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Investigation on Some Bis (cyclopentadienyl) Derivatives of Titanium.

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Bis(cyclopentadienyl)dicarbonyltitanium is monomeric by cryoscopy in benzene and a tetrahedral arrangement of the ligands is accordingly suggested for this compound. Bis(cyclopentadienyl)titanium absorbs carbon monoxide very slowly to give bis(cyclopentadienyl)dicarbonyltitanium. Bis(cyclopentadienyl)dichlorotitanium can be reduced by dilithium dipyridyl to a monomeric blue-black compound of formula $Ti(C_5H_5)_2$ *dipy. The solution structure of bis(cyclopentadienyl)titanium is briefly discussed in the light of the new results.*

Introduction

Up to now the organometallic chemistry of titanium contains a few examples only of compounds in which the central metal atom is in a 2+ oxidation state. The cyclopentadienyl anion seems to be the most suitable ligand to stabilise this oxidation state and compounds such as bis(cyclopentadienyl)titanium[1,2] and $Ti(C_5H_5)_2(CO)_2$[3] have been reported in the literature. The structure of bis(cyclopentadienyl)titanium is not yet known, although the apparent molecular weight in solution corresponds to a dimeric formula.[2,4,5]

In this paper we wish to report some new results on bis(cyclopentadienyl) derivatives of titanium. The new findings can be correlated to the general chemical behaviour of titanium in low oxidation states and have some bearing with the still unsolved problem of the structure of the parent compound, bis(cyclopentadienyl)titanium.

Results and Discussion

We have found that bis(cyclopentadienyl)dicarbonyltitanium which we have prepared by the known method[3] is a monomer in benzene. High-resolution infrared spectra in heptane have two bands at 1975 and 1897 cm^{-1} in the carbonyl stretching region. The previously reported[3] values are 1965 and 1883 cm^{-1} in benzene or tetrahydrofuran. The measured molecular weight excludes the possibility, suggested by the rather low wavenumber value of the band at 1897 cm^{-1}, that the compound is a dimer with CO bridges. A symmetrical arrangement of centrally π-bonded cyclopentadienyl rings and the diamagnetism of the compound are suggested by the single sharp proton resonance peak observed at 4.94 τ in d_6-acetone or at 5.42 τ in d_6-benzene. The n.m.r. spectrum was unchanged by cooling to about —50°C, thus showing that we are not dealing with a phenomenon of «stereochemical non-rigidity» of the type observed in $Fe(\pi\text{-}C_5H_5)(\sigma\text{-}C_5H_5)(CO)_2$.[6] We conclude by saying that bis(cyclopentadienyl)dicarbonyltitanium is a monomeric species with a probable tetrahedral arrangement of the ligands around the metal. The cyclopentadienyl ring is regarded here as a monodentate ligand.

It is interesting to note that bis(cyclopentadienyl)titanium absorbs carbon monoxide with difficulty at room temperature and atmospheric pressure to give bis(cyclopentadienyl)dicarbonyltitanium. This contrasts with the behaviour of the $[V(C_5H_5)_2]^+$ cation. The latter, prepared *in situ*[7] by oxidation of $V(C_5H_5)_2$ with $V(CO)_6$, reacts instantly with CO to give the $[V(C_5H_5)_2(CO)_2]^+$ cation, isoelectronic with $Ti(C_5H_5)_2(CO)_2$.

Reduction of $Ti(C_5H_5)_2Cl_2$ with dilithium dipyridyl led to monomeric, blue-black $Ti(C_5H_5)_2$dipy.[8] This slightly paramagnetic compound ($\mu_{eff} = 0.6$ B.M. at 296°K) has two e.p.r. signals in toluene solution at $g = 1.983$ and 1.989, superimposed on a broad line. We prefer to regard this compound as a titanium(III) derivative containing the 2,2'-dipyridyl radical anion as ligand. The coordination around the metal is probably tetrahedral, with 2,2'-dipyridyl acting as a normal bidentate ligand. The reduced magnetic moment can be interpreted as due to partial coupling between the unpaired spins on titanium and on the ligand.

Very interestingly bis(cyclopentadienyl)titanium as prepared from bis(cyclopentadienyl)dichlorotitanium and sodium naphthalene does not react with 2,2'-dipyridyl at room temperature in toluene solution. However, when bis(cyclopentadienyl)titanium was heated in molten 2,2'-dipyridyl a black compound analysing

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(7) F. Calderazzo and S. Bacciarelli, *Inorg. Chem.*, *2*, 721 (1963).

(8) A compound of this composition has also been obtained by Prof. E. O. Fischer at Technische Hochschule, München.

correctly for bis(cyclopentadienyl)2,2′-dipyridyltitanium was obtained. The substance is paramagnetic (μ_{eff} = = 1.04 B.M. per titanium at 296°K) and gives one single e.p.r. signal at g = 1.989. We tentatively propose that in this dipyridyl derivative the probably binuclear units of the starting bis(cyclopentadienyl) titanium are retained. Dipyridyl in this case would function as a bridging bidentate ligand. Either intramolecular bridging within the same dimeric unit or alternatively intermolecular bridging to give a polymeric substance are possible. We were unable to determine the molecular weight of this compound because of its low solubility. The possibility for 2,2′-dipyridyl to act as a bidentate bridge has been recently considered.[9]

The general reluctance of bis(cyclopentadienyl) titanium to give the monomeric bis(cyclopentadienyl) 2,2′-dipyridyltitanium or bis(cyclopentadienyl)dicarbonyltitanium suggests that bis(cyclopentadienyl) titanium is not a monomeric ferrocene-like compound as originally postulated.[1] A rapid equilibrium of binuclear bis(cyclopentadienyl)titanium to a monomeric π-sandwiched form in solution is also to be excluded on the basis of the present findings. Work is now in progress aimed at establishing the solution structure of bis(cyclopentadienyl)titanium.

Experimental Section

In view of the very high air-sensitivity of the compounds described in this paper, all the operations were carried out in an atmosphere of prepurified nitrogen.

The infrared spectra were measured on a Perkin-Elmer mod. 521 instrument equipped with grating.

The proton resonance spectra were measured on a Varian DP6OA instrument using tetramethylsilane (= 10 τ) as internal standard. The magnetic susceptibilities were measured with a Gouy balance which will be described in a forthcoming publication.[5]

Bis(cyclopentadienyl)titanium was prepared by reducing bis(cyclopentadienyl)dichlorotitanium with sodium naphthalene according to the procedure of Watt and coworkers.[2]

Bis(cyclopentadienyl)dicarbonyltitanium was prepared by reducing bis(cyclopentadienyl)dichlorotitanium with sodium cyclopentadienide in tetrahydrofuran in the presence of carbon monoxide under pressure, according to a slight modification of the known procedure.[3] After filtration, the reaction mixture was evaporated to dryness, and the solid residue extracted with heptane. The resulting brown solution was filtered, and cooled to dry ice temperature. The crude product was collected by filtration and dried *in vacuo* (22% yield). The compound was then purified by sublimation at 40°C/~10^{-3} mm. The molecular weight determined by cryoscopy in benzene was 245 (calcd. 234). The infrared spectrum has two bands at 1975 (m-s) and 1897 (s) cm^{-1} in heptane. Other infrared bands (nujol mull) were at 1423 (m), 1263 (w), 1110 (w), 1060(s), 1058(m-s), 1015(s), 1000(s), 892(w), 840(s), 830 (s), 810 (vs), 795 (vvs), 725 (w), 665 (m), 618 (w), 555 (s-m), 490 (m), 462 (s) and 405 (m) cm^{-1}.

Bis(cyclopentadienyl)titanium in toluene slowly absorbed carbon monoxide at atmospheric pressure at 20°C. In about 4 hrs. only 10% of the volume of CO expected for the conversion to $Ti(C_5H_5)_2(CO)_2$ was absorbed. The toluene solution showed the bands characteristic for the dicarbonyl compound in the C-O stretching region.

Bis(cyclopentadienyl)2,2′-dipyridyltitanium. To a suspension of $Ti(C_5H_5)_2Cl_2$ (10.0 g; 40.2 mmoles) in 250 ml tetrahydrofuran a green solution of dilithium-2,2′-dipyridyl[10] (40.2 mmoles) in tetrahydrofuran (250 ml) was added dropwise in about 2 hrs. under vigorous stirring at room temperature. The solvent was then evaporated at reduced pressure and the solid residue treated with toluene (300 ml). From the filtered toluene solution the titanium compound was then precipitated by addition of heptane. After filtration and drying *in vacuo* 10.9 g (81.2% yield) of bis(cyclopentadienyl)2,2′-dipyridyltitanium were obtained as dark blue crystals. *Anal.* Calcd. for $C_{20}H_{18}N_2Ti$: C, 71.86; H, 5.43; N, 8.38; Ti, 14.33; MW, 334.3. Found: C, 71.17; H, 5.75; N, 8.00; Ti, 14.57; MW, 321 (cryoscopy in benzene). The compound is soluble in aromatic hydrocarbons and acetone and is rapidly oxidised by air.

Infrared spectrum (nujol and halocarbon mulls): 3100 (w), 3070 (m), 3010 (w-sh), 2915 (w), 1980 (m), 1600 (m), 1582 (m), 1560 (m), 1500 (s), 1420 (m), 1285(m-w), 1270(m), 1148(m-s), 1122(w), 1090(w), 1060 (w), 1040 (w), 1010 (s), 960 (m-s), 895 (w), 828 (w), 815 (m), 795 (s), 755 (w), 730 (s), 710 (w), 680 (m-w), 665 (w), 650 (w), and 440 (w) cm^{-1}.

A *bis(cyclopentadienyl)2,2′-dipyridyltitanium* of unknown molecular weight was obtained by treating bis(cyclopentadienyl)titanium (1.19 g; 6.68 mmoles) with 2,2′-dipyridyl (2.08 g; 13.3 mmoles; m.p. 70.1°C) at 105°C for 2 hr. At the end of the reaction, the excess 2,2′-dipyridyl was partly sublimed off at 110°C/0.1 mm and partly dissolved in heptane. The titanium compound was then crystallised from heptane as dark-blue crystals (2.15 g; 96.3% yield). The solubility of this compound in organic solvents is lower than that of the previously described monomeric dipyridyl derivative. *Anal.* Calcd. for $[C_{20}H_{18}N_2Ti]_n$: C, 71.86; H, 5.43; N, 8.38; Ti, 14.33. Found: C, 71.63; H, 5.82; N, 8.16; Ti, 14.76.

Magnetic susceptibility measurements gave the results reported in Table I. The magnetic moment decreases

Table I. Magnetic Susceptibility Data[a] of $[Ti(C_5H_5)_2dipy]_n$.

T (°K)	$\chi_M^{corr} \times 10^6$ (c.g.s.u.)	μ_{eff}/titanium (B.M.)
296	457	1.04
240	482	0.97
210	529	0.95
180	575	0.91
150	660	0.89
120	800	0.88
90	1004	0.85

[a] The diamagnetic correction used for this compound and for the corresponding monomeric derivative was -213×10^{-6} c.g.s.u.

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slightly at decreasing temperature and the magnetic susceptibility follows the Curie-Weiss law quite well below 210°K with $\theta = +32°$.

The compound has an e.p.r. signal at $g = 1.989$ in the solid state. In tetrahydrofuran solution some hyperfine structure can be observed due to the two isotopes ^{47}Ti and ^{49}Ti of natural abundance 7.75 and 5.51% and with nuclear spins of 5/2 and 7/2, respectively.

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