On the Existence of the Anion Trichloro(η-cyclopentadienyl)titanate(1 −). Crystal Structure of the Salt $[Co(C_5H_5)_2][Ti(C_5H_5)Cl_3]$ †

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We have isolated, and characterised by elemental and *X*-ray crystal structure analysis, and e.s.r. and n.m.r. spectroscopy, the salt $[Co(C_5H_5)_2][Ti(C_5H_5)Cl_3]$. The results show that the ion $[Ti(C_5H_5)Cl_3]^-$ is a stable species of not unexpected properties, despite an earlier report that it readily loses chloride. This represents the first structural analysis of a (cyclopentadienyl)trihalogenotitanate(1 −) species.

We have recently described the isolation of the complex $[TiLCl_3]^-$ [L = tris(pyrazolyl)borate], and remarked upon the apparent non-existence of an analogue $[Ti(C_5H_5)Cl_3]^-$.[1] In reductions of $[Ti(C_5H_5)Cl_3]$ which might be expected to yield $[Ti(C_5H_5)Cl_3]^-$ the product generally contains $Ti(C_5H_5)Cl_2$, either as a dimer or as an adduct with a Lewis base. Evidently one chloride in $[Ti(C_5H_5)Cl_3]^-$ is labile, and this inference is supported by an earlier e.s.r. analysis which shows that $[Ti(C_5H_5)Cl_3]$ in methyltetrahydrofuran irradiated at 77 K with ^{60}Co γ-rays produces a species {supposed to be $[Ti(C_5H_5)Cl_3]^-$} which, upon annealing at some higher temperature, produces $[Ti(C_5H_5)Cl_2]$.[2] The e.s.r. spectrum of the latter species was in agreement with literature data, but the spectrum of $[Ti(C_5H_5)Cl_3]^-$ was considered to be uninterpretable.[2]

Much more recently, and without reference to these data, the synthesis of some complexes $[Co(C_5H_5)_2][M(C_5H_4Me)Cl_3]$ (M = Ti or V) and the e.s.r. spectrum of the former titanium complex were reported.[3] The reported spectrum is quite different from that attributed to $[Ti(C_5H_5)Cl_3]^-$, and the cyclic voltammograms of the titanium derivative were consistent with the presence in solution in CH_2Cl_2 of $[Co(C_5H_5)_2]^+$ and of an oxidisable counter ion; the reduction of $[Ti(C_5H_4Me)Cl_3]$ is reversible. These results argue for a significant stability for $[Ti(C_5H_4Me)Cl_3]^-$ and are in direct contradiction to the earlier report. We have carried out experiments to resolve this confusion.

Results and Discussion

Using the method of Morse *et al.*,[3] we have prepared a complex analysing for $[Co(C_5H_5)_2][Ti(C_5H_5)Cl_3]$ by the reaction of $[Co(C_5H_5)_2]$ with $[Ti(C_5H_5)Cl_3]$ in dichloromethane. Recrystallisation from CH_2Cl_2–hexane yielded dark green crystals which were subjected to *X*-ray crystal structure analysis.

The structure shows clearly the presence of both $[Co(C_5H_5)_2]^+$ and $[Ti(C_5H_5)Cl_3]^-$ as displayed in the Figure. Clearly, $[Ti(C_5H_5)Cl_3]^-$ has considerable stability in the solid state and in solution, consistent with the findings of Morse *et al.*[3] and in disagreement with Symons and Mishra.[2]

Description of Crystal Structure.—The crystals are composed of discrete $Ti(C_5H_5)Cl_3$ and $Co(C_5H_5)_2$ moieties, separated by van der Waals contacts. The cobalt atom is sandwiched between virtually parallel, eclipsed cyclopentadienyl residues, in the manner typical of metallocenes. The distances Co–C(5*) and Co–C(6*) have a mean value of 1.631(4) Å [the asterisked positions in Tables 1 and 2 denote the centroids of the cyclopentadienyl rings], and the C(5*)–Co–C(6*) arrangement is virtually linear. This length compares with independent Co–C(*) distances of 1.623 and 1.624 Å in $[Co(C_5H_5)_2]$-$[2\text{-}[\{(Me_3Si)_2CH\}C]B_{10}H_{16}]$,[4] 1.651 Å in $[Co(C_5Me_5)_2]$-$[C_2(CN)_4]$,[5] and 1.653 Å in $[Co(C_5Me_5)_2][(NC)_2CC_6H_4C(CN)_2]$,[6] which all contain cobaltocene(1 +) ions. The distances are all shorter than the corresponding distance in $[Co(C_5H_5)_2]$, 1.726 Å,[7] and this supports the contention that our crystals contain $[Co(C_5H_5)_2]^+$ ions rather than the neutral species.

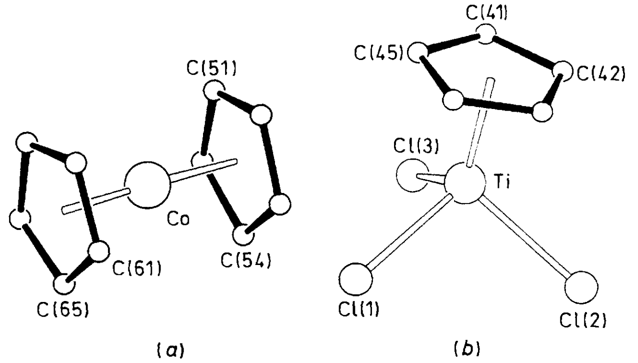

Figure. Representation of the structures of the ions $[Co(C_5H_5)_2]^+$ (*a*) and $[Ti(C_5H_5)Cl_3]^-$ (*b*), showing the numbering scheme

For the $Ti(C_5H_5)Cl_3$, moiety, the co-ordination pattern is essentially a three-legged piano-stool arrangement, as found for $[Ti(C_5H_5)Cl_3]$.[8] However, the bond distances are all slightly longer than in the titanium(IV) molecule, our mean Ti–Cl separation being 2.349(8) Å compared with 2.222(8) for $[Ti(C_5H_5)Cl_3]$, and Ti–C(4*) is 2.027 compared to 2.01 Å in $[Ti(C_5H_5)Cl_3]$. These distances are fully consistent with our formulation of a titanium(III) anion $[Ti(C_5H_5)Cl_3]^-$. Tables 1 and 2 contain final atomic parameters, and selected molecular dimensions.

Thus, the crystal appears best formulated as $[Co(C_5H_5)_2]$-$[Ti(C_5H_5)Cl_3]$, containing the hitherto unreported $[Ti(C_5H_5)Cl_3]^-$ anion, inconsistent with the suggestions of Symons and Mishra[2] but in full agreement with the findings of Morse *et al.*[3] concerning the closely related $[Ti(C_5H_4Me)Cl_3]^-$, based upon e.s.r. studies.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

Table 1. Final atomic co-ordinates (fractional × 10^4) with estimated standard deviations (e.s.d.s) in parentheses for $[Co(C_5H_5)_2][Ti(C_5H_5)Cl_3]$

Atom	*x*	*y*	*z*
Ti	3 696.5(3)	3 239.5(4)	8 308.0(4)
Cl(1)	2 323.6(5)	2 447.1(6)	6 781.7(7)
Cl(2)	4 246.3(5)	4 705.1(7)	7 100.3(7)
Cl(3)	2 870.5(6)	4 652.9(7)	9 214.3(6)
C(41)	4 643(3)	2 488(4)	10 201(3)
C(42)	5 274(2)	2 759(3)	9 552(4)
C(43)	5 076(2)	1 902(4)	8 583(3)
C(44)	4 329(3)	1 123(3)	8 644(3)
C(45)	4 054(3)	1 495(4)	9 634(4)
Co	1 468.1(2)	−2 495.9(3)	6 471.1(3)
C(51)	2 408(2)	−1 822(3)	8 060(3)
C(52)	2 916(2)	−2 305(3)	7 333(3)
C(53)	2 638(2)	−1 619(3)	6 242(3)
C(54)	1 940(3)	−707(3)	6 299(3)
C(55)	1 799(2)	−838(3)	7 442(3)
C(61)	946(3)	−3 691(4)	5 059(3)
C(62)	1 170(3)	−4 376(3)	6 119(4)
C(63)	620(4)	−3 881(5)	6 791(3)
C(64)	60(3)	−2 902(5)	6 127(6)
C(65)	264(3)	−2 802(4)	5 060(4)
Calculated co-ordinates of the centres of the C_5H_5 rings			
C(4*)	4 675	1 953	9 323
C(5*)	2 340	−1 458	7 075
C(6*)	612	−3 531	5 831

Table 2. Dimensions about the metal atoms (bond lengths in Å, angles in °) with e.s.d.s in parentheses

Ti–Cl(1)	3.250(1)	Ti–C(43)	2.361(3)
Ti–Cl(2)	2.364(1)	Ti–C(44)	2.360(3)
Ti–Cl(3)	2.334(1)	Ti–C(45)	2.324(3)
Ti–C(41)	2.325(3)	Ti–C(4*)	2.027
Ti–C(42)	2.332(3)		
Co–C(51)	2.037(3)	Co–C(61)	2.002(3)
Co–C(52)	2.021(3)	Co–C(62)	2.010(3)
Co–C(53)	2.004(3)	Co–C(63)	1.994(3)
Co–C(54)	2.006(3)	Co–C(64)	1.986(3)
Co–C(55)	2.028(3)	Co–C(65)	2.002(3)
Co–C(5*)	1.635	Co–C(6*)	1.627
Cl(1)–Ti–Cl(2)	97.9(1)	Cl(1)–Ti–C(4*)	118.4
Cl(1)–Ti–Cl(3)	97.5(1)	Cl(2)–Ti–C(4*)	117.7
Cl(2)–Ti–Cl(3)	100.1(1)	Cl(3)–Ti–C(4*)	120.8
C(5*)–Co–C(6*)	178.1		

We determined the e.s.r. spectrum of powdered and frozen solution (CH_2Cl_2) samples of $[Co(C_5H_5)_2][Ti(C_5H_5)Cl_3]$ at 4 K and have compared them with that assigned to $[Ti(C_5H_5)Cl_3]^-$ and reported for $[Ti(C_5H_4Me)Cl_3]^-$. Symons and Mishra[2] reported a 'nearly axial' spectrum for powdered $[Ti(C_5H_5)Cl_3]^-$ at 77 K, with g = 1.962, 1.962, and 1.945, g_{av} = 1.956. Morse *et al.*[3] show a very different spectrum for powdered $[Co(C_5H_5)_2][Ti(C_5H_4Me)Cl_3]$ at 4 K with invariant $g_{\parallel}$ = 1.733 and $g_{\perp}$ = 1.938, plus minor signals which varied in intensity with sample rotation. Our data, which give $g_{\parallel}$ = 1.743 and $g_{\perp}$ = 1.973 under similar conditions, are much more like the latter than the former.

We also confirmed that $[Ti(C_5H_5)Cl_3]^-$, like $[Ti(C_5H_4Me)Cl_3]^-$, is stable in solution. An n.m.r. spectrum of 1:1 mixture of $[Co(C_5H_5)_2]$ and $[Ti(C_5H_5)Cl_3]$ in solution at *ca.* 25 °C showed a strong sharp singlet at δ 6.13, assigned to cobaltocene(1+) protons, and a very broad signal centred at about 27.5 and with a width of about 4 p.p.m., of the right intensity to correspond with $[Ti(C_5H_5)Cl_3]^-$. Morse *et al.*[3] report a similar signal at about δ 29 for their species in CD_2Cl_2 at 30 °C.

It is clear that species $[Ti(C_5R_5)Cl_3]^-$ (R = H or alkyl) are stable in the solid state and in solution in CH_2Cl_2.

Experimental

All compounds were manipulated under pure dry dinitrogen in dry degassed solvents. The following spectrometers were used: JEOL GSX-270 for n.m.r., Bruker ER 200-D for e.s.r. The starting materials, $[Co(C_5H_5)_2]$[9] and $[Ti(C_5H_5)Cl_3]$,[10] were prepared by literature methods.

Bis(η^5-*cyclopentadienyl*)*cobalt*(1+) *trichloro*(η^5-*cyclopentadienyl*)*titanate*(1−).—Solutions of cobaltocene (0.38 g, 2 mmol) in CH_2Cl_2 (20 cm^3) and trichloro(cyclopentadienyl)titanium (0.45 g, 2 mmol) in CH_2Cl_2 (20 cm^3) were mixed under N_2. The resulting dark green solution was stirred for 1 h. The solvent was then removed under vacuum to leave a green solid which was washed with toluene (2 × 5 cm^3) and dried *in vacuo*. The solid was extracted with CH_2Cl_2 (5 × 10 cm^3), the extract was filtered and taken to dryness, affording analytically pure $[Co(C_5H_5)_2][Ti(C_5H_5)Cl_3]$ (yield 50%). Single crystals can be obtained by layering a concentrated solution of $[Co(C_5H_5)_2][Ti(C_5H_5)Cl_3]$ in CH_2Cl_2 with hexane (Found: C, 44.1; H, 3.40. $C_{15}H_{15}Cl_3CoTi$ requires C, 44.1; H, 3.65%). I.r. spectrum (Nujol and hexachlorobutadiene mulls): 3 936w, 3 102m, 1 815w, 1 720w, 1 638w, 1 415s, 1 262s, 1 112s, 1 018vs, 942w, 865vs, 805vs,br, 740ms, 667w, 603w, 501m, 461br,vs, 434s, 417s, and 391br,vs cm^{-1}.

X-*Ray Crystallographic Analysis of* $[Co(C_5H_5)_2][Ti(C_5H_5)Cl_3]$.—*Crystal data.* $C_{15}H_{15}Cl_3CoTi$, M = 408.5, monoclinic, a = 14.404(1), b = 10.365(1), c = 11.591(1) Å, β = 108.256(7)°, U = 1 643.4 Å^3, space group $P2_1/a$ (equivalent to no. 14), Z = 4, D_c = 1.651 g cm^{-3}, $F(000)$ = 820, μ(Mo-K_α) = 19.7 cm^{-1}, λ(Mo-$K_{\bar{\alpha}}$) = 0.710 69 Å.

Crystals of this sample were very air-sensitive dark green prisms. One, *ca.* 0.33 × 0.38 × 0.62 mm, was sealed under dinitrogen in a capillary, and after preliminary photographic examination was transferred to an Enraf-Nonius CAD4 diffractometer (monochromated molybdenum radiation) for measurement of cell parameters (from the centred settings of 25 reflections in each of four diffracting orientations) and diffraction intensities (to $\theta_{max.}$ = 25°). Two reflections monitored throughout the data collection showed no significant changes in intensity. During processing, corrections were made for Lorentz-polarisation effects, absorption (by semi-empirical ψ-scan methods), and negative intensities (by Bayesian statistical methods).

Data for 2 879 unique reflections (2 518 of which had $I > 2\sigma_I$) were input to the SHELX program system for structure determination[11] (which was by the heavy-atom method) and refinement (by full-matrix, least-squares methods). Convergence was reached at R = 0.035, R' = 0.038[11] for all 2 879 data weighted $w = \sigma_F^{-2}$. Hydrogen atoms were included in idealised positions, with thermal parameters riding on those of their bonded carbon atoms. A final difference map showed features in the range −0.55 to +0.29 e Å^{-3} only.

Scattering curves for neutral atoms were taken from ref. 12. All computing was carried out on a MicroVAX II machine, using programs noted above and in Table 4 of ref. 13.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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