Journal of Organometallic Chemistry, 301 (1986) C5—C8
Elsevier Sequoia S.A., Lausanne — Primted in The Netherlands

Preliminary communication

SYNTHESIS, NMR, AND STRUCTURAL CHARACTERIZATION OF THE $[Ni_9Pt_3(CO)_{21}H_{4-n}]^{n-}$ (n = 4, 3, 2) ANIONIC CLUSTERS

ALESSANDRO CERIOTTI, FRANCESCO DEMARTIN, GIULIANO LONGONI*, MARIO MANASSERO*, GIANLUIGI PIVA, GIAMPIETRO PIRO and MIRELLA SANSONI,

Dipartimento di Chimica Inorganica e Metallorganica, Centro del CNR ed Istituto di Chimica Strutturistica Inorganica, Via G. Venezian 21, 20133 Milano (Italy)

and BRIAN T. HEATON*

Chemical Laboratory, The University of Kent, Canterbury CT2 7NH, (Great Britain)

(Received October 21st, 1985)

Summary

The preparations of bimetallic carbonyl clusters having the general formula $[Ni_9Pt_3(CO)_{21}H_{4-n}]^{n-}$ (n = 4, 3, 2) are described. X-ray studies on $[NEt_4]_3[Ni_9Pt_3(CO)_{21}H]$ show that it is isostructural with $[Ni_{12}(CO)_{21}H]^{3-}$, with the platinum atoms occupying the inner triangle of the central Ni_3Pt_3 planar triangulated array. The interstitial coordination of the hydride atoms in these compounds is inferred from ^1H and ^{195}Pt NMR and X-ray data.

During the synthesis of the clusters $[Ni_{38}Pt_6(CO)_{48}H_{6-n}]^{n-}$ (n = 6, 5, 4, 3), by reaction of $[Ni_6(CO)_{12}]^{2-}$ with K_2PtCl_4 in a ca. 1/1 molar ratio, we also obtained analytical and spectroscopic evidence for formation of a series of bimetallic Ni—Pt clusters of the general formula $[Ni_{12-x}Pt_x(CO)_{21}H_{4-n}]^{n-}$ (x = 2, 3, 6; n = 4, 3, 2) as side products [1,2]. We now report the synthesis and ^1H and ^{195}Pt NMR studies of the $[Ni_9Pt_3(CO)_{21}H_{4-n}]^{n-}$ (n = 4, 3, 2) clusters and the crystal structure of the trianion. These derivatives were selectively synthesized through the route shown in Scheme 1 and equation 1. As shown in Scheme 1 the reaction of $[Ni_6(CO)_{12}]^{2-}$ with K_2PtCl_4 in ca. 2/1 molar ratio gives uncharacterized brown anion(s) and small amounts of $[Ni_9Pt_3(CO)_{21}H]^{3-}$; subsequent controlled degradation of the former with carbon monoxide (25°C, 1 atm) selectively affords $[Ni_9Pt_3(CO)_{21}]^{4-}$ in 60—70% yield (based on platinum).

0022-328X/86/$03.50

SCHEME 1

$$\begin{array}{l} \qquad 2\,[\mathrm{Ni_6(CO)_{12}}]^{2-} + \mathrm{K_2PtCl_4} \\ \qquad\qquad\qquad \downarrow \\ \text{Brown anion(s)} + [\mathrm{Ni_9Pt_3(CO)_{21}H}]^{3-} \\ \qquad\qquad \searrow^{\mathrm{CO}} \\ \qquad [\mathrm{Ni_9Pt_3(CO)_{21}}]^{4-} + \mathrm{Ni(CO)_4} \end{array}$$

The $[Ni_9Pt_3(CO)_{21}]^{4-}$ tetra-anion is readily and reversibly protonated by acids to the corresponding mono- and di-hydride (eq. 1).

$$[\mathrm{Ni_9Pt_3(CO)_{21}}]^{4-} \xrightleftharpoons[\mathrm{OH^-,\ DMSO}]{\mathrm{H^+,\ CH_3CN}} [\mathrm{Ni_9Pt_3(CO)_{21}H}]^{3-} \xrightleftharpoons[\mathrm{OH^-,\ acetone}]{\mathrm{H^+,\ acetone}} [\mathrm{Ni_9Pt_3(CO)_{21}H_2}]^{2-} \qquad (1)$$

A comparison of the chemical behavior of these clusters with that of the corresponding homometallic $[Ni_{12}(CO)_{21}H_{4-n}]^{n-}$ (n = 4, 3, 2) derivatives [3] reveals a few significant differences. Thus, while $[Ni_9Pt_3(CO)_{21}H]^{3-}$ is readily deprotonated to $[Ni_9Pt_3(CO)_{21}]^{4-}$ by several alkaline reagents, such as alkali hydroxides and t-butylates, a correspondingly clean and ready deprotonation of $[Ni_{12}(CO)_{21}H]^{3-}$ was not observed [3]. Furthermore, $[Ni_9Pt_3(CO)_{21}H_2]^{2-}$ slowly decomposes in solution at room temperature, whereas $[Ni_{12}(CO)_{21}H_2]^{2-}$ is reported to decompose only above 60°C [3,4]. The tetrasubstituted ammonium salts of the tetra-anion are soluble in acetonitrile, sparingly soluble in acetone, and insoluble in tetrahydrofuran (THF). The corresponding salts of the di- and tri-anion are more soluble in acetone and THF. Crystals of $[NEt_4]_3[Ni_9Pt_3(CO)_{21}H]$ were grown from acetone by precipitation with isopropyl alcohol.

Crystal data for $[NEt_4]_3[Ni_9Pt_3(CO)_{21}H]$: $C_{45}H_{61}N_3Ni_9O_{21}Pt_3$, M = 2093.7, monoclinic, Space group $P2_1/c$ (No. 14), a 13.620(5), b 17.503(6), c 25.780(9) Å; β 93.49(3)°, V 6134(7) Å^3, D_c 2.267 g cm^{-3} for Z = 4, μ(Mo-K_α) 96.63 cm^{-1}, $F(000)$ = 4024. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares on the basis of 3121 independent absorption-corrected reflections having $I \geqslant 3\sigma(I)$. Current R and R_W are 0.050 and 0.058, respectively*.

An ORTEP drawing of the $[Ni_9Pt_3(CO)_{21}H]^{3-}$ is shown in Fig. 1. The overall stereochemistry is related to that of $[Ni_{12}(CO)_{21}H]^{3-}$ [5], with the three platinum atoms occupying the inner triangle of the central hexametallic layer. The preference of platinum for the highest metal-connected sites has been previously observed in bimetallic (Fe—Pt and Rh—Pt) carbonyl clusters [6,7]. The most significant interatomic separations are listed in the legend to

---

*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 (Great Britain). Any request should be accompanied by a full literature citation for this communication.

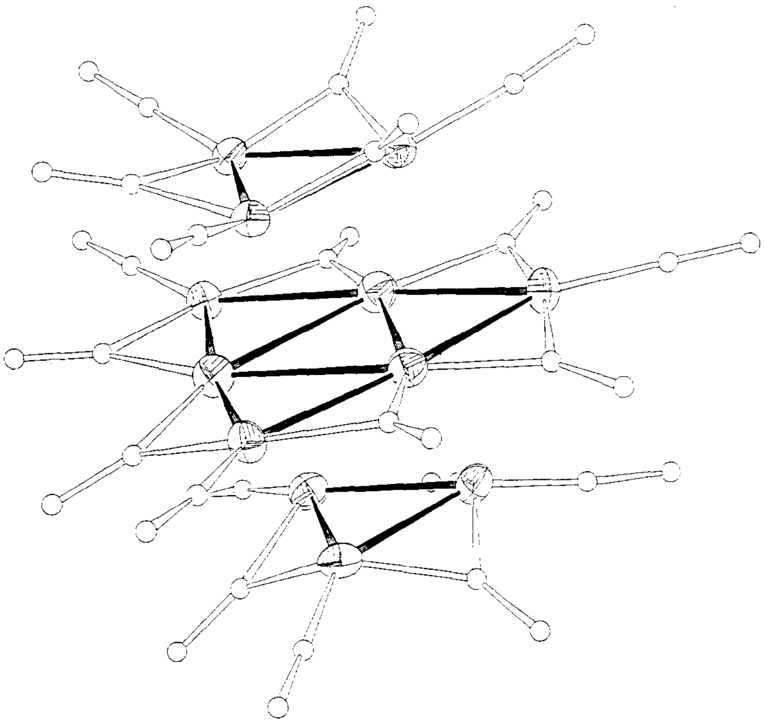

Fig. 1. ORTEP drawing of the $[Ni_9Pt_3(CO)_{21}H]^{3-}$ trianion (interlayer bonds are omitted for clarity). Average bonding distances (Å): Ni—$Ni_{in\text{-}layer}$ 2.451; Ni—$Ni_{inter\text{-}layer}$ 2.886 (lower half), 2.950 (upper half); Ni—$Pt_{in\text{-}layer}$ 2.541; Ni—$Pt_{inter\text{-}layer}$ 2.922 (lower half), 2.944 (upper half); Pt—Pt 2.845; Ni—$C_{terminal}$ 1.684; Ni—$C_{bridging}$ 1.896; Pt—$C_{bridging}$ 1.922; C—$O_{terminal}$ 1.168; C—$O_{bridging}$ 1.194. Typical esd's on single distances are Pt—Pt 0.003, Pt—Ni 0.004, Ni—Ni 0.004, Pt—C and Ni—C 0.03.

Fig. 1. The unique hydride atom could not be directly located; but comparison of the interlayer bond distances in the two halves of $[Ni_9Pt_3(CO)_{21}H]^{3-}$ reveals that the average Ni—Pt and Ni—Ni contacts are longer (by 0.022 and 0.064 Å, respectively) in the upper half of the metallic skeleton. A similar lengthening was found in $[Ni_{12}(CO)_{21}H]^{3-}$, but was absent in $[Ni_{12}(CO)_{21}]^{4-}$ and $[Ni_{12}(CO)_{21}H_2]^{2-}$ [5,8]; a subsequent neutron diffraction study showed the hydride to occupy the expanded trigonal-antiprismatic cavity of this hexagonal closed packed fragment [5]. A similar stereochemistry of the hydride is suggested by analogy for $[Ni_9Pt_3(CO)_{21}H]^{3-}$.

The interstitial location of the hydride atoms in these hydride clusters is confirmed by the ^{1}H and ^{195}Pt NMR spectra (see Table 1). Thus, the ^{195}Pt spectrum of $[Ni_9Pt_3(CO)_{21}H_{4-n}]^{n-}$ consists of a singlet ($n = 4$), a doublet ($n = 3$), and a triplet ($n = 2$), and the latter two resonances become singlets on broad-band proton-decoupling. The ^{1}H NMR spectra of $[Ni_9Pt_3(CO)_{21}H_{4-n}]^{n-}$ ($n = 3, 2$), at room and low temperature (—90°C), consist of five lines arising from ^{1}H—^{195}Pt coupling from the different isotopomers within the inner Pt_3 triangle; seven lines with relative intensities of 0.08/1/4.3/7.3/4.3/1/0.08 would be expected but the two outer lines are probably to weak to be observed. Of particular significance is the very small

TABLE 1

INFRARED AND NMR SPECTRA (25°C) OF $[Ni_9Pt_3(CO)_{21}H_{4-n}]^{n-}$ (n = 4, 3, 2)

Compound	ν(CO) (cm^{-1})	$\delta(^1H)$ (ppm)	$\delta(^{195}Pt)$[c] (ppm)	J(Pt—H) (Hz)
$[Ni_9Pt_3(CO)_{21}]^{4-}$ [a]	1970, 1790	—	+185(s)	—
$[Ni_9Pt_3(CO)_{21}H]^{3-}$ [b]	1997, 1828	−20.0 [d]	−222(d)	260.4
$[Ni_9Pt_3(CO)_{21}H_2]^{2-}$ [b]	2030, 1860	−17.8 [d]	−323(t)	201.1
$[Ni_9Pt_3(CO)_{21}\,{}^1H^2H]^{2-}$ [b]	2030, 1860	—	−325.5	[e]

[a] In acetonitrile. [b] In acetone. [c] 0 ppm = 21.4 MHz at such a magnetic field that the protons in TMS resonance at exactly 100 MHz; high frequency shifts are positive. s, singlet; d, doublet; t, triplet. [d] Non-binomial quintet, with average relative intensities of 1/5.6/7.4/5.8/1.3. [e] $J(^{195}Pt-^2H)$ 27.3 Hz.

value of $J(^1H-^{195}Pt)$. Such a small value is unlikely to be due to a one-bond coupling constant expected for a static structure but could arise from a fast H-migration involving trigonal antiprismatic/tetrahedral hole jumps within the metallic skeleton, similar to that already established for $[Rh_{13}(CO)_{24}H_x]^{(5-x)-}$ (x = 1, 2, 3, 4) [9,10] and $[Rh_{14}(CO)_{25}H]^{3-}$ [11].

It should also be noted that the hydrogen interchange is slow on the NMR time scale, as evidenced by the reaction of $[Ni_9Pt_3(CO)_{21}H]^{3-}$ with $CF_3CO_2{}^2H$ to give $[Ni_9Pt_3(CO)_{21}\,{}^1H^2H]^{2-}$. The ^{195}Pt-{^{1}H} NMR spectrum of the latter consists of 3 equally intense lines due to $J(^{195}Pt-^2H)$ 27.3 Hz: in addition there is a singlet at higher frequency due to a small amount of $[Ni_9Pt_3(CO)_{21}\,{}^1H_2]^{2-}$ (isotope shift 2.5 ppm).

Acknowledgements. We are grateful to the S.E.R.C. for financial support (to B.T.H.), and thank Dr. E. Occhiello for recording the ^{195}Pt NMR spectrum of $[Ni_9Pt_3(CO)_{21}]^{4-}$.

References

1 A. Ceriotti, F. Demartin, G. Longoni, M. Manassero, M. Marchionna, G. Piva and M. Sansoni, Angew. Chem., 97 (1985) 708.
2 A. Ceriotti, F. Demartin, P. Ingallina, G. Longoni, M. Manassero, M. Marchionna and M. Sansoni: unpublished results.
3 A. Ceriotti, P. Chini, R. Della Pergola and G. Longoni, Inorg. Chem., 22 (1983) 1595.
4 G. Longoni, B.T. Heaton and P. Chini, J. Chem. Soc. Dalton Trans., (1980) 1537.
5 W. Broach, L.F. Dahl, G. Longoni, P. Chini, A.J. Schultz and J.M. Williams, Adv. Chem. Ser., 167 (1978) 93.
6 G. Longoni, M. Manassero and M. Sansoni, J. Am. Chem. Soc., 102 (1980) 7973.
7 A. Fumagalli, S. Martinengo and G. Ciani, J. Organomet. Chem., 273 (1984) C46.
8 P. Chini, G. Longoni and S. Martinengo, Chim. Ind., (Milano), 12 (1978) 989.
9 S. Martinengo, B.T. Heaton, R.J. Goodfellow and P. Chini, J. Chem. Soc., Chem. Comm., (1977) 39.
10 B.T. Heaton, Phil. Trans. Royal Soc. (London) A, 308 (1982) 95.
11 B.T. Heaton, C. Brown, D.O. Smith, L. Strona, R.J. Goodfellow, P. Chini and S. Martinengo, J. Am. Chem. Soc., 102 (1980) 6175.