Oxidative Additions to Dicarbonylbiscyclopentadienyltitanium(II)

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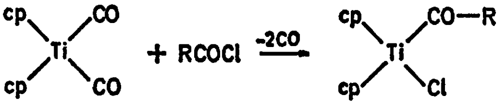
Summary Oxidative additions of alkyl and acyl halides to dicarbonylbiscyclopentadienyltitanium(II), $Ti(cp)_2(CO)_2$, yielded acyl derivatives of titanium, while the reaction with 9,10-phenanthraquinone (paq) gave $Ti(cp)_2(paq)$.

In connection with the current interest in oxidative additions[1] we report our results on $Ti(cp)_2(CO)_2$ (I) (cp = C_5H_5),[2] which can be considered as a model d^2 system for this general class of reactions. The so-called titanocene dimer has not been used much[3] in oxidative additions, possibly since the dimer[4] is not a genuine source of carbene-like $Ti(cp)_2$.



(1)

(I) (II; R = Ac) (III; R = Bz)

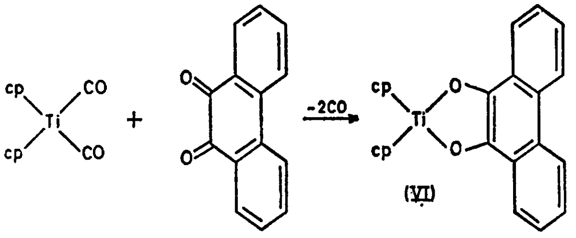
Complex (I) was treated with various reagents which take part in oxidative additions, such as acyl and alkyl halides, 9,10-phenanthraquinone, and halogens. All reactions were carried at room temperature in toluene.

Compound (I) reacts with acetyl chloride and benzoyl chloride, according to the stoicheiometry in reaction (1), to give yellow-orange needles of (II) and (III) respectively (*ca.* 80%) after 1 day. The products are insoluble in hydrocarbons, but soluble in $CHCl_3$ and, unusually for organometallic derivatives of titanium, stable in air. They were characterised by their i.r. and n.m.r. spectra [ν(C=O acyl) (Nujol) 1620 cm^{-1} for (II) and 1595 cm^{-1} for (III); τ ($CDCl_3$) 7·0 (3H, s) and 4·2 (10H, s) for (II), and 4·1 (10H, s) and 2·1 (5H, m), and elemental analyses.† Complex (II) gives a peak at *m/e* 256 (M^+) in its mass spectrum; (III) is monomeric in $CHCl_3$ (*M* 324).

Complex (I) also reacts with methyl and ethyl iodide to give the acyl derivatives $Ti(cp)_2(COMe)I$ (IV)† and $Ti(cp)_2(COEt)I$ (V),† respectively (*ca.* 80%) [ν(C=O) (Nujol) 1610 cm^{-1} for (IV) and 1605 cm^{-1} for (V); τ ($CDCl_3$) 7·0 (s) and 4·2 (s) (low solubility precluded measurement of reproducible integrated areas) for (IV) and 8·6 (3H,t), 6·72 (2H, q), and 4·2 (10H, s) for (V). The reactions were accompanied by evolution of CO (1 mol. equiv. per g-atom of Ti).

The reactions leading to (IV) and (V) may involve alkyl migration to a carbonyl group (or carbon monoxide insertion) as one step in the overall oxidative addition. Our results are similar to those obtained in oxidative additions of methyl and ethyl iodide to $Rh(cp)(CO)PPh_3$.[5] A kinetic investigation is planned in order to elucidate the mechanism of this reaction.

Reaction of (I) with 9,10-phenanthraquinone was similar to the oxidative addition to d^8 and d^{10} systems,[6] and led to (VI).



(VI) (2)

Reaction (2) takes place within the time of mixing, giving a deep-green solution, from which (VI)† crystallised upon addition of heptane. Complex (VI) is very soluble in aromatic hydrocarbons and the resulting solution is air-stable; it melts at 155° without decomposition {τ [$(CD_3)_2CO$] 1·3 (2H, m), 2·0 (2H, m), and 2·5 (4H, m) (phenanthrene fragment) and 3·9 (10H, s, cyclopentadienyl)}. It is monomeric in benzene (*M* 382), and shows the parent peak at *m/e* 386 in its mass spectrum.

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† Satisfactory elemental analytical data were obtained.

Reaction of (I) with halogens is exemplified by oxidation with I_2 in toluene, which gave the known[7] $Ti(cp)_2I_2$ in substantially quantitative yield.

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[1] J. Halpern, *Accounts Chem. Res.*, 1970, **3**, 386.

[2] J. G. Murray, *J. Amer. Chem. Soc.*, 1961, **83**, 1287.

[3] H. Köpf and B. Block, *Z. Naturforsch.*, 1968, **23b**, 1536; G. Schmid, W. Petz, W. Arloth, and H. Nöth, *Angew. Chem.*, 1967, **79**, 683.

[4] H. H. Brintzinger and J. E. Bercaw, *J. Amer. Chem. Soc.*, 1970, **92**, 6182.

[5] A. J. Hart-Davis and W. A. G. Graham, *Inorg. Chem.*, 1970, **9**, 2658.

[6] J. S. Valentine and D. Valentine, *J. Amer. Chem. Soc.*, 1970, **92**, 5795.

[7] G. Wilkinson and J. M. Birmingham, *J. Amer. Chem. Soc.*, 1954, **76**, 4281.