Journal of Organometallic Chemistry, 424 (1992) 159–161
Elsevier Sequoia S.A., Lausanne
JOM 22285

Synthesis and characterization of the paramagnetic niobium(III) complex $[Nb(\eta\text{-}C_5Me_5)Cl_2(PMe_3)_2]$ and its reaction with carbon monoxide

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(Received August 29, 1991)

Abstract

$[Nb(\eta\text{-}C_5Me_5)Cl_2(PMe_3)_2]$ (**1**) has been prepared by magnesium reduction of $[Nb(\eta\text{-}C_5Me_5)Cl_4]$ in the presence of PMe_3 and reacts with carbon monoxide to give purple $[Nb(\eta\text{-}C_5Me_5)Cl_2(CO)_2(PMe_3)]$ (**2**).

Introduction

The chemistry of niobium complexes containing the pentamethylcyclopentadienyl ligand remains largely unexplored. To date, only the hydrolytic behaviour of $[Nb(\eta\text{-}C_5Me_5)Cl_4]$ [1], its high pressure carbonylation to $[Nb(\eta\text{-}C_5Me_5)(CO)_4]$ [2], fluorination to $[Nb(\eta\text{-}C_5Me_5)F_4]$ [3] and its use as a precursor to butadiene derivatives [4] have been reported. In recent work, we have found that the paramagnetic pentamethylcyclopentadienyl tantalum(III) complex $[Ta(\eta\text{-}C_5Me_5)Cl_2(PMe_3)_2]$ is a versatile precursor to half-sandwich C_5Me_5 tantalum derivatives in a variety of oxidation states [5–7]. Here, we describe the analogous niobium compound and its reaction with carbon monoxide.

Results and Discussion

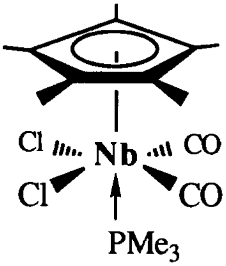
$[Nb(\eta\text{-}C_5Me_5)Cl_2(PMe_3)_2]$ (**1**) is prepared *via* reduction of $[Nb(\eta\text{-}C_5Me_5)Cl_4]$ in tetrahydrofuran (THF) with a slight excess of magnesium in the presence of trimethylphosphine (eq. 1).

$$[Nb(\eta\text{-}C_5Me_5)Cl_4] + Mg \xrightarrow[THF]{2PMe_3} \underset{(\mathbf{1})}{[Nb(\eta\text{-}C_5Me_5)Cl_2(PMe_3)_2]} + MgCl_2 \qquad (1)$$

(**1**) forms dark red crystals which are strongly paramagnetic. Nevertheless, contact-shifted resonances may be observed in the ^1H NMR spectrum at δ 72.6 ($\nu_{1/2}$ 30 Hz) and 14.8 ($\nu_{1/2}$ 60 Hz) integrating for 15 and 18 protons respectively;

these signals are therefore assigned to the methyl hydrogens of the C_5Me_5 ring and PMe_3 ligands. The infrared spectrum also shows the presence of coordinated PMe_3, as a broad absorption at 950 cm^{-1} [ν(P–C)]. Additional bands at 1025 cm^{-1} and in the region 260–380 cm^{-1} are attributable to a C_5Me_5 ring-breathing mode and Nb–Cl stretches respectively.

1 reacts with carbon monoxide (*ca.* 1 atm) in toluene to give [Nb(η-C_5Me_5)$Cl_2(CO)_2(PMe_3)$] (**2**) as a purple microcrystalline solid in 95% yield. Its Nujol mull infrared spectrum reveals bands at 2000, 1920 and 1900 cm^{-1} due to CO stretches; three bands rather than the two anticipated are observed which is similar to the tantalum analogue [7] and may reflect a solid-state splitting of one of the bands. The bands for **2** also occur 12–20 wavenumbers higher than those found for the tantalum compound consistent with reduced π-back donation from the less electropositive centre of **2**. The remaining spectroscopic data are similar in virtually all respects to the tantalum complex and therefore, an analogous structure [7] is postulated with *cis*-chloro and *cis*-carbonyl ligands and with the PMe_3 ligand lying *trans* to the C_5Me_5 ring (see below).



We envisage that **1** will prove to be a useful synthetic precursor to a wide range of pentamethylcyclopentadienyl niobium compounds.

Experimental

All manipulations were carried out under dinitrogen by use of standard Schlenk and cannula techniques or a conventional glovebox. Solvents were distilled from an appropriate drying agent and degassed prior to use. Elemental analyses were performed by the microanalytical services of the Department of Chemistry, Durham University. The following instruments were used: NMR spectra, Varian VXR 400S (399.952 MHz, ^1H; 100.577 MHz, ^{13}C), Bruker AC 250 (250.13 MHz, ^1H; 62.90 MHz, ^{13}C; 101.26 MHz, ^{31}P), chemical shifts are referenced to the residual protio impurities of the deuterated solvent, and, where necessary, assignments of ^{13}C resonances were made using proton coupled or DEPT spectra; IR spectra (Nujol mulls, CsI windows), Perkin–Elmer 577 and 457 grating spectrophotometers. [Nb(η-C_5Me_5)Cl_4] [8] and PMe_3 [9] were prepared by previously published procedures.

Preparations

[Nb(η-C_5Me_5)$Cl_2(PMe_3)_2$] (1). Trimethylphosphine (2.33 g, 30.6 mmol) was condensed onto [Nb(η-C_5Me_5)Cl_4] (1.87 g, 5.1 mmol), magnesium turnings (0.128 g, 5.2 mmol) and THF (20 cm^3) in a large "rotoflo" ampoule cooled to −196°C. Upon warming to room temperature, 1 atm of nitrogen was introduced. The

mixture was stirred at room temperature for 18 h by which time the THF solution was red. Removal of the volatile components under reduced pressure gave a dark red residue which was extracted with n-pentane (40 cm^3). Filtration of the extract, followed by cooling to ca. −50°C afforded dark red crystals which were collected and dried *in vacuo*. Yield, 1.25 g (54%). Anal. Found: C, 43.04; H, 7.63. Calc. for $C_{16}H_{33}Cl_2NbP_2$ (451.20): C, 42.59; H, 7.37. ^1H NMR (400 MHz, [$^2H_6$]-benzene, 296 K): δ 14.77 [s(br) ($\nu_{1/2}$ 60 Hz), 18 H, PMe_3], 72.58 [s(br) ($\nu_{1/2}$ 30 Hz), 15 H, C_5Me_5]. IR (Nujol, CsI, cm^{-1}): 1025w, 950s(br), 720s, 370m, 335w, 320s, 280w, 265w.

[Nb(η-C_5Me_5)$Cl_2$$(CO)_2$($PMe_3$)] (2). A toluene (10 cm^3) solution of [Nb(η-C_5Me_5)$Cl_2$$(PMe_3)_2$] (0.2 g, 0.44 mmol) was degassed in a 400 cm^3 thick-walled "rotoflo" ampoule. The ampoule was then cooled in a CO_2/acetone slush bath and carbon monoxide (1 atm) introduced. After warming to room temperature, the mixture was stirred for 24 h to give a purple solution. The volatile components were removed under reduced pressure to give a purple microcrystalline solid, which was collected, washed with pentane (2 × 5 cm^3) and dried *in vacuo*. Yield 0.18 g (95%). Anal. Found: C, 41.84; H, 5.75. Calc. for $C_{15}H_{24}Cl_2NbO_2P$ (431.14): C, 41.79; H, 5.61. ^1H NMR (400 MHz, [$^2H_6$]-benzene, 296 K): δ 1.24 [d, $^2J(PH) = 9.6$ Hz, 9 H, PMe_3], 1.63 [s, 15 H, C_5Me_5]; $^{13}C\{^1H\}$, δ 11.7 [$C_5\mathit{Me}_5$], 15.5 [d, $^1J(PC) = 25$ Hz, PMe_3], 107.5 [C_5Me_5]; $^{31}P\{^1H\}$, δ −19.8. IR (Nujol, CsI, cm^{-1}): 2000s, 1920s, 1900s, 1020w, 970s, 955s, 735m, 720m, 480w, 450w, 395w, 370w, 280w, 255m.

Acknowledgements

We thank the Research and Initiatives committee of the University of Durham for financial support. U.S. is grateful to the Deutsche Forschungsgemeinschaft for a post-doctoral fellowship.

References

1 J de la Mata, R Fandos, M Gomez, P Gomez-Sal, S Martinez-Carrera and P Royo, Organometallics, 9 (1990) 2846.
2 W.A Herrmann, W Kalcher, H Biersack, I. Bernal and M Creswick, Chem Ber, 114 (1981) 3558
3 H W Roesky, M Sotoodeh, Y M Xu, F. Schrumpf and M Noltemeyer, Z Anorg Allg Chem, 580 (1990) 131
4 T Okamoto, H. Yasuda, A Nakamura, Y Kai, N Kanehisa and N Kasai, J Am Chem Soc 110 (1988) 5008
5 V.C Gibson, T.P. Kee and W. Clegg, J Organomet Chem, 353 (1988) C23
6 V.C Gibson and T.P Kee, J Chem Soc, Chem Commun, (1989) 656
7 V C. Gibson, T P Kee and W Clegg, J Chem Soc, Dalton Trans, (1990) 3199
8 H Yasuda, T Okamoto and A. Nakamura, Organomet Synth, 4 (1988) 20
9 W Wolfsberger and H Schmidbauer, Synth React Inorg Metal.-Org Chem, 4 (1974) 149