Journal of Organometallic Chemistry, 253 (1983) C64—C66
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

Preliminary communication

GOLD CLUSTERS. REACTIVITY OF $[Au_9(PPh_3)_8]^{3+}$ AND $[Au_8(PPh_3)_7]^{2+}$ TOWARDS ISOPROPYL ISOCYANIDE

W. BOS*, J.J. BOUR, J.W.A. VAN DER VELDEN, J.J. STEGGERDA,
Inorganic Chemistry, Faculty of Science, Toernooiveld, 6525 ED Nijmegen
(The Netherlands)
A.L. CASALNUOVO and L.H. PIGNOLET
Department of Chemistry, University of Minnesota, Minneapolis, MN 55455 (U.S.A.)

(Received May 24th, 1983)

Summary

Isopropyl isocyanide reacts with $[Au_9(PPh_3)_8]^{3+}$ or $[Au_8(PPh_3)_7]^{2+}$ in CH_2Cl_2 to give the cluster complex $[Au_9(PPh_3)_6(i\text{-}PrNC)_2]X_3$ ($X = NO_3$ or PF_6), in which the peripheral Au atoms are bonded to PPh_3 or i-PrNC. The complex has been characterized by elemental analysis, molecular weight, NMR, IR and Mössbauer spectroscopy.

Reactions with isocyanides are well-known in gold chemistry and a great number of gold(I)- and gold(III)-isocyanide complexes have been synthesized [6—9]. Since isocyanide complexes can undergo reactions with nucleophiles such as amines and alcohols, it seemed of interest to synthesize gold cluster compounds with isocyanide ligands. In the reactions with isocyanides, $[Au_9(PPh_3)_8]^{3+}$ and $[Au_8(PPh_3)_7]^{2+}$ were used, since these gold clusters have proved to be convenient starting materials for the synthesis of various new gold clusters [1].

An excess of 0.5 ml (5.5 mmol) isopropyl isocyanide was added with stirring to 500 mg (0.12 mmol) $[Au_9(PPh_3)_8](NO_3)_3$ [4] dissolved in 10 ml of CH_2Cl_2. A gold mirror formed on the reaction vessel wall upon standing for 1.5 h at room temperature. After 6 h the mixture was added to 100 ml of diethyl ether. The orange precipitate was filtered off and redissolved in 15 ml of acetone. The acetone solution was filtered through Celite 505 to remove metallic gold and added to 100 ml hexane. The orange-red product was filtered off and washed with a little diethyl ether. Yield 58%. (256 mg). The same procedure but starting from $[Au_8(PPh_3)_7]^{2+}$ gave the identical product (^{31}P NMR and IR) after a reaction time of 18 h.

0022-328X/83/$03.00

Beautiful square pyramidal orange-red crystals were obtained by the diffusion of diethyl ether into a dichloromethane solution. Anal. Found: C, 36.81; H, 3.03; Au, 48.70; N, 1.73; P, 4.03. $C_{116}H_{104}Au_9N_5O_9P_6$, M = 3670.72. calcd.: C, 37.96; H, 2.86; Au, 48.29; N, 1.91; O, 3.92; P, 5.06%.

$[Au_9(PPh_3)_6(i\text{-}PrNC)_2](PF_6)_3$. 200 mg (0.055 mmol) $[Au_9(PPh_3)_6(i\text{-}PrNC)_2](NO_3)_3$ was dissolved in 5 ml of CH_2Cl_2 and added dropwise to 50 ml of ethanol saturated with NH_4PF_6. The orange-brown precipitate was filtered off, washed with ethanol and redissolved in 5 ml CH_2Cl_2. After filtration over Celite 505 the orange product was precipitated by adding 50 ml of hexane, filtered off, and washed with a little hexane. Orange-red square pyramidal crystals were obtained in the way described for $[Au_9(PPh_3)_6(i\text{-}PrNC)_2](NO_3)_3$. Elemental analysis: Found: C, 35.35; H, 2.76; Au, 45.20; F, 8.55; N, 0.72; P, 7.27. $C_{116}H_{104}Au_9F_{18}N_2P_9$, M = 3919.62, calcd.: C, 35.55; H, 2.67; Au, 45.23; F, 8.73; N, 0.71; P, 7.11%.

The new cluster $[Au_9(PPh_3)_6(i\text{-}PrNC)_2]^{3+}$ is the first example of a gold cluster containing isocyanide. The composition was confirmed by elemental analysis, osmometric molecular weight measurements and electric conductivity, Mössbauer, and NMR data. The molecular weight of the nitrate as determined in $CHCl_3$, assuming the complex to be a 1/3 electrolyte is 3500, (theoretical, 3671). Extrapolation of the conductivity Λ to infinite dilution yields Λ_0 in methanol of 270 Ω^{-1} cm^2 mol^{-1}, which is in the range found for 1/3 electrolytes. The $^{31}P\{^1H\}$ NMR spectrum of a CH_2Cl_2 solution shows a single sharp line at +53.95 ppm downfield relative to TMP, which is in the range normally found for gold-phosphine cluster compounds [5]. ^1H NMR (CD_2Cl_2. δ (ppm)): 0.95 doublet ($CH{-}(CH_3)_2$, J 6.6 Hz); 3.6 heptet ($CH{-}(CH_3)_2$, J 6.6 Hz); 6.7—7.4 multi (phenyl protons). The integrated proton NMR intensities are in good agreement with a ligand ratio of 6 PPh_3 to 2 i-PrNC. The infrared spectra show, along with the vibrations of triphenylphosphine and the uncoordinated anions NO_3^- (1360 cm^{-1}) or PF_6^- (840 cm^{-1}), a ν(CN) stretch vibration at 2200 cm^{-1} (representing a shift of 60 cm^{-1} to higher frequencies compared to the free isopropyl isocyanide). The Mössbauer data can be assigned by assuming three different gold sites, which results in one singlet and two quadrupole pairs with parameters as listed in Table 1. The singlet is attributed to a central Au atom, in accordance with data for $[Au_9(PPh_3)_8]^+$, $Au_{11}(PPh_3)_7(SCN)_3$ and $[Au_8(PPh_3)_7]^{2+}$. The doublet with the isomer shift of 1.81 mm/sec is assigned to peripheral

TABLE 1

^{197}Au MÖSSBAUER PARAMETERS [a]

Compound	Au-site	Q.S.	I.S.	Line-width	Intensity
t-BuNC AuCl	—	7.97	2.24	1.95	—
LAuCl	—	7.50	2.93	2.1	—
$[Au_9L_6(i\text{-}PrNC)_2]^{3+}$	central	0.0	2.93	2.02	0.8
$[Au_9L_6(i\text{-}PrNC)_2]^{3+}$	Au—P	6.78	1.81	2.02	2.2
$[Au_9L_6(i\text{-}PrNC)_2]^{3+}$	Au—CN	6.79	0.91	2.02	1

[a] L = PPh_3, Q.S., I.S. and linewidth in mm/sec. I.S. relative to ^{197}Pt-source. The Mössbauer spectra were recorded at 4.2 K with the apparatus described earlier [2,3].

gold atoms bonded to PPh_3 [10], the quadrupole pair at 0.91 mm/sec is assigned to peripheral gold coordinated to i-PrNC (see Table 1). The new cluster is clearly closely related to $[Au_9(PPh_3)_8]^{3+}$ with two PPh_3 ligands replaced by 2 i-PrNC. The formation of $[Au_9(PPh_3)_6\ (\text{i-PrNC})_2]^{3+}$ from $[Au_8(PPh_3)_7]^{2+}$ and i-PrNC looks somewhat puzzling, but the interconversion of Au_9 and Au_8 clusters is well known in other reactions [1].

The addition of primary amines to gold(I) isocyanide complexes leads to the formation of formamidine complexes [6—9]. The magnitude of the ν(CN) shift is significant for the reactivity of the isocyanide ligand; although the shift of 60 cm^{-1} for the $[Au_9(PPh_3)_6\ (\text{i-PrNC})_2]^{3+}$ seems low, the compound reacts with primary amines to carbene cluster compounds. Further details of this reaction will be reported later.

Acknowledgment

Acknowledgment is made to the Netherlands Foundation for Chemical Research (S.O.N.) and to N.A.T.O. for an exchange grant to Prof. L.H. Pignolet and Prof. J.J. Steggerda.

References

1 J.J. Steggerda, J.J. Bour and J.W.A. van der Velden, Recl. Trav. Chim. Pays-Bas, 101 (1982) 164 and ref. therein.

2 M.P.A. Viegers and J.M. Trooster, Phys. Rev. B, 15 (1977) 72.

3 M.P.A. Viegers, Ph.D. Thesis, University of Nijmegen, Nijmegen, The Netherlands, 1976.

4 F. Coriati and L. Naldini, J. Chem. Soc. Dalton Trans., (1972) 2286; J.W.A. van der Velden, J.J. Bour, J.H. Noordik and W.P. Bosman, Inorg. Chem., to be published.

5 J.W.A. van der Velden, Ph.D. Thesis, University of Nijmegen, Nijmegen, The Netherlands, 1983.

6 J.E. Parks and A.L. Balch, J. Organomet. Chem., 71 (1974) 453.

7 G. Minghetti, F. Bonati and G. Banditelli, Inorg. Chem., 15 (1976) 1718.

8 J.A. Mc. Cleverty and M.M.M. da Motta, J. Chem. Soc. Dalton Trans., (1973) 2571.

9 R. Uson, A. Laguna, P. Brun, M. Laguna, and M. Abad, J. Organomet. Chem., 218 (1981) 265.

10 F.A. Vollenbroek, J.W.A. van der Velden, J.J. Bour and J.M. Trooster, Recl. Trav. Chim. Pays-Bas, 100 (1981) 375.

JOURNAL OF ORGANOMETALLIC CHEMISTRY, VOL. 253 (1983)

AUTHOR INDEX

Alberti, A., 291
Angerer, W., C36
Asfandiarov, N.L., 301
Avilès, T., 39

Bakos, J., 249
Barr, N., 391
Bartocci, C., 253
Behrens, H., 217
Benn, R., 93
Biran, C., C13
Bloodworth, A.J., 1
Bos, W., C64
Bougeard, P., 117
Bour, J.J., C64
Breunig, H.J., C21
Brodie, A.M., C1
Brunner, H., 93
Bunton, C.A., C33

Casalnuovo, A.L., C64
Casellato, U., 317
Chen, J., 231
Clark, P.W., 399
Cocolios, P., 65
Comasseto, J.V., 131
Coutsolelos, A., 273
Cowan, D.O., C43
Czisch, P., C9

Dagnac, P., 123
Davies, A.G., 1
De C.T. Carrondo, M.A.A.F., 53
Degl'innocenti, A., 291
Delgado-Peña, F., C43
Dobson, C.B., C27
Dobson, G.R., C27
Doherty, J., 81
Domingos, A.M.T.S., 53
Dunoguès, J., C13
Dyke, H.J., 399
Dyke, S.F., 391, 399

Efendene, B., C13