Journal of Organometallic Chemistry, 316 (1986) 315–318
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

INSERTION REACTIONS OF t-Bu(η^5-C_5H_5)Fe$(CO)_2$

KEITH H. PANNELL, TONY GIASOLLI, and RAMESH N. KAPOOR

Department of Chemistry, The University of Texas at El Paso, El Paso, TX 79968-0513 (U.S.A.)

(Received June 16th, 1986)

Summary

The complex t-Bu(η^5-C_5H_5)Fe$(CO)_2$ has been treated with triphenylphosphine in refluxing THF to produce t-BuCO(η^5-C_5H_5)Fe(CO)(PPh_3). The large steric bulk of the t-butyl group suggests that this reaction should be faster than the reaction involving the methyl group, and a kinetic investigation illustrates this to be the case. The same steric bulk predicts that the reaction with SO_2 should be slow, and indeed we have been unable to effect the related SO_2 insertion reaction. Attempts to prepare the corresponding t-Bu(η^5-C_5H_5)W$(CO)_3$ led to formation of the related isobutyl complex.

Introduction

The complex, t-BuFp (Fp = (η^5-C_5H_5)Fe$(CO)_2$) was reported by Rosenblum et al. as the first, and subsequently only, example of a t-butyl derivative of a transition metal carbonyl [1]. It is the object of this article to comment upon the reactions of the complex with triphenylphosphine and SO_2, both reagents that lead to facile "insertion" reactions with other alkyl derivatives of the Fp system. We have also attempted to make the related complex t-Bu(η^5-C_5H_5)W$(CO)_3$.

Experimental

The complex t-BuFp was prepared using the general procedure outlined by Giering and Rosenblum with minor modification. In the published procedure, treatment of isobutenyl-Fp with HBF_4 in acetic anhydride produced the salt $[(CH_3)_2C{=}CH_2(\eta^5\text{-}C_5H_5)Fe(CO)_2]^+$ BF_4^-. Subsequent treatment of this salt with $NaBH_4$ yielded the desired t-butyl complex. We find that the formation of the salt is better performed in diethyl ether at −78°C. The salt begins to precipitate out immediately the HBF_4 is added dropwise and filtration yields a pure, easily obtained product. With acetic anhydride as solvent, the precipitation process was not smooth, and a sticky product was generally obtained.

0022-328X/86/$03.50

Reaction of t-BuFp with triphenylphosphine

In a typical reaction, 0.5 g (2.1 mmol), of the complex t-BuFp was dissolved in 50 ml of dry, oxygen free, THF together with a 100% excess of triphenylphosphine, (1.1 g, 4.2 mmol). The mixture was refluxed until infrared monitoring indicated little or no starting material present in solution (24 h), but the spectrum exhibited new CO stretching frequencies at 1908 and 1598 cm^{-1} indicative of t-BuCO(η^5-C_5H_5)-Fe(CO)(PPh_3). The THF was removed in vacuo and the resultant oily residue dissolved in the minimum of a methylene chloride/hexane (50/50) mixture, and placed upon an alumina column. Elution with hexane separated any starting materials, and subsequent elution with a 50/50 methylene chloride/hexane solution led to collection of an orange band. Removal of the solvent, and recrystallization of the solid residue led to a 65% yield of the insertion complex. Analysis, performed by Galbraith Laboratories, Knoxville, TN. Analysis: Found, C, 70.3; H, 5.91. $C_{29}H_{29}FeO_2P$ calcd.: C, 70.2; H, 5.88%. Infrared, ν(CO) (hexane) 1917, 1601 cm^{-1}. ^1H NMR, ppm, ($CDCl_3$), C_6H_5, 7.51, 7.28, C_5H_5, 4.33 (d, *J* 2 Hz), Me, 0.72(s). ^{31}P NMR 73.6 (relative to phosphoric acid).

Related reactions using the above procedure with the N ligands acetonitrile, pyridine, and triethylamine were attempted. In all cases after a few hours it became apparent from infrared monitoring that decomposition of the t-butyl complex was occurring, resulting in the formation of Fp_2.

Attempted preparation of t-Bu(η^5-C_5H_5)W(CO)$_3$

To a cooled (0°C) solution of (η^5-C_5H_5)W$(CO)_3^-$ Na^+ prepared from 7.0 g (0.02 mmol) of $W(CO)_6$, was added dropwise methallyl chloride to produce the corresponding methallyltungsten complex, ν(CO) (hexane) 2016, 1934, and 1925 cm^{-1}. Subsequent treatment of this complex with HBF_4 as described above produced a yellow solid butenyl salt, ν(CO) (THF) 2056, 2009, 1972, and 1951 cm^{-1}.

Using the same techniques as Giering and Rosenblum we treated the corresponding butenyl-(η^5-C_5H_5)W$(CO)_3$ tetrafluorborate salt (2.0 g, 4.2 mmol) with an excess of sodium borohydride (0.6 g, 1.5 mmol) as a suspension in THF at °C. After complete addition, 30 min, the solution, a yellow brown colour, was refluxed for 30 min. The solvent was removed, and the resulting oil purified by chromatography on an alumina column, eluting with hexane. A 45% yield of the isobutyltungsten complex was obtained, with no evidence for the formation of any t-butyl complex. Analysis: Found, C, 36.92; H, 3.91. $C_{12}H_{14}O_3W$ calcd.: C, 36.92; H, 3.59%. Infrared, ν(CO) (hexane) 2016, 1924 cm^{-1}. ^1H NMR ($CDCl_3$)(η^5-C_5H_5), 5.0; Me_2, 0.59 (d, *J* 6.6 Hz); CH_2, 1.17 (d, *J* 6.6 Hz); *CH*Me_2 1.5(m).

Kinetic studies

Kinetic experiments were performed in THF, monitoring the appearance of the CO stretching frequencies of the t-BuCOFp complex at 1908 and 1598 cm^{-1} over a range of temperatures from 30 to 55°C, with triphenylphosphine concentrations ranging from a 20 to 60 fold excess, preserving pseudo first order conditions for the reaction. The kinetic data for the t-butyl complex and a comparison kinetic study on the corresponding CH_3Fp complex were obtained at 1.2 mmol PPh_3 (60 fold excess over the Fp complexes), 50°C and are as follows: *k*(t-butyl) 5.0×10^{-3} min^{-1}, *k*(methyl) 4.0×10^{-5} min^{-1}. The activation parameters for the t-butyl reaction are ΔH 97.0 kJ mol^{-1}, ΔS -27.6 J K^{-1} mol^{-1}.

Reactions with SO_2

The reaction of the complex t-BuFp with SO_2 was performed by dissolving 0.5 g of the complex in approximately 20 ml of sulphur dioxide, and permitting the liquid to evaporate gradually under an atmosphere of dinitrogen. The resulting oil was purified by column chromatography, and shown to be exclusively unreacted starting material.

Results and discussion

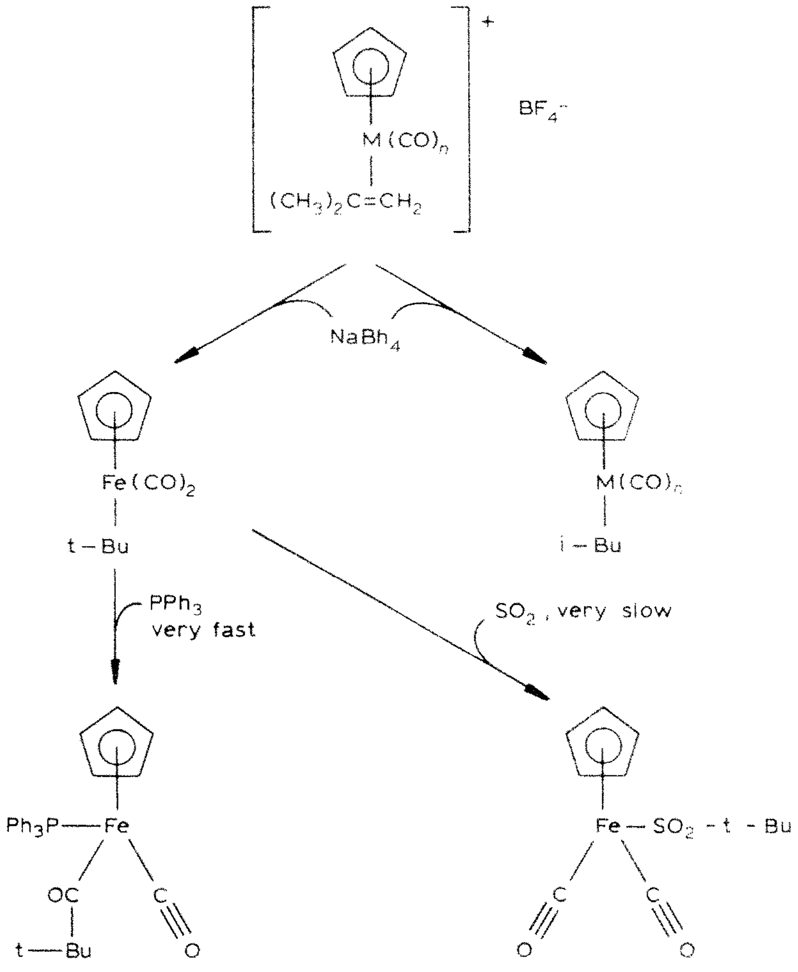
It is apparent that the title complex reacts in two distinct fashions with the typical insertion reaction type ligands triphenylphosphine and sulphur dioxide. With the former, a rapid reaction occurs leading to the expected acyl complex t-BuCO(η^5-C_5H_5)Fe(CO)(PPh_3). A kinetic analysis of this reaction showed that the reaction was zero order in triphenylphosphine, over the concentration range of phosphine used, and first order with respect to the Fp complex. Such a result is in keeping with the kinetic investigation of the insertion reaction between triphenylphosphine and the CH_3Fp complex [2,3]. The reaction of the t-butyl complex is some 2 orders of magnitude faster than the methyl derivative, reflecting the greater steric bulk of the alkyl group, consistent with previous studies on the series MeFp, EtFp, and PrFp [3,5]. Comparison of the activation parameters is difficult since the other reported reactions used either a different phosphine or solvent. However, the enthalpy of activation is on the low end of a range reported in a comprehensive study on such insertion reactions with varying alkylFp complexes, i.e. our value of 97.0 kJ mol^{-1} compared to a range from 94.6 to 115.1 kJ mol^{-1} [5]. It was further claimed that variations of solvent and phosphine may not be particularly important. A current review of the carbonylation reactions has recently appeared [6].

Attempts to decarbonylate the new acyl complex were uniformly unsuccessful. Both thermal and photochemical treatment led to the formation of Fp_2 as monitored by infrared spectroscopy. In a related reaction involving photochemical treatment of t-BuFp in the presence of the phosphine, only formation of Fp_2 was noted.

Attempts to perform an SO_2 insertion reaction with the t-butyl complex were uniformly unsuccessful over the short term reaction times, 2–4 h, that we employed. No reaction took place, under conditions that lead to high yield insertion reactions with the related methyl complex. It has been previously reported that the t-butyl complex reacts to 10% completion after 30 h reaction time [4]. Mechanistic investigations into the insertion of SO_2 into alkylFp complexes have shown the mechanism to involve an S_N2 nucleophilic attack by SO_2 at the carbon atom attached to the iron atom. In keeping with S_N2 reactions, increasing steric bulk around this carbon atom retard the rate of reaction. In the case of the t-butyl group this is so marked as to effectively prevent short term chemical reactivity.

In summary (Scheme 1), we have shown that the reactivity of the t-butyl group is characteristic of its large steric requirement. Migration from Fe to a carbonyl ligand which involves release of steric strain at the metal atom is enhanced, whereas insertion of SO_2 which involves a very crowded transition state is not readily observed.

Attempts to synthesize the related t-butyltungsten complex were unsuccessful, and only the isobutyl complex, $(CH_3)_2CHCH_2$(η^5-C_5H_5)W$(CO)_3$ was formed. The



SCHEME 1

reason for this difference of chemical reactivity between the two transition metals, Fe and W, is not clear.

Acknowledgements

Support of this research by the Petroleum Research Fund administered by the American Chemical Society, the Robert A. Welch Foundation, Houston, Texas, and the NIH (RR 08012) is greatly acknowledged.

References

1 W.P. Giering and M. Rosenblum, J. Organomet. Chem., 25 (1970) C71.
2 I.S. Butler, F. Basolo, and R.G. Pearson, Inorg. Chem., 6 (1967) 2074.
3 M. Green and D.J. Westlake, J. Chem. Soc. A, (1971) 367.
4 S.E. Jacobson and A. Wojcicki, J. Am. Chem. Soc., 95 (1973) 6962.
5 J.D. Cotton, G.T. Crisp, and L. Latif, Inorg. Chim. Acta, 47 (1981) 171.
6 J.J. Alexander, in F.R. Hartley and S. Patai (Eds.), The Chemistry of the Metal-Carbon Bond, Volume 2, J. Wiley and Sons Ltd., New York, 1985.