Journal of Organometallic Chemistry, 341 (1988) 415–419
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

Organometalloidal derivatives of the transition metals

XVI *. Thermal decarbonylation of (η^5-C_5H_5)Fe(CO)(PPh_3)COR (R = CH_3, CH_2SiMe_3, and CH_2SiMe_2Ph) **

Keith H. Pannell and John R. Rice

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

(Received July 29th, 1987)

Abstract

Thermal decarbonylation of (η^5-C_5H_5)Fe(CO)(PPh_3)COR proceeds via the initial formation of (η^5-C_5H_5)Fe$(CO)_2$R and PPh_3 as the kinetically favoured process. A kinetic investigation of this initial step for the title complexes exhibits a relative rate of phosphine loss $Me_3SiCH_2 > Me_2PhSiCH_2 > CH_3$ reflecting the steric bulk of the groups involved.

Introduction

There have been many papers and reviews concerning the decarbonylation of transition metal acyl complexes [2–4]. The most common techniques for achieving decarbonylations are thermal and photochemical.

Decarbonylation of the type of complex [(η^5-C_5H_5)Fe(CO)(L)COR] has been particularly well studied because, inter alia, it is an excellent system for studying the stereochemistry of the process at the metal centre, either with optically active complexes or with a known mixture of diastereoisomerically related isomers. Indeed Wojcicki [5], Brunner [6], and Davison [7] have studied the system from this standpoint and shown that whereas the photochemical decarbonylation proceeds

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* For part XV see ref. 1.

** Dedicated to Professor Colin Eaborn in recognition of his crucial role in the development of organosilicon chemistry.

0022-328X/88/$03.50

with > 85% inversion of configuration at the Fe atom, the thermal reaction proceeds with essential racemization.

Thus, in the photochemical process, loss of CO produces a trigonal intermediate with stereochemical integrity, while this is not true for the thermal process.

We long ago reported for the first time that this was due to the fact that the thermal reaction, by contrast to the photochemical reaction, proceeds initially via the loss of the phosphine ligand to produce $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ with immediate loss of optical activity, and it is this dicarbonyl species that reacts again with PPh_3 to ultimately form the observed and isolated decarbonylated product $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)R$ [8,9]. This loss of phosphine was later shown to involve an intramolecular substitution of the ligand by the acetyl group with stereospecific formation of an η^2-acetyl intermediate which may be trapped by other ligands L′, or rearrange to the dicarbonyl complex as we had reported [10].

This article contains the data concerned with the earlier reports together with a kinetic investigation into the loss of the phosphine ligand from the complexes $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COR$ ($R = CH_3$, CH_2SiMe_3, and CH_2SiMe_2Ph).

Experimental

The starting acyl complexes were synthesized using published techniques [11,12]. Thermal decarbonylations were studied using 1% solutions in refluxing 2,2,4-trimethylpentane, b.p. 98 °C, monitoring the reactions directly via infrared spectroscopy. A typical sequence of infrared spectra obtained over a 54 h time period is presented in Fig. 1, while a sequence over the first 10–20 min is presented in Fig. 2. The concentrations in these two examples are not equivalent, thus any comparison of the relative amounts of reactants and products in the two reactions is inappropriate. From the kinetic data collected over the initial stages of the reactions we

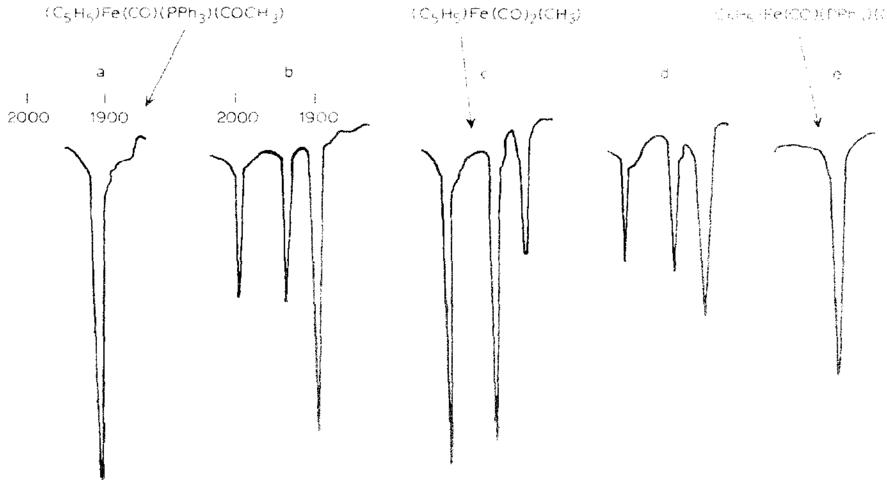


Fig. 1. Overall monitoring of thermal decarbonylation of $(C_5H_5)Fe(CO)(PPh_3)CoR$. (a) t 0, (b) 1 h, (c) 16 h, (d) 46 h, (e) 54 h.

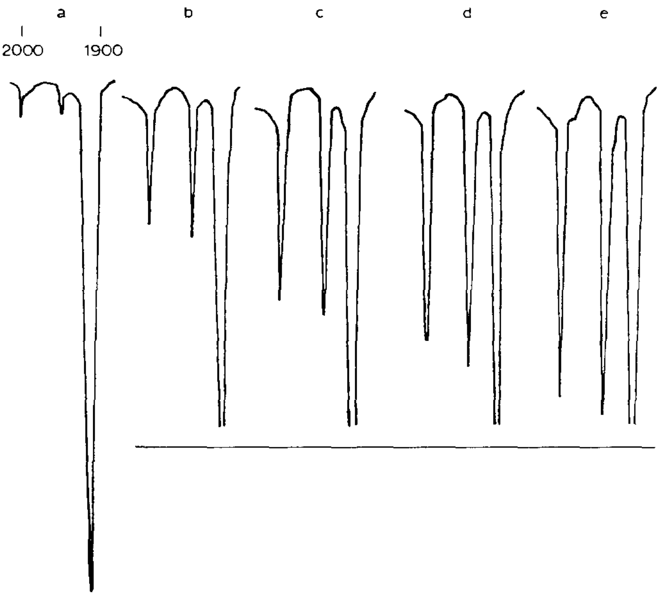


Fig. 2. Initial appearance of $(C_5H_5)Fe(CO)_2R$ upon thermal treatment of $(C_5H_5)Fe(CO)(PPh_3)COR$. (a) *t* 1 min, (b) 6 min, (c) 10 min, (d) 14 min, (e) 19 min.

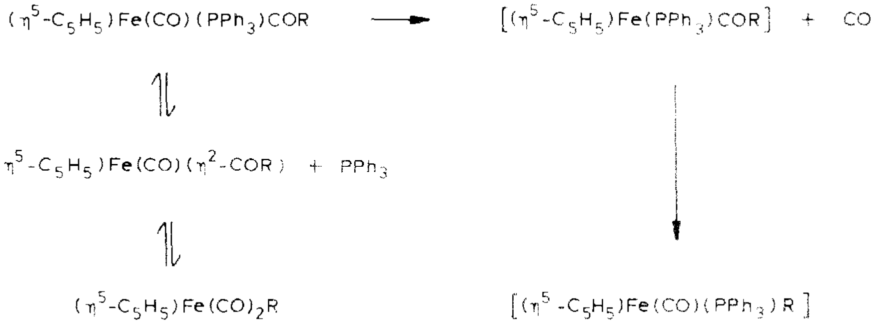
have obtained the first order rate constants for the appearance of $(\eta^5$-$C_5H_5)Fe(CO)_2R$ via loss of phosphine from the three complexes studied.

Results and discussion

The initial report on the thermal decarbonylation of $(\eta^5$-$C_5H_5)Fe(CO)$-$(PPh_3)COCH_3$ noted that traces of $(\eta^5$-$C_5H_5)Fe(CO)_2CH_3$ were obtained along with the major product $(\eta^5$-$C_5H_5)Fe(CO)(PPh_3)CH_3$ [11]. Monitoring of the reaction as noted in Figs. 1 and 2 clearly demonstrates that the reaction does not proceed directly but via the dicarbonyl complex, which reacts with the phosphine in such a non-polar solvent to form the product. If the reaction is stopped at such a time when maximum amounts of the dicarbonyl complex are observed by infrared monitoring we have been able to recover up to 30% of the dicarbonyl complex [9].

The kinetically controlling step in the thermal decarbonylation is thus the initial loss of PPh_3 to form $(\eta^5$-$C_5H_5)Fe(CO)_2R$ via $(\eta^5$-$C_5H_5)Fe(CO)(\eta^2$-acyl), thus demonstrating that racemization of optically active starting acyl complexes during the decarbonylation is not related to the methyl migration process.

The results of the kinetic investigation into the loss of PPh_3, as measured by the initial appearance of the dicarbonyl complexes (up to 6% conversion), exhibit distinct rate variations between the methyl and silylmethyl complexes. Thus, the first order rate constants for the appearance of $(\eta^5$-$C_5H_5)Fe(CO)_2R$ are, $R = CH_3$, k 4.2×10^{-4} min^{-1}; $R = CH_2SiMe_3$, k 1.8×10^{-3} min^{-1}; $R = CH_2SiMe_2Ph$, k 1.4×10^{-3} min^{-1}. The two silylacetyl ligands expel the phosphine ligand more rapidly than the simple unsubstituted acetyl ligand. The extinction coefficients of the carbonyl bands in the dicarbonyl are greater than those of the related mono-



Scheme 1

carbonyls, and hence attempts to measure the rate of loss of the starting acyl complex via monitoring the reduction of the single CO band was impractical for the purposes of obtaining accurate rate data. Several studies have shown that the steric bulk of phosphine ligands contribute significantly to the rate of decarbonylation [3,4,13], i.e. greater steric bulk at the metal centre enhances expulsion reactions. It seems reasonable that the greater steric bulk of the silylacetyl groups is thus responsible for the rate enhancement observed in this study. The small but reproducible difference in rate between the trimethylsilyl- and dimethylphenylsilyl-acetyl groups may also be interpreted in this manner.

It is of interest that our attempts to decarbonylate the extremely bulky t-butyl complex $(\eta^5\text{-}C_5H_5)Fe(CO)(PPh_3)COBu^t$ uniformly failed [14]. In such experiments only decomposition of the complex was observed. It seems that the $COBu^t$ group is too bulky to undertake the intramolecular phosphine displacement reaction to form the π^2-acyl species. It appears that optimum size may be important in controlling the rate of these decarbonylations.

The significance of the facile loss of PPh_3 from acyl phosphine complexes may be further exemplified by a recent report concerning the catalysis by PPh_3 of the σ–π transformation, $(\eta^5\text{-}C_5H_5)Mo(CO)_3R$, (R = cyclopropylmethyl) → $(\eta^5\text{-}C_5H_5)Mo(CO)_2(\eta^3\text{-allyl})$. In the absence of phosphine the thermal σ–π transformation does not occur due to the higher energy requirement for CO loss compared to PPh_3 loss from a transient intermediate phosphino acyl complex [15].

Acknowledgements

This research was supported by the Robert A. Welch Foundation, Houston, Texas.

References

1 K.H. Pannell, J.M. Rozell, and J.M. Zeigler, Macromolecules, in press.

2 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.

3 A. Wojcicki, Advan. Organomet. Chem., 11 (1973) 87.

4 F. Caldarazzo and K. Noack, Coordin. Chem. Rev., 1 (1968) 118.

5 T.G. Attig, P. Reich-Rohrwig, and A. Wojcicki, J. Organomet. Chem., 51 (1973) C21.

6 H.R. Brunner and J. Strutz, Z. Naturforsch. B, 29 (1974) 446.
7 A. Davison and N. Martinez, J. Organomet. Chem., 74 (1974) C17.
8 K.H. Pannell, 29th Ann. Southwest Reg. Meet. Am. Chem. Soc., El Paso, TX, December 1973, abstract No. 35.
9 K.H. Pannell and J.R. Rice, J. Organomet. Chem., 78 (1974) C35.
10 H. Brunner and H. Vogt, Ang. Chem. Int. Ed. 20 (1981) 405.
11 S.R. Wu and A. Wojcicki, J. Organomet. Chem., 27 (1971) 231.
12 K.H. Pannell, Transition Met. Chem., 1 (1975/6) 36.
13 K.W. Barnett, T.G. Pollman, and W.T. Solomon, J. Organomet. Chem., 36 (1972) C23.
14 K.H. Pannell, A. Giasolli, and R.N. Kapoor, J. Organomet. Chem., 316 (1986) 315.
15 K.H. Pannell, R.N. Kapoor, M. Wells, A. Giasolli, and L. Parkanyi, Organometallics, 6 (1987) 663.