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The Synthesis and Characterization of Tri-μ-chlorobis{di(η^5-cyclopentadienyl)tantalum(III, IV)} [$Ta_2(\mu\text{-}Cl)_3Cp_4$] (Cp = cyclopentadienyl)

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The synthetic efforts in Group VB complexes have received little attention [1–5]. We report the synthesis and characterization of the first binuclear chloro-bridged tantalum organometallic complex.

A solution of 2.0 g $LiPPh_2$ in 50 ml of THF and 9.71 g of 18% NaCp in THF was added to a suspension containing 3.55 g $TaCl_5$ in 100 ml THF. The reaction mixture was stirred for 12 hr at 25 °C in an argon atmosphere. The mixture turned dark green after several hours. The reaction product was filtered to remove any insoluble salts, after which the volume of the solution was reduced by rotary evaporation inside the dry box, leaving a green oil. The latter was heated in a sublimator and white solid product, **1**, was collected at 60 °C and 10^{-6} torr and identified as tetraphenylbiphosphine, P_2Ph_4 by elemental analysis, infrared spectrophotometry, mass spectroscopy and by its melting point, 123 °C, (120 °C, lit.). The temperature of the sublimator was raised to 120 °C for several days with constant removal of a crystalline purple solid, **2**. *Anal.* Calcd for $C_{20}H_{20}Cl_3Ta_2$: C, 33.01; H, 2.75; Cl, 14.14; Ta, 49.79. Found: C, 33.36; H, 3.47; Cl, 14.69; Ta, 49.78%. The melting point of **2** was > 370 °C.

The supporting analytical data for tri-μ-chlorobis{di(η^5-cyclopentadienyl)tantalum(III, IV)} consist of X-ray fluorescence, elemental analysis, mass spectral analysis, and its magnetic susceptibility, infrared, and far infrared spectra. The complex is paramagnetic and oxidatively unstable. Although it is considerably decomposed in air over short periods of time, it can be stored in the dry box in an inert atmosphere for months with no apparent decomposition.

The synthesis of $Ta_2(\mu\text{-}Cl)_3Cp_4$ is reproducible although in relatively low yield (< 20%). The difficulties in developing synthetic routes for systems of the type reported herein are numerous [6].

The mass spectral analysis of the purple solid **2** showed no parent ion but had ions, m/e = 316, 318, 320 and m/e = 346, 348, indicative of $TaCl_2(C_5H_5)^+$ and $TaCl(C_5H_5)_2^+$ respectively.

The results of magnetic measurements of $Ta_2(\mu\text{-}Cl)_3Cp_4$ in the temperature range 4.4°–300 °K are consistent with the model of a dimer where there are mixed oxidation states (Ta(III)/Ta(IV)) for the metal. The dimer is paramagnetic with a magnetic moment of 1.32 B.M. (temperature range 4.4–300 °K) with θ = 10° which corresponds to one unpaired electron per unit of $Ta_2(\mu\text{-}Cl)_3Cp_4$.

The Ir spectrum showed ν_{CH}(Cp) at 30 cm^{-1} and ν_{Ta-Cl} (recorded with a Beckman IR 11 spectrophotometer). The vibrational frequencies in the Ta–Cl region (380, 368, 330, 315, 300, 286, 271 cm^{-1}) are consistent with an idealized molecular symmetry of C_{2v} [8].

Further characterization of **2** by vapor pressure osmometry to prove unequivocally the dimeric nature of **2** was impossible because of the low solubility.

The fact that tetraphenylbiphosphine was generated is noteworthy since this elimination most likely occurs thermally through an unstable intermediate. The reaction of $TaCl_5$ with NaCp alone did not generate $Ta_2(\mu\text{-}Cl)_3Cp_4$ nor did the reaction of $TaCl_5$ with $LiPPh_2$ generate P_2Ph_4.

This reaction with tantalum appears to be unique for Group VB since a similar sequence of steps does not produce the niobium analog. The difference between the structure and reactivity of niobium and tantalum complexes has been noted. It has been asserted that the activity of the Nb cyclopentadienyl complexes in hydrogenation reactions is greater than that of the corresponding Ta complexes [6, 7].

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References

1 E. K. Barfield, G. W. Parshall and F. N. Tebbe, *J. Am. Chem. Soc., 92,* 5234 (1970).
2 J. A. Labinger and J. Schwartz, *J. Am. Chem. Soc., 97,* 1596 (1975).
3 D. T. Hawkins, *J. Chem. Soc., 16,* 0000 (1976).
4 A. Van Baalen, C. J. Groenenboom and H. J. De Liefde Meijer, *J. Organometal. Chem., 74,* 245 (1974).
5 J. E. Huheey, "Inorganic Chemistry: Principles of Structure and Reactivity", Harper and Row, New Nork, 1972, pp. 441–442.
6 J. L. Martin and J. Takats, *Inorg. Chem., 14,* 73 (1975).
7 F. N. Tebbe and G. W. Parshall, *J. Am. Chem. Soc., 93,* 3793 (1971).
8 G. L. Carlson, *Spectrochim. Acta, 19,* 1291 (1963).