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Preliminary communication

SYNTHESIS AND CRYSTAL STRUCTURE OF $[(Ph_3P)_2N][Ni_2(CO)_6H]$

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Summary

The interstitial dihydride dianion $[Ni_{12}(CO)_{21}H_2]^{2-}$ is readily converted by carbon monoxide (25°C, 1 atm) into a mixture of tetracarbonylnickel and a new colourless hydride carbonyl monoanion, which has been characterized by X-ray diffraction as $[Ni_2(CO)_6H]^-$.

Deep red-violet THF solutions of the recently reported interstitial dihydride $[Ni_{12}(CO)_{21}H_2]^{2-}$ dianion [1] are readily decolourized by carbon monoxide (25°C, 1 atm) owing to the occurrence of reaction (1). This new hydride

$$[Ni_{12}(CO)_{21}H_2]^{2-} + 23\ CO \rightarrow 2\ [Ni_2(CO)_6H]^- + 8\ Ni(CO)_4 \qquad (1)$$

carbonyl monoanion shows IR absorptions in THF at 2005m and 1950s cm^{-1} and a ^1H NMR signal at τ 18.6 ppm. The same compound was previously obtained in solution through reaction 2:

$$[Ni_5(CO)_{12}]^{2-} + H_2O + 6\ CO \xrightarrow{THF} [Ni_2(CO)_6H]^- + 3\ Ni(CO)_4 + OH^- \qquad (2)$$

On the basis of the close similarity of its IR spectrum to that of the $[Ni(CO)_3X]^-$ (X = Cl,Br,I) species [2], it was tentatively formulated as $[Ni(CO)_3H]^-$ [3,4].

Past failures to isolate the $[Ni_2(CO)_6H]^-$ monoanion must be attributed to its lability; initial attempts to isolate the compound resulted either in recondensation to a mixture of $[Ni_5(CO)_{12}]^{2-}$ and $[Ni_6(CO)_{12}]^{2-}$, when tetrasubstituted ammonium cations were used, or in formation of $Ni(CO)_3L$ (L = phosphine or arsine) when tetrasubstituted phosphonium or arsonium cations were used. Moreover, in the presence of excess water and under carbon monoxide atmosphere according to reaction 2 decomposition of $[Ni_2(CO)_6H]^-$ to $Ni(CO)_4$, has often been observed.

Only recently, by using reaction 1, which can be carried out in anhydrous conditions, and by taking advantage of the particular stability of the bis(triphenylphosphine)imminium cation (PPN) [5], we have been able to isolate in the solid state the PPN salt of $[Ni_2(CO)_6H]^-$ by evaporation in vacuum of the solvent. $[PPN][Ni_2(CO)_6H]$ has been successfully crystallized by extraction in toluene and precipitation by slow diffusion of n-heptane.

In order to establish both the stoichiometry and the molecular structure of the compound, a single crystal X-ray diffraction study has been carried out.

Crystal data

$[(Ph_3P)_2N][Ni_2(CO)_6H]$, mol. wt. 824.4, monoclinic, space group $P2_1/c$; a 13.44(1), b 21.09(1), c 14.46(1) Å; β 90.45(5)°; V 4098 Å^3, $Z = 4$, D_m 1.34(2), D_c 1.34 g cm^{-3}. Intensities up to 2θ 50° were collected on a Basic diffractometer [6] using graphite monochromatized Mo-K_α radiation. The structure was solved by Patterson and Fourier methods and refined by block matrix least squares to the current R of 0.054 by using 2094 independent intensities having $\sigma(I)/I \leqslant 0.25$.

As shown in Fig. 1 the structure of the $[Ni_2(CO)_6H]^-$ monoanion consists of two tetrahedral $Ni(CO)_3$ moieties joined by a Ni—Ni bond of 2.864(3) Å, and with the carbonyls in an eclipsed conformation (Ni—C$_{(av)}$ 1.734 Å; C—O$_{(av)}$ 1.175 Å). Within each $Ni(CO)_3$ moiety the C—Ni—C angles are nearly as expected for a tetrahedral arrangement, and range from 112.8(6) to 115.2(7)° (114.0° on the average). The idealized symmetry of the anion is only C_{2v} owing to a significant bending of the two $Ni(CO)_3$ units with respect to the Ni—Ni axis. Thus, with reference to the symmetry plane containing C(1), Ni(1), Ni(2) and C(4), the two in-plane C—Ni—Ni angles are 116.8° (av), while the remaining four out-of-plane C—Ni—Ni angles decrease to an average of 96.0°. This bending is clearly

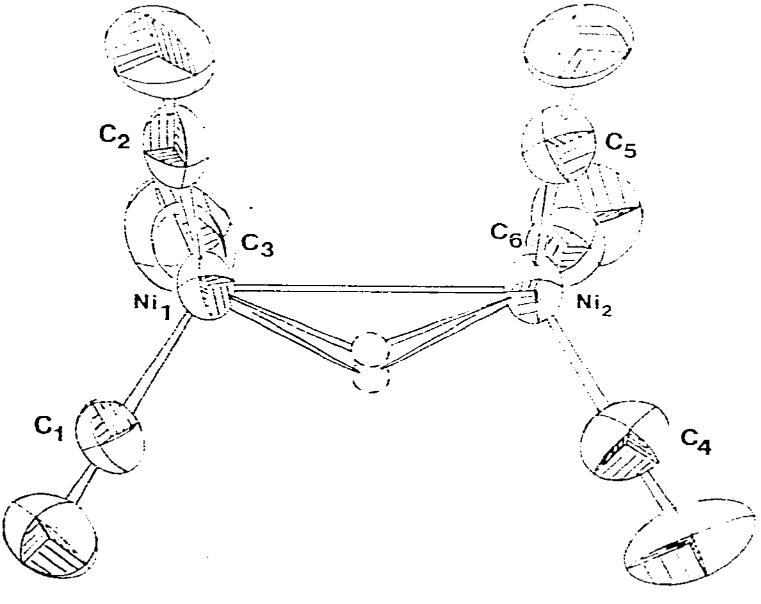

Fig. 1. ORTEP view of $[Ni_2(CO)_6H]^-$ showing the unique hydrogen atom in the two available symmetry-related bridging sites described in the text.

reflected by the C···C non bonding contacts (C(1)···C(4) 4.39(2); C(2)···C(5) 3.27(3): C(3)···C(6) 3.38(2) Å) and suggested the possibility that the hydrogen atom bridges the two nickel atoms close to the cited mirror plane.

Potential energy maps calculations [7] confirmed this view by excluding the presence of a terminally bonded hydrogen atom on the ground of non bonding contacts, and revealed two possible symmetry-related bridging sites on the mirror plane bisecting the Ni—Ni bond and 0.5 Å respectively above and below the C(1), Ni(1), Ni(2), C(4) mirror plane, as shown in Fig. 1. The two sites are at ca. 1.70 Å from both the two nickel atoms and as far as ca. 2.40 Å from the nearest carbon atom. Although the two minima are not perfectly equivalent, their values are very close and suggest the possibility that the hydrogen atom is randomly distributed between the two bridging sites. This would also explain the higher thermal parameters of some atoms of the $Ni_2(CO)_6$ group.

A further feature of the crystal structure of $[PPN][Ni_2(CO)_6H]$ is that the PPN cation has the unusual linear form, as in the recently described $[PPN][V(CO)_6]$ [8]. The most significant molecular parameters of the PPN cation are: P—N 1.549 Å; P—C 1.792 Å; P—N—P 175.9(8)°; N—P—C 111.2°; C—P—C 107.6°.

In the light of this structure determination, the close similarity between the infrared spectra of $[Ni_2(CO)_6H]^-$ and $[Ni(CO)_3X]^-$ (X = Cl, Br, I) [2] suggested the possibility that the latter should be reformulated as $[Ni_2(CO)_nX]^-$. Preliminary results, however, confirm that the formulation in the literature is correct, since the molecular weight resulting from unit cell and density determination on a pale yellow crystal of $[PPN][Ni(CO)_3I]$ (812) is in close agreement with the calculated value (808.23).

The unstable cinnabar-red $Ni_2(CO)_6H_2 \cdot 4NH_3$ (obtained some years ago by reduction of $Ni(CO)_4$ with sodium metal in liquid ammonia, probably being formed by ammonolysis of the initially formed $[Ni_2(CO)_6]^{2-}$ dianion [9,10]) may be related to $[Ni_2(CO)_6H]^-$, and so we reinvestigated this reaction. Owing to solvent absorption we could not directly monitor the reaction by IR. However, after evaporation of the ammonia and extraction of the residue in THF, we obtained a light-coloured solution showing the strongest IR absorption at 1870 cm^{-1}, in agreement with the presence in solution of an anionic species such as, for instance, $[Ni_2(CO)_6]^{2-}$. After standing a few days under nitrogen the solution turned red, and at the same time there was a growth in the IR bands characteristic of the colourless $[Ni_2(CO)_6H]^-$ and of traces of more oxidized nickel carbonyl clusters [3]. The conversion into $[Ni_2(CO)_6H]^-$ was greatly accelerated by addition of trace amounts of water, but we found no evidence for a di-hydride species.

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