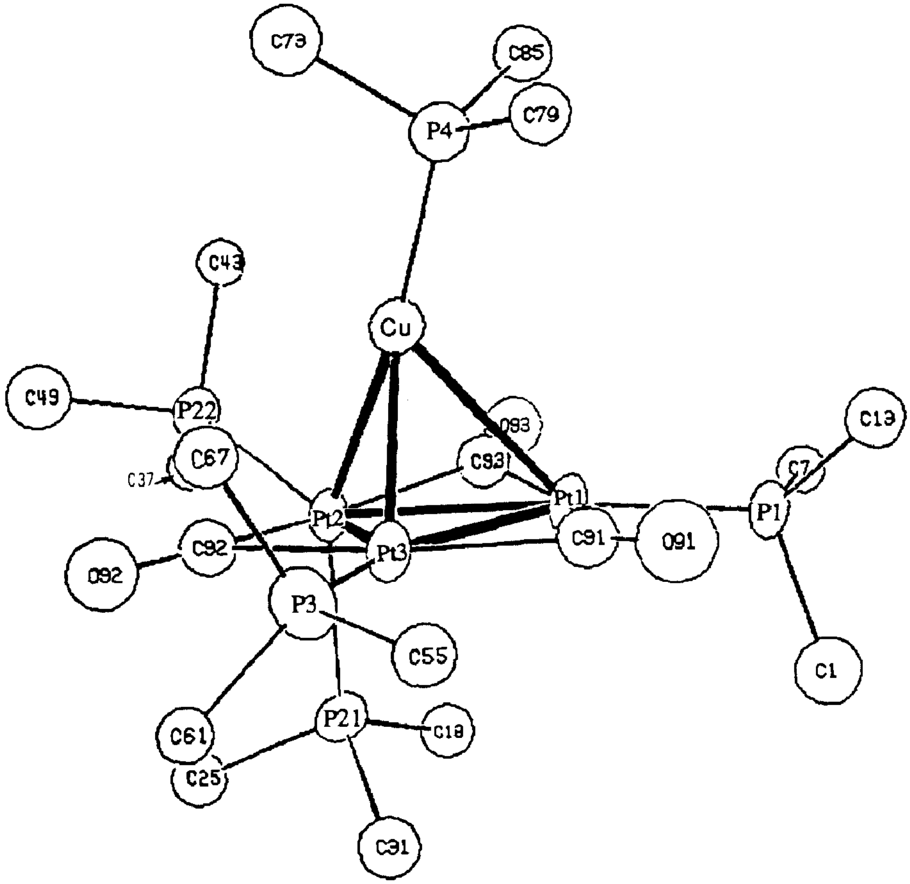

Fig. 1. Molecular structure of $[CuPt_3(\mu\text{-}CO)_3(PPh_3)_5](BF_4)$. The phenyl groups are represented by their *ipso* carbons only. Selected dimensions in the cation: Pt(1)–Pt(2) 2.709(1), Pt(1)–Pt(3) 2.667(1), Pt(1)–Cu 2.735(3), Pt(1)–P(1) 2.267(6), Pt(1)–C(91) 2.10(3), Pt(1)–C(93) 2.11(2), Pt(2)–Pt(3) 2.712(1), Pt(2)–Cu 2.577(3), Pt(2)–P(21) 2.409(7), Pt(2)–P(22) 2.334(6), Pt(2)–C(92) 2.11(3), Pt(2)–C(93) 2.09(2), Pt(3)–Cu 2.664(3), Pt(3)–P(3) 2.277(6), Pt(3)–C(91) 2.05(3), Pt(3)–C(92) 2.12(2), Cu–P(4) 2.212(8) Å; Pt(2)–Pt(1)–Pt(3) 60.58(3), Pt(2)–Pt(1)–Cu 56.51(7), Pt(2)–Pt(1)–P(1) 151.8(2), Pt(3)–Pt(1)–Cu 59.08(7), Pt(3)–Pt(1)–P(1) 145.3(2), Cu–Pt(1)–P(1) 137.0(2), Pt(1)–Pt(2)–Pt(3) 58.95(3), Pt(1)–Pt(2)–Cu 62.26(7), Pt(1)–Pt(2)–P(21) 94.5(2), Pt(1)–Pt(2)–P(22) 140.7(2), Pt(3)–Pt(2)–Cu 60.42(7), Pt(3)–Pt(2)–P(21) 99.3(2), Pt(3)–Pt(2)–P(22) 141.0(2), Cu–Pt(2)–P(21) 154.4(2), Cu–Pt(2)–P(22) 96.4(2), P(21)–Pt(2)–P(22) 109.0(2), Pt(1)–Pt(3)–Pt(2) 60.47(3), Pt(1)–Pt(3)–Cu 61.73(7), Pt(1)–Pt(3)–P(3) 155.4(2), Pt(2)–Pt(3)–Cu 57.29(7), Pt(2)–Pt(3)–P(3) 144.0(2), Cu–Pt(3)–P(3) 126.9(2), Pt(1)–Cu–Pt(2) 61.23(7), Pt(1)–Cu–Pt(3) 59.19(7), Pt(1)–Cu–P(4) 125.8(2), Pt(2)–Cu–Pt(3) 62.29(8), Pt(2)–Cu–P(4) 166.9(2), Pt(3)–Cu–P(4) 130.4(2)°.

The best yield reported for the synthesis of $[Pt_3(\mu\text{-}CO)_3(PCy_3)_3]$ from readily available precursors is 85% (based on Pt) [14]. Mingos and co-workers [2] have reported a yield of 85% (based on Pt) for eq. 1, so that the overall yield for this $AuPt_3$ cluster is ca. 72% (based on Pt). Eq. 2 makes use of simpler precursor complexes but $[AuPPh_3]^+$ is needed to strip off phosphine ligands from $[Pt(PPh_3)_3]$ [5]. The yield reported is 66% (based on Pt), and only 1/6 of the gold used is found in the $AuPt_3$ cluster.

Herein we report a one-pot procedure (eq. 3) which gives a yield of ca. 90%

(based on Pt) and in which 2/3 of the gold is present in the desired cluster owing to the smaller amount of phosphine present.

$$3\ AuCl(SC_4H_8) + 6\ Pt(PPh_3)_2(C_2H_4) + CO \xrightarrow[Tl[PF_6]]{acetone}$$

$$2[AuPt_3(\mu\text{-}CO)_3(PPh_3)_5]PF_6 + [Au(PPh_3)_2]PF_6 + 3\ TlCl + C_2H_4 \quad (3)$$

This optimized procedure has been extended to the preparation of the related $[AgPt_3]^+$ and $[CuPt_3]^+$ clusters (see Fig. 1). These reactions are very rapid, and the $[MPt_3]^+$ clusters (M = Cu, Ag, Au) are air-stable in the solid state. Their IR spectra display two bands in the ν(CO) region corresponding to the bridging CO's. The $^{31}P\{^1H\}$ NMR spectra show four groups of signals at ca. −70 °C of relative intensities 2/1/1/1 (see Fig. 2). The resonances assigned to P(3), P(1) and P(22) coalesce when the temperature is raised, indicating fluxional behaviour.

The X-ray structural analysis * of the new complex $[CuPt_3(\mu\text{-}CO)_3(PPh_3)_5][BF_4]$ shows that it adopts a tetrahedral structure (see Fig. 1), related to that of the corresponding $AgPt_3$ [11] and $AuPt_3$ [5] clusters. The C(carbonyl) atoms, P(1) and P(3) are almost coplanar with the Pt_3 triangle (max. deviation for C(93): −0.47(2) Å), whereas the PPh_3 ligands at Pt(2) are situated on either side of this plane (P(21): 2.38(1), P(22): −1.06(1) Å). In this 56 valence electron cluster, the mean Cu–Pt distance of 2.650 Å is a little longer than that recently found in the sandwich cluster $[Cu\{Pt_3(\mu\text{-}CO)_3(PPh_3)_3\}_2]PF_6$ [6]. Owing to the greater asymmetry in our cluster, these heterometallic distances span a wider range 2.735(3)–2.577(3) Å than these in the $Cu[Pt_3]_2$ cluster.

Experimental

Methods and instruments were as given in ref. 12.

Preparation of $[AuPt_3(\mu\text{-}CO)_3(PPh_3)_5]PF_6$. To a solution of 748 mg (1 mmol) of $[Pt(PPh_3)_2(C_2H_4)]$ [15] in 25 ml of acetone were added 160 mg (0.5 mmol) of $[AuCl(SC_4H_8)]$ and 170 mg (0.5 mmol) of $TlPF_6$ under CO. The solution immediately turned orange. This mixture was vigorously stirred during 15 min and filtered. Diethyl ether was added to the filtrate to give 700 mg of orange plates. The yield is 90% based on Pt and 60% based on Au.

Anal. Found: C, 47.95; H, 3.21. $C_{93}H_{75}AuF_6O_3P_6Pt_3$ calc: C, 48.09; H, 3.25%. Dec. 184 °C. IR(KBr) ν(CO): 1844vs, 1820vs cm^{-1}. $^{31}P\{^1H\}$ NMR

---

* *Crystal data* for: $C_{93}H_{75}BCuF_4O_3P_5Pt_3$, $M = 2131$. monoclinic, space group $P\ 2_1/n$, a 14.06(2), b 25.17(2), c 24.28(4) Å, β 90.95(6), U 8587 Å^3, $Z = 4$, D_c 1.44 g cm^{-3}, $F(000) = 3784$, μ(Mo-K_α) 6.16 cm^{-1}, λ(Mo-K_α) 0.71069 Å, intensities of 12865 reflections with $1 < \theta < 23°$ were measured on a Enraf–Nonius CAD4 diffractometer, $\omega/2\theta$ scan mode with ω scan width $= 1 + 0.35 \tan \theta$, dimensions of crystal selected 0.36×0.14×0.015 mm. Intensities were corrected for Lorentz and polarisation effects. The metal atoms were found by direct methods [18], and the remaining non-hydrogen atoms from subsequent difference Fourier syntheses. Calculations were performed on a PDPII computer with SPD system [17]. The structure was refined by full matrix-least squares using 6015 data with $I/\sigma(I) \geq 3.0$ to $R = 0.10$ and $R_w = 0.102$ with the error in an observation of unit weight of 1.79. The disordered BF_4^- anion was not refined and anisotropic thermal parameters were assigned to the metals and phosphorus atoms. Scattering factors were from ref. 19. Tables of atomic coordinates, a list of bond lengths and angles, a list of thermal parameters and a list of structure factors have been deposited with the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. They may be obtained on request from the Director by citing the full literature reference for this communication.

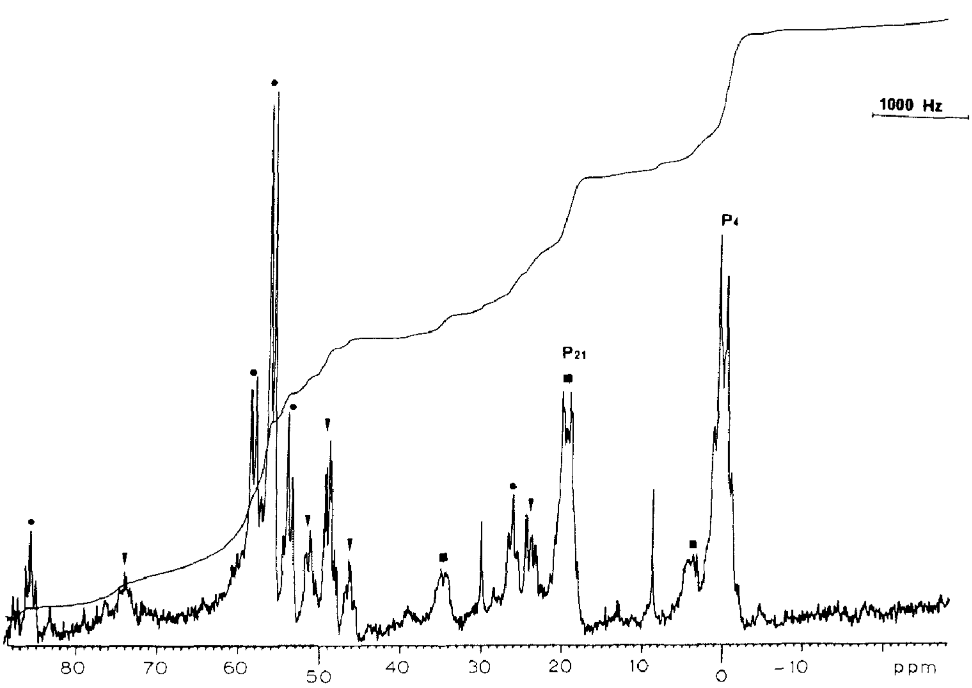

Fig. 2. $^{31}P\{^1H\}$ NMR spectrum (at $-75\,^\circ C$ in CD_2Cl_2) of $[CuPt_3(\mu\text{-}CO)_3(PPh_3)_5]BF_4$. The various signs identify the satellites due to coupling with ^{195}Pt.

(CD_2Cl_2/CH_2Cl_2, ref. H_3PO_4 ext., room temperature): δ 50.6 (s with complex Pt satellites, 3P), 40.8 (m with Pt satellites, 1P), 31.5 (d, Au-P), − 143.6 (septet, PF_6); at − 60 °C: δ 52.8 (m with Pt satellites, 2P), 51.0 (m with Pt satellites, 1P), 40.9 (m with Pt satellites, 1P), 31.5 (m, Au-P), − 143.6 (septet, PF_6).

Preparation of $[AgPt_3(\mu\text{-}CO)_3(PPh_3)_5]NO_3$. The reaction was carried out in a Schlenk flask wrapped with foil to exclude light. To a solution of 748 mg (1 mmol) of $[Pt(PPh_3)_2(C_2H_4)]$ in 25 ml of acetone were added 77 mg (0.5 mmol) of $AgNO_3$ under CO. The solution immediately turned orange. This mixture was stirred vigorously for 15 min then filtered. Diethyl ether was added to the filtrate, to give 570 mg of red plates. The yield is 80% based on Pt and 53% based on Ag.

Anal. Found: C, 51.73; H, 3.50; N, 0.70. $C_{93}H_{75}AgNO_6P_5Pt_3$ calc: C, 51.94; H, 3.51; N, 0.65%. Dec. 148 °C. IR(KBr) $\nu(CO)$: 1837vs, 1803vs cm^{-1}, $\nu(NO_3^-)$: 1381 cm^{-1}. $^{31}P\{^1H\}$ NMR (CD_2Cl_2/CH_2Cl_2, room temperature): δ 53.5 (s with complex Pt satellites, 3P), 26.8 (m with Pt satellites, 1P), 9.8 (d, Ag-P); at − 75 °C: δ 55.8 (m with Pt satellites, 2P), 49.7 (m with Pt satellites, 1P), 27.2 (m with Pt satellites, 1P), 10.1 (m, Ag-P).

Preparation of $[CuPt_3(\mu\text{-}CO)_3(PPh_3)_5]BF_4$. Contact between the product and metal spatula was avoided in this synthesis. To a solution of 748 mg (1 mmol) of $[Pt(PPh_3)_2(C_2H_4)]$ in 25 ml of acetone were added 157 mg (0.5 mmol) $[Cu(CH_3CN)_4]BF_4$ [16] under CO. This solution was stirred vigorously for 15 min then filtered. Diethyl ether was added to the filtrate to give 600 mg of deep orange plates. Recrystallisation was from THF/hexane. The yield is 85% based on Pt and 57% based on Cu.

Anal. Found: C, 52.48; H, 3.49. $C_{93}H_{75}BCuF_4O_3P_5Pt_3$ calc: C, 52.40; H, 3.55%. Dec. 169 °C. IR(KBr) $\nu(CO)$: 1832vs, 1813vs cm^{-1}, $\nu(BF_4)$: 1044 cm^{-1}. $^{31}P\{^1H\}$

NMR: (CD_2Cl_2/CH_2Cl_2, room temperature): δ 52.6 (s with complex Pt satellites, 3P), 20.6 (m with Pt satellites, 1P), 1.8 (m, Cu-P); at − 75 °C: 55.9 (d with Pt satellites, 2P), 48.8 (m with Pt satellites, 1P), 18.6 (m with Pt satellites, 1P), − 1.4 (m, Cu-P) (see Fig. 2).

Acknowledgement. We are grateful to the CNRS and Atochem for financial support, and to the Johnson Matthey Technology Center for a generous loan of $PtCl_2$.

References

1 P. Braunstein, H. Lehner, D. Matt, A. Tiripicchio, and M. Tiripicchio Camellini, Angew. Chem. Int. Ed. Engl., 23 (1984) 304.
2 C.E. Briant, R.W.M. Wardle, and D.M.P. Mingos, J. Organomet. Chem., 267 (1984) C49.
3 C.E. Briant, D.I. Gilmour, and D.M.P. Mingos, J. Organomet. Chem., 267 (1984) C52; J. Chem. Soc., Dalton Trans., (1986) 835; D.M.P. Mingos, and R.W.M. Wardle, J. Chem. Soc., Dalton Trans., (1986) 73; D.M.P. Mingos, P. Oster, and D.J. Sherman, J. Organomet. Chem., 320 (1987) 257.
4 G.J. Arsenault, L. Manojlović-Muir, K.W. Muir, R.J. Puddephatt, and I. Treurnicht, Angew. Chem. Int. Ed. Engl., 26 (1987) 86; L. Manojlović-Muir, K.W. Muir, I. Treurnicht, and R.J. Puddephatt, Inorg. Chem., 26 (1987) 2418.
5 J.J. Bour, R.P.F. Kanters, P.P.J. Schlebos, W. Bos, W.P. Bosman, H. Behm, P.T. Beurskens, and J.J. Steggerda, J. Organomet. Chem., 329 (1987) 405.
6 M.F. Hallam, D.M.P. Mingos, T. Adatia, and M. McPartlin, J. Chem. Soc., Dalton Trans., (1988) 335.
7 T. Blum, P. Braunstein, A. Tiripicchio, and M. Tiripicchio Camellini, in P. Braunstein (Guest Ed.), 'Recent Advances in Di- and Polynuclear Chemistry', New J. Chem., 12 (1988) in press; and ref. cited therein.
8 R. Usón, J. Forniés, B. Menjon, F.A. Cotton, L.R. Falvello, and M. Thomas, Inorg. Chem., 24 (1985) 4651.
9 A. Albinati, K.-H. Dahmen, A. Togni, and L.M. Venanzi, Angew. Chem. Int. Ed. Engl., 24 (1985) 766; L.M. Venanzi, M.K. Wolfer, A. Albinati, and F. Demartin, ibid., 27 (1988) 563.
10 R. Uson, J. Forniés, M. Thomas, J.M. Casas, F.A. Cotton, and L.R. Falvello, Inorg. Chem., 26 (1987) 3482.
11 S. Bhaduri, K. Sharma, P.G. Jones, and C. Freire Erdbrügger, J. Organomet. Chem., 326 (1987) C46.
12 For example, P. Braunstein, J. Rosé, A. Dedieu, Y. Dusausoy, J.-P. Mangeot, A. Tiripicchio, and M. Tiripicchio-Camellini, J. Chem. Soc., Dalton Trans., (1985) 225; and ref. cited therein.
13 P. Braunstein, and J. Rosé, in I. Bernal (Ed.), 'Stereochemistry of Organometallic and Inorganic Compounds', Elsevier: Amsterdam, 1988, Vol. III; and ref. cited therein.
14 A. Moor, P.S. Pregosin, and L.M. Venanzi, Inorg. Chim. Acta, 48 (1981) 153.
15 N. Nagel, Chem. Ber., 115 (1982) 1998.
16 G.J. Kubas, Inorg. Synth., (1979) 90.
17 B.A. Frenz, in H. Schenk, R. Olthof-Hazekamp, H. van Koningsveld, and G.C. Bassi, (Eds.), "Computing in Crystallography"; University Press: Delft, The Netherlands, 1978, p. 64–71.
18 G. Germain, P. Main, M.M. Woolfson, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., A27 (1971) 368.
19 International Tables for X-ray Crystallography, Kynoch Press, Birmingham, 1974, Vol. 4, p. 99.