An Electron Spin Resonance Study of Some Cyclopentadienyl–Organophosphide Complexes of Titanium(III) and Zirconium(III)

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E.S.R. INVESTIGATIONS[1,2] of cyclopentadienyl derivatives of titanium(III) have suggested the formation of anion-radicals of the type, $[(\pi\text{-}C_5H_5)_2TiX_2]^-$, where X = H, or alkyl.[1] Confirmation that the dihydro-species are negatively charged comes from the observation of strong interactions with sodium and lithium cations.[2]

We present evidence for the formation of similar anion-radicals in the reaction of titanocene or zirconocene dichlorides with organophosphines in the presence of alkali-metals

Under similar reaction conditions the diamagnetic, dimeric complexes $[(\pi\text{-}C_5H_5)_2MPR_2]_2$ (M = Ti or Zr; R = Et or Bu^n) have been isolated.[3]

Addition of titanocene dichloride, under conditions of high vacuum, to an excess of sodium dimethylphosphide, prepared from tetramethyldiphosphine with a sodium-mirror in tetrahydrofuran, immediately gave an e.s.r. spectrum consisting of a large doublet with coupling constant of 20·5 G, at $g = 1{\cdot}988$.† The ^{47}Ti (7·7% abundance, I 5/2) and ^{49}Ti (5·5%, 7/2) isotope patterns were clearly seen underlying the main spectrum with a titanium coupling constant of 10·8 G. Further reaction at room temperature gave a second spectrum (Figure 1) at g 1·992.

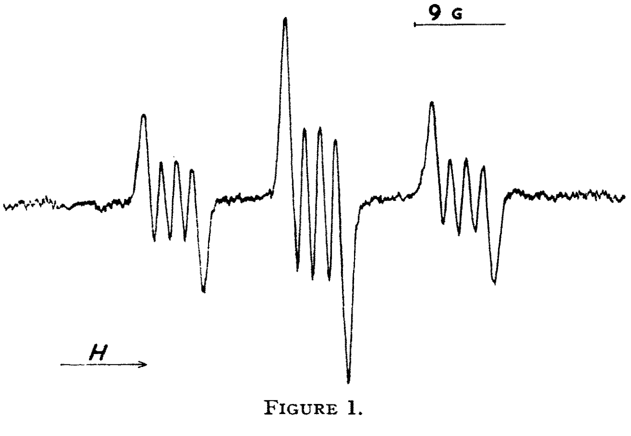

FIGURE 1.

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† g-Values were measured by comparison with solid DPPH ($g = 2{\cdot}0036$) and $(\pi\text{-}C_5H_5)_2$ TiCl ($g = 1{\cdot}980$) (ref. 1).

This spectrum consists of a triplet (12·7 G) of quartets (1·3 G). Splitting of *ca.* 9 G from ^{47}Ti and ^{49}Ti isotopes could be seen at higher gain. Reaction with $LiPMe_2$ gave a 1 : 2 : 1 triplet (12·6 G) with no evidence of a quartet splitting.

Sodium diphenylphosphide, from sodium and either tetraphenyldiphosphine, diphenylphosphine or triphenylphosphine, gave, on reaction with titanocene dichloride, similar spectra to those observed above, namely a doublet (7·74 G, g = 1·980) and a triplet (9·4 G, g = 1·989). Coupling to the ^{47}Ti and ^{49}Ti isotopes was observed in both cases, and in the triplet spectrum, the coupling constant (9·5 G) is very nearly equal to the main triplet splitting. This results in the coincidence of some of the lines, which gives an unusually intense satellite spectrum (Figure 2). Comparison of the intensities of the satellite lines with the major lines in this spectrum has enabled us to determined the number of Ti nuclei/paramagnetic molecule. In order to eliminate effects from differential broadening, and imperfect overlap of components, the spectrum was doubly integrated. The calculated ratio of the integrated intensity of line x to line y (Figure 2), for one Ti nucleus/molecule is 0·073. The experimental ratio was 0·072, thus confirming the presence of only one Ti nucleus/molecule.

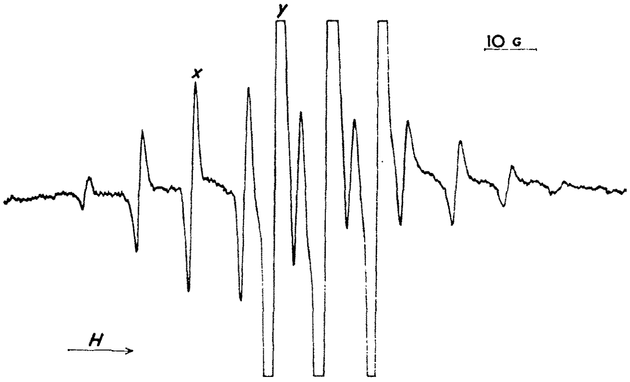

FIGURE 2.

We believe that the doublet spectra result from coupling to a single phosphorus nucleus, and may be attributed to the species $(\pi\text{-}C_5H_5)_2Ti^{III}PR_2$, where R = Me or Ph. Phosphorus couplings of a similar magnitude have been observed in other paramagnetic organometallic complexes.[4,5]

The triplet splittings are attributed to two phosphorus nuclei, and the quartet (1 : 1 : 1 : 1) splitting in the second spectrum (Figure 1) to coupling to a sodium nucleus (I = 3/2). On the assumption that the phenyl and the methyl compounds are similar in structure, we interpret the second spectrum from the dimethylphosphine complex as from the ion pair $[(\pi\text{-}C_5H_5)_2Ti^{III}(PMe_2)_2]^-$ Na^+, and the spectrum from the diphenyl complex as from the anion $[(\pi\text{-}C_5H_5)_2Ti^{III}(PPh_2)_2]^-$. The absence of alkali-metal splitting with the latter complex may be the result of steric hindrance to ion-pair formation by the relatively bulky phenyl groups. Henrici-Olivé and Olivé[2] found that the alkali-metal splitting in their dihydro-species decreased by a factor of 2·5 in going from sodium to lithium. A similar decrease in our experiment would explain the non-observation of alkali-metal splitting in the lithium complex.

The observation that there is only one titanium nucleus/molecule eliminates the possibility that the signals result from dimeric bridged species, similar to the mono-anion radical $[Me_2PCr(CO)_4]_2^-$,[4] or from triplet-state neutral species similar to that proposed for $[(\pi\text{-}C_5H_5)_2TiCl]_2$.[6]

Spectra have also been obtained by reduction of zirconocene dichloride with alkali-metal organophosphides. Thus, with $NaPPh_2$ a triplet spectrum, from two equivalent phosphorus nuclei, of coupling 11·7 G, g = 1·989 was obtained.

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[1] H. Brintzinger, *J. Amer. Chem. Soc.*, 1967, **89**, 6871.
[2] G. Henrici-Olivé and S. Olivé, *Angew. Chem. Internat. Edn*, 1968, **7**, 386.
[3] K. Issleib and H. Hackert, *Z. Naturforsch.*, 1966, **21b**, 19.
[4] R. E. Dessy, P. M. Weissman, and R. L. Pohl, *J. Amer. Chem. Soc.*, 1966, **88**, 5117.
[5] H. D. Murdock and E. A. C. Lucken, *Helv. Chim. Acta*, 1964, **47**, 1517.
[6] R. L. Martin and G. Winter, *J. Chem. Soc.*, 1965, 4709.