Novel Diphenylketene Derivatives of Dicyclopentadienylvanadium and -titanium

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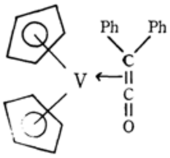
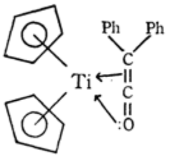
The interaction of cumulative carbon-carbon double bond systems with various organometallic compounds has been reported from this laboratory.[1] Because the comparison between the two kinds of interactions of ketene- and allene-systems with organometallic compounds is an interesting problem, we now wish to report on the isolation and on some properties of the diphenylketene derivatives of vanadium and titanium.

When a solution of diphenylketene (I) (3.7 g., 1.91 mmol.) and dicyclopentadienylvanadium (3.3 g., 1.82 mmol.) in toluene (20 ml.) was stirred under nitrogen at 60°C for 1 hr., the color of the reaction mixture changed from violet to dark green. After the mixture had then cooled to room temperature, dark green crystals separated. Recrystallization from toluene gave 5.5 g. (81% yield) of air-sensitive dark green crystals ((II); m. p. 159—163°C in a sealed tube under nitrogen). Found: C, 76.83; H, 5.30; mol. wt. (in benzene), 386. Calcd. for $C_{24}H_{20}OV$: C, 76.79; H, 5.37; mol. wt., 375. IR (KBr disk): 1618 and 1580 cm^{-1}, and no absorption in the region of 1620—2800 cm^{-1}.

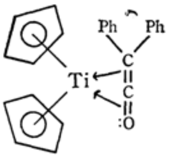
II is paramagnetic; its electron paramagnetic resonance spectrum of a benzene solution shows a *g*-factor of 1.9976 and a ^{51}V hyperfine splitting of 45.5 gauss. This splitting and *g*-value are almost the same as those of the acetylene derivatives of dicyclopentadienylvanadium.[2] This fact suggests that the diphenylketene is bound to the metal as tightly as acetylene, although infrared data excludes such a cyclic structure as that of the acetylene derivatives. In view of the facts mentioned above, we postulate II as the most probable structure; in it the metal is coordinated through the C=C double bond in the ketene.



(II)



(III-a)



(III-b)

A similar reaction of I (1.4 g.) with dicyclopentadienyltitanium dicarbonyl (1.1 g.) in hexane has been found to form dicyclopentadienyldiphenylketene-titanium (III) in a yield of 90%. III crystallizes as orange-yellow prisms from the reaction mixture, m. p. 215—217°C (decomp.), in a sealed tube under nitrogen. Found: C, 77.07; H, 5.49; O, 4.74; Ti, 13.6; mol.wt. 367 (vapor pressure osmometer, in benzene). Calcd. for $C_{24}H_{20}OTi$: C, 77.42; H, 5.41; O, 4.30; Ti, 13.0%; mol. wt. 372. IR (KBr disk): 1575 and 1555 cm^{-1}, and no absorption in the region of 1580—2800 cm^{-1}.

The NMR spectrum of III in methylene chloride or deuterochloroform shows that the relative intensity of π-cyclopentadienyl and phenyl protons is approximately 1 : 1. although the decomposition of the complex with the chlorinated solvents prevents precise measurements. To obtain the effective atomic number of krypton, the titanium atom must be supplied with 4 electrons from the π-complexed diphenylketene. Of the two most probable structures, a and b, the former, which involves the coordination of the diphenylketene group through the π-complexing C=C bond and the lone pair of the oxygen, is favored on the basis of a consideration of the steric requirement and its similarity with the cyanoamido complex.[3]

The reaction of II and III with such proton-donors as alcohol, hydrochloric acid, water and acetic acid were of considerable interest. These reagents decomposed the diphenylketene complexes, with the liberation of tetraphenylethane (IV). For example, when treated with glacial acetic acid, the III complex yielded IV, with a vigorous gas evolution, in a yield of 53%. Similarly, the vanadium complex, II, gave IV in a 25% yield, when treated with ethanol. The formation of IV in the above reactions suggests that the carbon-carbon double bond in the ketene is weakened by bonding to the metal.

Further work on the interaction of ketenes with organometallic π-compounds is in progress.

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1) a) A. Nakamura, P.-J. Kim and N. Hagihara, *J. Organometal. Chem*, **3**, 7 (1965); ibid., **3**, 355 (1965). b) A. Nakamura, This Bulletin, **38**, 1868 (1965); **39**, 543 (1966).

2) R. Tsumura and N. Hagihara, ibid., **38**, 861 (1965).

3) H. Bock and H. Dieck, *Ber.*, **99**, 213 (1966).