

## C.I.D.N.P. Enhancement of both Organometallic and Organic Compounds in the Thermal Reaction of $[\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}(\eta\text{-C}_5\text{H}_5)_2]$ with $\text{CCl}_4$

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The thermal reaction of  $[\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}(\eta\text{-C}_5\text{H}_5)_2]$  with  $\text{CCl}_4$  in  $[\text{}^2\text{H}_6]$ benzene solution gives enhanced signals for both the starting titanium compound and product  $\text{PhCH}_2\text{CCl}_3$ , but not in titanocene dichloride or bibenzyl which are also produced; a mechanism accounting for these observations is proposed.

We report the first thermal C.I.D.N.P. signal observed in a transition metal organometallic derivative, and also in one of the organic products of its reaction with carbon tetrachloride.† When  $[\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}(\eta\text{-C}_5\text{H}_5)_2]$  dissolved in  $[\text{}^2\text{H}_6]$ -benzene is treated with  $\text{CCl}_4$  at ambient temperature, a reaction occurs forming  $[\text{TiCl}_2(\eta\text{-C}_5\text{H}_5)_2]$  ( $\delta$  5.92) as the only significant cyclopentadienyl-containing compound and  $\text{PhCH}_2\text{-CCl}_3$  [ $\delta(\text{CH}_2)$  3.51] and  $(\text{PhCH}_2)_2$  [ $\delta(\text{CH}_2)$  2.74] as the organic products.‡ During the reaction both the benzyl protons of the starting organometallic compound and those of  $\text{PhCH}_2\text{CCl}_3$

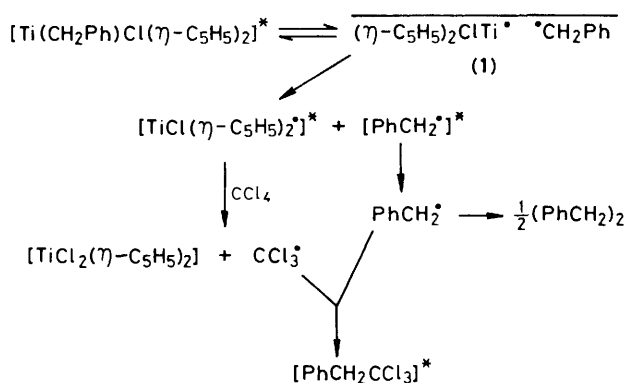
show enhanced absorption.§ Use of Kaptein's equation for the net C.I.D.N.P. effect<sup>1</sup> and the  $g$  values and hyperfine coupling constants for the reacting radicals¶ reveals that the enhanced polarisation of the starting material is consistent with a cage recombination reaction, whereas  $\text{PhCH}_2\text{CCl}_3$  is formed by a diffusive encounter of its constituent radicals. These conclusions are further supported by an experiment carried out in the presence of the radical trap norbornadiene, when the organic product was not observed (diffusive radicals

† A recent paper reports both thermal and photochemical decomposition of  $[\text{TiMe}_2(\eta\text{-C}_5\text{H}_5)_2]$ ; however no mention is made of C.I.D.N.P. effects in the organometallic products during the thermal reactions.

‡ The relative molar proportions of  $\text{PhCH}_2\text{CCl}_3$  and  $(\text{PhCH}_2)_2$  depend on the experimental conditions. In a typical experiment in which 10  $\mu\text{l}$  of  $\text{CCl}_4$  were added to 0.5 ml of a 79 mM solution of  $[\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}(\eta\text{-C}_5\text{H}_5)_2]$ , 28% of  $\text{PhCH}_2\text{CCl}_3$  and 72% of  $(\text{PhCH}_2)_2$  were formed.

§ Enhancements were calculated from peak integrals measured on single pulse spectra (to minimise effects due to the different relaxation times of various species) with respect to analogous peaks of the same species either before (for starting materials) or after (for products) the reaction, when nuclear polarisations were assumed to be equilibrium values. A smaller enhancement was also seen at  $\delta$  2.12 p.p.m., where toluene absorbs; however spectra at the end of the experiment show that toluene is formed only in trace amounts.

¶  $\text{PhCH}_2$ ,  $g = 2.0026$ ,  $^{2a}a(\text{CH}_2) = -1.628$  mT;  $^{2b}\text{CCl}_3$ ,  $g = 2.0091$ .<sup>3</sup> For  $[\text{TiCl}(\eta\text{-C}_5\text{H}_5)_2]$ ,  $g_{\text{av}} = 1.98$ .<sup>4</sup>



**Scheme 1.** Species (1) represents a cage pair (see text); asterisks represent species with non-equilibrium nuclear polarisations.

reacting preferentially with the trap) while enhancement of the titanium compound remained essentially unaltered. A plausible mechanism giving rise to these effects is shown in Scheme 1. A feature of the reaction which is not clear in Scheme 1 is the role of carbon tetrachloride in initiating the reaction, although it must have this function as decomposition of  $[\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}(\eta\text{-C}_5\text{H}_5)_2]$  is extremely slow in pure  $[\text{}^2\text{H}_6]$ -benzene. It appears that there is an interaction between the benzyltitanium compound and  $\text{CCl}_4$  which yields a more reactive species than the starting material, and that this gives

rise to a cage species containing benzyl and  $[\text{TiCl}(\eta\text{-C}_5\text{H}_5)_2]$  radicals, which we have approximated in Scheme 1 by (1). Further information on the nature of these species and details of their formation cannot however, be extracted from our present experimental data. Nevertheless, it appears that this reaction is quite unusual. Although it is known, for example, that  $[\text{Ti}(\text{CH}_2\text{Ph})\text{Cl}(\eta\text{-C}_5\text{H}_5)_2]$  reacts with chloroform,<sup>5</sup> the reaction is slower than that with carbon tetrachloride, and we have been unable to observe C.I.D.N.P. effects. Further,  $[\text{M}(\text{CH}_2\text{Ph})_2(\eta\text{-C}_5\text{H}_5)_2]$  (M = Ti or Zr) or  $[\text{Zr}(\text{CH}_2\text{Ph})\text{Cl}(\eta\text{-C}_5\text{H}_5)_2]$  are stable in the dark in the presence of  $\text{CDCl}_3$  or  $\text{CCl}_4$ , although they do react *via* radical pathways photochemically.<sup>6</sup> Mechanistic and C.I.D.N.P. studies of these systems are currently in progress.

Received, 21st October 1981; Com. 1234

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