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Preliminary communication

A NEW METHOD FOR THE PREPARATION OF SOME CARBONYL METALATE ANIONS

FAUSTO CALDERAZZO* and GUIDO PAMPALONI
Istituto Chimica Generale, University of Pisa, Via Risorgimento 35, 56100 Pisa (Italy)
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Summary

Reaction of anhydrous metal halides with sodium metal in the presence of cyclooctatetraene in tetrahydrofuran under carbon monoxide at atmospheric pressure yields the hexacarbonyl metalate anions of vanadium, niobium and tantalum, $[M(CO)_6]^-$. Yields as high as 85% of $[V(CO)_6]^-$ were achieved by this method.

Carbonyl metalate anions, $[M(CO)_n]^-$ are usually prepared by reductive carbonylation of metal salts in anhydrous solvents with CO above atmospheric pressure at elevated temperature in the presence of highly electropositive metals [1]. A few cases are known in which the reductive carbonylation to the carbonyl metalates or to the zerovalent compound can be carried out under mild conditions of temperature and pressure, the examples being essentially limited to Group VIII metals, namely $Co_2(CO)_8$ [2], the tetracarbonyl cobaltate(–I) anion [3], $Ru_3(CO)_{12}$ [4], $Rh_4(CO)_{12}$ [5], $Ir_4(CO)_{12}$ [6], and to the $[M_2(CO)_{10}]^{2-}$ anions of Group VIB metals [7].

In a search for safer and simpler preparative methods for Group V metal carbonyl derivatives, we recently reported [8] a room temperature and atmospheric pressure synthesis of the hexacarbonyl niobate anion, $[Nb(CO)_6]^-$, involving the treatment of the pentachloride of niobium with the reductively carbonylating system Mg-Zn-CO-pyridine. We now report that the reduction of anhydrous VCl_3 with sodium sand in tetrahydrofuran (THF) under carbon monoxide at atmospheric pressure produces the corresponding carbonyl metalate [9] in excellent yields, provided cyclooctatetraene (COT) is used as electron-transfer agent:

$$VCl_3 + 4\,Na + 6\,CO \xrightarrow{COT} Na[V(CO)_6] + 3\,NaCl \qquad (1)$$

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Filtration of the crude reaction mixture [10] followed by washing with additional THF and cooling to dry-ice temperature gives a 85% yield of the hexacarbonyl vanadate. This is the first low pressure and low temperature preparation of $[V(CO)_6]^-$ to be reported. The reaction can be carried out with catalytic amounts of COT, the typical COT/V molar ratio being 0.5. The new reductive carbonylation system was found to work, though less efficiently, with Nb_2Cl_{10} (COT/Nb = 3, 60 h, 40°C, 46% yield) and with Ta_2Cl_{10} (COT/Ta = 1.4, 72 h, 40°C, 12% yield).

In order to throw some light into the mechanism of this reaction, the following facts were established: (a) Na_2COT, as prepared from COT and sodium sand in THF [12] did not react with CO under the same experimental conditions as for reaction (1); (b) the anthracene radical-anion, which is known [13], so be unreactive towards CO, did not induce any appreciable reductive carbonylation of VCl_3; (c) VCl_3 was not carbonylated by using sodium alone as reducing agent under the same conditions.

It is believed that cyclooctatetraene complexes of Group V metals are formed as intermediates in the reaction. In this connection, it is important to note that $[Nb(COT)_3]^-$ was reported [14] to be carbonylated to $[Nb(CO)_6]^-$, but the rather drastic conditions used (50 atm, 100°C) suggest that in our system carbonylation starts at a stage before the formation of binary COT complex [15]. This is substantiated by the observation that only a small yield of $[V(CO)_6]^-$ (about 10% in 48 h) was obtained when $V(COT)_2$ [15a] was treated with CO under the conditions of reaction 1.

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9 In a typical experiment, 5.56 g (35.3 mmol) of anhydrous VCl_3 in THF (300 cm^3) contained in a 2 l flask were cooled to dry-ice temperature and 3.21 g (0.14 mol) of sodium sand were added. To this suspension, COT (2.0 cm^3, 17.7 mmol) in THF (50 cm^3) was added during 30 min under a CO atmosphere. The temperature was then allowed to rise and the mixture was stirred for 72 h at 40°C, while carbon monoxide absorption corresponding to 92% of the expected volume was observed.
10 An alternative procedure to separate the $Na[V(CO)_6]$ involves careful addition of water to the dry reaction mixture after evaporation of the solvent under reduced pressure, followed by diethyl ether extraction and recrystallization from THF [11].
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12 The strongly exothermic reaction to give Na_2COT was carried out under argon at dry-ice temperature by slowly adding (5 h) a THF (50 cm^3) solution of COT (6.5 cm^3, 57.4 mmol) to a suspension of sodium sand (2.73 g, 0.119 mol) in the same solvent (300 cm^3). The suspension was stirred for 2 h at room temperature and then cooled overnight at −30°C. The pale yellow precipitate was filtered off and dried in vacuo (92% yield).
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