*Journal of Organometallic Chemistry*, 233 (1982) C41—C45
Elsevier Sequoia S.A., Lausanne — Printed in The Netherlands

**Preliminary communication**

# THE HEXACARBONYLNIOBATE(–I) ANION

FAUSTO CALDERAZZO*, GUIDO PAMPALONI
*Istituto Chimica Generale, University of Pisa, Via Risorgimento 35, 56100 Pisa (Italy)*
and GIANCARLO PELIZZI
*Istituto Chimica Generale, University of Parma, Via Massimo D'Azeglio 85, 43100 Parma (Italy)*

(Received April 15th, 1982)

## Summary

Some new hexacarbonylniobate(–I) derivatives have been prepared; the bis(triphenylphosphine)iminium derivative, which has been shown by X-ray diffraction methods to be isostructural with the corresponding hexacarbonylvanadate(–I) compound, contains essentially linear and octahedral $[(PPh_3)_2N]^+$ and $[Nb(CO)_6]^-$ ions, respectively.

The hexacarbonylmetalates of niobium(–I) and tantalum(–I) were reported some years ago [1] and their syntheses have recently been improved [2,3]. However, "the chemistry of these anions is still largely unexplored" [3].

We now report some new hexacarbonylniobate derivatives and the crystal and molecular structure of one of them. When possible, comparison is made with the corresponding compounds of the hexacarbonylvanadate(–I) anion.

The sodium derivative $NaNb(CO)_6$ (I) stabilized by tetrahydrofuran, was isolated as a yellow-orange solid sensitive to air and light. By treatment of I with the appropriate chloride, the following compounds were isolated: the red-brown phenanthrolinenickel, $[Ni(phen)_3][Nb(CO)_6]_2$ (II) and the yellow bis(triphenylphosphine)iminium derivative, [PPN] $[Nb(CO)_6]$ (III). The latter was recrystallized from dichloromethane/diethyl ether to give single crystals for the crystal and molecular structure determination by X-ray diffraction methods. Preliminary crystal examination and subsequent data collection were performed on a computer-controlled Siemens AED diffractometer using Mo-$K_\alpha$ radiation ($\lambda$ 0.71069 Å) at a takeoff angle of 4°. Crystal data: space group $R\bar{3}$ (rhombohedral); $a$ 9.832(4) Å, $\alpha$ 91.98(5)°, $Z = 1$. The positional and thermal (anisotropic for nonhydrogen atoms, isotropic for hydrogen atoms) parameters were refined by a full-matrix least-squares procedure converging to a conven-

0022-328X/82/0000—0000/$02.75 © 1982 Elsevier Sequoia S.A., Lausanne

tional $R$ of 0.0391 for 732 independent reflections ($5.0° < 2\vartheta < 52.0°$) having $I \geqslant 2\sigma(I)$ [4]. The compound is isostructural with the corresponding vanadium derivative [5], although the unit cell parameters are larger because of the longer Nb—C bonds. As there is only one molecule per unit cell, both cation and anion have the crystallographically imposed $\bar{3}$ symmetry, with Nb and N lying on the inversion $\bar{3}$ axis at the special positions $\frac{1}{2}\ \frac{1}{2}\ \frac{1}{2}$ and 0 0 0, respectively, and with the phosphorus atom lying on a threefold axis.

The structure consists of $[Nb(CO)_6]^-$ anions and $[(Ph_3P)_2N]^+$ cations, whose geometries are in Fig. 1 and 2, respectively. In the anion the coordination geometry around the Nb atom is nearly perfectly octahedral (Nb—C, 2.089(5) Å: C—Nb—C, 89.2(3)°, C—0,1.163(7) Å). The Nb—C—O linkage is nearly linear (177.8(4)°). As no $Nb(CO)_6$ systems have been structurally characterized

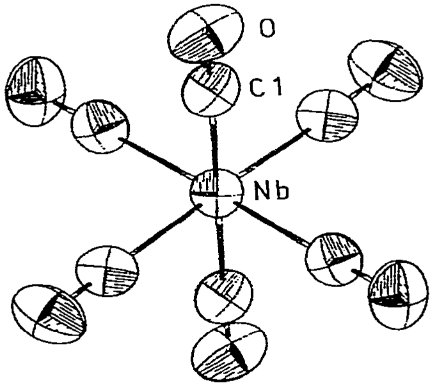

Fig. 1. Structural view of the $[Nb(CO)_6]^-$ anion.

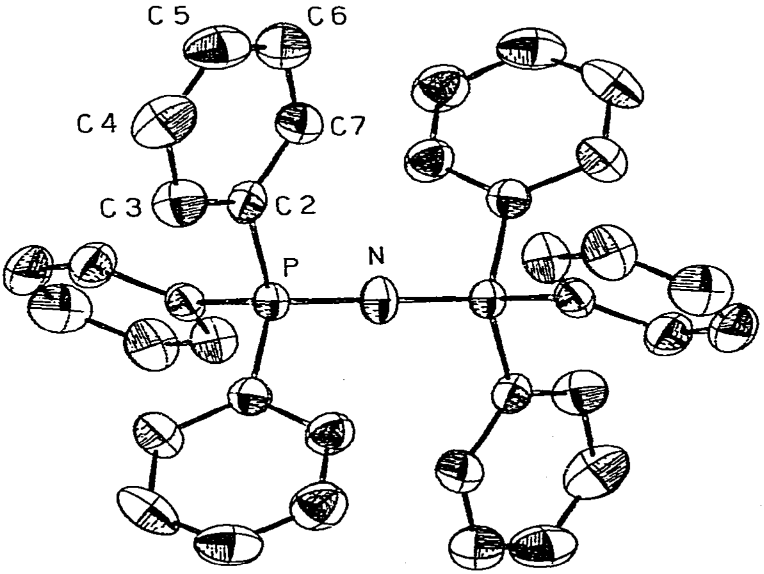

Fig. 2. Structural view of the $[(Ph_3P)_2N]^+$ cation.

previously, a comparison in terms of Nb—C, C—O and Nb—C—O parameters must be made with carbonylniobium complexes containing the cyclopentadienyl ring as ancillary ligand. The values found for our hexacarbonylniobate(−I) anion are in agreement with the literature data [6] for terminally bonded carbonyl groups in Nb complexes in oxidation states I and above.

In the cation, the P—N—P group is explicitly linear for symmetry requirements. Relevant structural parameters are: P—N, 1.547(2); P—C, 1.791(4); C—C(av.), 1.376(7) Å; N—P—C, 110.7(3); C—P—C, 108.2(4); C—C—P, 122.2(5) and 118.7(5); C—C—C(av.), 120.0(9)°. These values are similar to those found for the corresponding vanadium compound [5].

In accord with its nearly perfect octahedral structure, the hexacarbonylniobate(−I) anion has one main carbonyl stretching vibration in aqueous solution, see Table 1. The shift of the unique band for niobium to higher wavenumbers with respect to vanadium is consistent with the generally assumed lower degree of $\pi$-back donation for *4d* transition elements with respect to their *3d* homologues [7]. In agreement with this, hexacarbonylniobate(−I) derivatives show a lower thermal stability than the corresponding vanadium complexes. In solvents of low dielectric constant, such as diethyl ether, more bands were observed due to the deformation by the cation, as noted for other carbonylmetalates [8].

TABLE 1

SPECTROSCOPIC DATA OF HEXACARBONYL DERIVATIVES OF VANADIUM(−I) AND NIOBIUM(−I)

| Compound | $\tilde{\nu}$(CO) (cm$^{-1}$) | | | Medium | Ref. |
|---|---|---|---|---|---|
| NaV(CO)$_6$ | 1923w | 1877s | 1775m | Et$_2$O | 9 |
| | 1880sh | 1851s | | THF | This work |
| | | 1862s | | H$_2$O$^a$ | This work |
| NaNb(CO)$_6$ (I) | 1908w | 1876s | 1778m | Et$_2$O | This work, 10 |
| | 1887sh | 1860s | 1835sh | THF | This work |
| | | 1875s | | H$_2$O$^a$ | This work |
| [Ni(phen)$_3$]<br>[Nb(CO)$_6$]$_2$ (II) | 1916w | 1889s | 1838m | Nujol | This work |
| | | 1860s | | Acetone | This work |
| [(PPh$_3$)$_2$N]<br>[Nb(CO)$_6$] (III) | | 1845s | | Nujol | This work |
| | 1895w | 1869s | | Et$_2$O | This work |
| | 1887sh | 1857s | | THF | This work |
| | | 1864s | | Acetone | This work |

$^a$0.01 mm CaF$_2$ cell.

## *Experimental*

All operations were carried out under prepurified carbon monoxide or argon. The IR spectra were recorded with a Perkin—Elmer model 283 instrument equipped with grating, and each spectrum was calibrated with both CO and water vapour.

*NaNb(CO)$_6$*. The sodium salt, stabilized by tetrahydrofuran, was isolated as a yellow-orange solid sensitive to air and light by aqueous sodium hydroxide treatment of the products resulting from the reductive carbonylation [13] of $NbCl_5$, followed by diethyl ether extraction and recrystallization from tetrahydrofuran. The salt was finally dried in vacuo at room temperature for 3—4 h. Complete decomposition was sometimes noted during attempts to eliminate tetrahydrofuran from the sodium derivative by prolonged treatment in vacuo. Anal. Found: CO, 48.0; Nb, 25.0. $NaNb(CO)_6\cdot$tetrahydrofuran calcd.: $C_{10}H_8NaNbO_7$: CO, 47.2; Nb, 26.1%.

*$[Ni(phen)_3][Nb(CO)_6]_2$*. The sodium salt (0.48 mmol) dissolved in water (20 $cm^3$) was treated with a large excess of an aqueous solution of $[Ni(phen)_3]^{2+}$. The brick-red precipitate obtained was filtered off, washed with water and dried in vacuo (51% yield). Anal. Found: C, 51.3; H, 2.7; N, 7.2. $[Ni(phen)_3][Nb(CO)_6]_2$, $C_{48}H_{24}N_6NbNiO_{12}$ calcd.: C, 51.4; H, 2.2; N, 7.5%.

*$[(PPh_3)_2N][Nb(CO)_6]$*. The sodium derivative (2.2 mmol) was suspended in dichloromethane (18 $cm^3$) and treated with 2.1 mmol of $(PPh_3)_2NCl$. The reaction was over in a few minutes as evidenced by the formation of a yellow-orange solution and precipitation of sodium chloride. After filtration, diethyl ether was added to the filtered solution in order to decrease the solubility of the bis(triphenylphosphine)iminium derivative. After cooling to about −30°C, the yellow crystalline product was collected by filtration and dried in vacuo (30% yield). Anal. Found: C, 62.9; H, 3.7; N, 1.7. $[(PPh_3)_2N][Nb(CO)_6]$, $C_{42}H_{30}NNbO_6P_2$ calcd.: C, 63.1; H, 3.8; N, 1.8%.

The authors thank the National Research Council (C.N.R., Rome), Programma Finalizzato, for financial support, Mr. Ullrich Englert (Studienstiftung des Deutschen Volkes, Universität Tübingen) for technical assistance at the University of Pisa, and the Scuola Normale Superiore of Pisa for the award of a postdoctoral fellowship to G. Pampaloni.

## References

1 R.P.M. Werner and H.E. Podall, Chem. Ind. (London), (1961) 144.
2 R.P.M. Werner, A.H. Filbey and S.A. Manastyrskyi, Inorg. Chem., 2 (1964) 298.
3 J.E. Ellis and A. Davison, Inorg. Syn., 16 (1976) 68.
4 (a) International Tables for X-Ray Crystallography, Vol. 4, Kynoch Press, Birmingham, England, 1974; (b) G.M. Sheldrick, SHELX-76, A Program for Crystal Structure Determination, University of Cambridge, Cambridge, England, 1976.
5 R.D. Wilson and R. Bau, J. Amer. Chem. Soc., 96 (1974) 7601.
6 R.J. Doedens and L.F. Dahl, J. Amer. Chem. Soc., 87 (1965) 2576; A.N. Nesmeyanov, A.I. Gusev, A.A. Pasynskii, K.N. Anisimov, N.E. Kolobova and Yu.T. Struchkov, Chem. Commun., (1968) 1365; A.N. Nesmeyanov, A.I. Gusev, A.A. Pasynskii, K.N. Anisimov, N.E. Kolobova and Yu.T. Struchkov, ibid., (1969) 277; A.N. Nesmeyanov, A.I. Gusev, A.A. Pasynskii, K.N. Anisimov, N.E. Kolobova and Yu.T. Struchkov, ibid., (1969) 739; N.I. Kirillova, A.I. Gusev and Yu.T. Struchkov, Zh. Strukt. Khim., 13 (1972) 473; N.I. Kirillova, A.I. Gusev, A.A. Pasynskii and Yu.T. Struchkov, ibid., 15 (1974) 288; N.I. Kirillova, N.E. Kolobova, A.I. Gusev, A.B. Antonova, Yu.T. Struchkov, K.N. Anisimov and O.M. Khitrova, ibid., 15 (1974) 651; W.A. Herrmann, H. Biersack, M.L. Ziegler and K. Weidenhammer, Angew. Chem., 91 (1979) 1026; K.S. Wong, W.R. Scheidt and J.A. Labinger, Inorg. Chem., 18 (1979) 136; M.A. Porai-Koshits, A.S. Antsyshkina, A.A. Pasynskii, G.G. Sadikov, Yu.V. Skripkin and V.N. Ostrikova, Inorg. Chim. Acta, 34 (1979) L285; W.A. Herrmann, H. Biersack, M.L. Ziegler and P. Wülknitz, Angew. Chem., Int. Ed. Engl., 20 (1981) 388; W.A. Herrmann, H. Biersack, M.L. Ziegler, K. Weidenhammer, R. Siegel and D. Rehder, J. Amer. Chem. Soc., 103 (1981) 1692.
7 F. Calderazzo, R. Ercoli and G. Natta, Metal Carbonyls: Preparation, Structure and Properties, in, I. Wender and P. Pino (Eds.), Organic Syntheses via Metal Carbonyls, Vol. 1, J. Wiley, New York, 1968.

8 W.F. Edgell, M.T. Yang and N. Koizumi, J. Amer. Chem. Soc., 87 (1965) 2563; W.F. Edgell and J. Lyford, ibid., 93 (1971) 6407; M. Darensbourg and C. Borman, Inorg. Chem., 15 (1976) 3121; M.Y. Darensbourg, D.J. Darensbourg, D. Burns and D.A. Drew, J. Amer. Chem. Soc., 98 (1976) 3127; W.F. Edgell, S. Hedge and A. Barbetta, ibid., 100 (1978) 1406; M.Y. Darensbourg and J.M. Hanckel, J. Organometal. Chem., 217 (1981) C9, and ref. therein.

9 F. Calderazzo, G. Pampaloni and D. Vitali, Gazz. Chim. Ital., 111 (1981) 455.

10 The $[Nb(CO)_6]^-$ anion as the $Et_4N^+$ derivative was reported to have one single carbonyl vibration at 1860 cm$^{-1}$ in tetrahydrofuran [11].

11 D. Rehder, personal communication. We are grateful to Dr. Rehder for sending a copy of the manuscript prior to publication [12].

12 H.C. Bechthold and D. Rehder, J. Organometal. Chem., in press.

13 F. Calderazzo, G. Pampaloni, U. Englert and R. Zamboni, unpublished results.