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PHOTOCHEMICAL STUDIES ON η^5-CYCLOPENTADIENYL(TRIPHENYLPHOSPHINE)NICKELALKYL AND -ARYL COMPOUNDS *

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Summary

Photo-induced degradation studies of a series of organonickel complexes of the type $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(R)$ (R = CH_3, C_2H_5, C_6H_5 and $C_6H_4CH_3$-*p*) as well as certain deuterated analogs have been undertaken. Photolysis of the methyl compound in benzene as well as benzene-d_6 gives methane as the major gaseous product, the photogenerated methyl group abstracting hydrogen from either the cyclopentadienyl ring, from the solvent, or from another methyl group. The photo-induced dealkylation of the ethyl compound gives both ethylene and ethane, and is explained by β-hydride elimination followed by subsequent reaction of the hydrido intermediate with additional ethyl compound. The photolysis of the phenyl and *p*-tolyl complexes in benzene solution leads to biaryl formation, both from the coupling of two coordinated aryl groups as well as interactions with the solvent. Triphenylphosphine is a product in all of these photo-decomposition studies.

Introduction

Recent studies in our laboratory have been concerned with photochemically-induced reactions of various σ-bonded organotransition metal compounds, including Group IVB metallocene dialkyls [1—6] and diaryls [4,7], $(\eta^5\text{-}C_5H_5)M(CO)_3CH_3$ (R = Cr, Mo, W) complexes [8,9], $(\eta^5\text{-}C_5H_5)Fe(CO)_2R$ (R = CH_3, C_2H_5, C_6H_5) complexes [10], as well as the homoleptic-type compounds tetraneopentylchromium and trimesitylchromium · tetrahydrofuranate [11]. In spite of an enormous amount of research concerning reactions of compounds which contain carbon—nickel σ-bonds [12], no detailed photochemical investi-

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gations on this important class of organometallic compounds have thus far been undertaken.

Our initial studies in this area, which are described in the present paper, have been concerned with the photo-induced degradation of alkyl- and aryl-nickel compounds of the type $(\eta^5\text{-}C_5H_5)Ni(PPh_3)R$ ($R = CH_3, C_2H_5, C_6H_5$, $p\text{-}C_6H_4CH_3$). This class of σ-bonded organonickel compounds was chosen for study, since a wide variety of derivatives containing various alkyl and aryl substituents are readily available [13,14], and since results of detailed thermal decomposition studies on these same compounds are available for comparison [15,16].

Results and discussion

Photolysis of $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(CH_3)$ and deuterated derivatives in benzene and benzene-d_6

Earlier studies [15,16] on the thermal degradation of $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(CH_3)$ indicated that methane was the principal gaseous product. Thermal degradation of the solid compound produced 92% methane and 8% ethane, whereas in xylene solution the methane/ethane ratio was 79/21. In our studies, when $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(CH_3)$ was photolyzed in benzene and the gas evolved was analyzed by gas chromatography, it was shown to contain 96% methane and 4% ethane. Photolysis of the methyl compound in benzene-d_6 resulted in 5% deuterated methane as CH_3D, which was identified by mass spectrometry (Table 1). Formation of methane could arise by abstraction of a hydrogen atom from the solvent, as shown by this experiment, from the cyclopentadienyl group, from a phenyl group, or from another methyl substituent. Ethane, however, must result from a bimolecular reaction. In order to further investigate the source of hydrogen in the formation of methane, certain deuterated analogs were employed.

Photolysis of $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(CD_3)$ resulted principally in the formation of CD_3H, although a small amount (6%) of CD_4 also resulted from bimolecular abstraction from another CD_3 group. Photolysis of this same compound in benzene-d_6 resulted as expected in a slightly increased yield of CD_4 (11%), however, the large percentage of CD_3H formed in this photolysis (56%) indicates that the principal photo-decomposition pathway involves hydrogen abstraction from a cyclopentadienyl ring. The relative large amount of CD_2H_2 (26—29%) formed in these photolyses may be indicative of methylene-nickel complexes as

TABLE 1

PERCENTAGE COMPOSITION OF THE GASEOUS PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(R)$ IN BENZENE AND BENZENE-d_6 SOLUTIONS

R	Solvent	CD_4	CD_3H	CD_2H_2	CH_3D	CH_4	C_2D_6	$C_2D_4H_2$	C_2H_6
CH_3	C_6H_6					96			4
CH_3	C_6D_6				5	92			3
CD_3	C_6H_6	6	60	26			5	3	
CD_3	C_6D_6	11	56	29			2	2	

TABLE 2

PERCENTAGE COMPOSITION OF THE GASEOUS PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF (η^5-C_5D_5)(PPh_3)Ni(R) IN BENZENE AND BENZENE-d_6 SOLUTIONS

R	Solvent	CD_4	CD_3H	CD_2H_2	CH_3D	CH_4	C_2D_6	C_2H_6
CH_3	C_6H_6				24	70		6
CH_3	C_6D_6				74	18		8
CD_3	C_6H_6	66	24				10	
CD_3	C_6D_6	90					10	

intermediates. These could abstract hydrogen atoms from either the cyclopentadienyl ring, or to a lesser extent, the solvent.

Photochemical studies on (η^5-C_5D_5)(PPh_3)NiR complexes are also consistent with these conclusions. When (η^5-C_5D_5)(PPh_3)Ni(CH_3) was photolyzed in benzene solution, 70% CH_4 and 24% CH_3D could be identified, whereas photolysis of this complex in benzene-d_6 lowered in CH_4/CH_3D ratio to 18/74 (Table 2). CD_4 was the principal product (66%) when (η^5-C_5D_5)(PPh_3)Ni(CD_3) was photolyzed in benzene solution, whereas similar photolysis in benzene-d_6 produced CD_4 as the sole methane product (90%). This latter result would seem to rule out hydrogen abstraction from the triphenylphosphine ligand as a source of methane formation.

Photolysis of (η^5-C_5H_5)(PPh_3)Ni(C_2H_5) in benzene and benzene-d_6

When (η^5-C_5H_5)(PPh_3)Ni(C_2H_5) was photolyzed in benzene solution, both ethylene and ethane were produced, in a 60/40 ratio (Table 3). This result is in marked contrast to earlier studies [15] on the thermal degradation of this compound in xylene solution, in which 99% ethylene and 1% ethane was reported to be produced. It is, however, consistent with related studies on the photoinduced degradation of (η^5-C_5H_5)Fe$(CO)_2C_2H_5$ [10] and of Mn$(CO)_5$(C_2H_5) [17,18] complexes, in which both ethylene and ethane are produced, with the former being obtained in slightly greater amount. As previously suggested in the thermal studies [15] on (η^5-C_5H_5)(PPh_3)Ni(C_2H_5) and in photochemical studies on related transition metal-ethyl systems [10,17], these results can best be interpreted in terms of a β-hydrogen elimination process to give an intermediate metal-ethylene hydride complex. The latter could serve as a source of the ethylene and also function as a reducing agent in the formation of ethane from another molecule of (η^5-C_5H_5)(PPh_3)Ni(C_2H_5). Photolysis of (η^5-C_5H_5)(PPh_3)Ni(C_2H_5) in benzene-d_6 afforded no deuterated ethane (Table 3), indicating that

TABLE 3

PERCENTAGE COMPOSITION OF THE GASEOUS PRODUCTS OBTAINED FROM THE PHOTOLYSIS OF (η^5-C_5H_5)(PPh_3)Ni(C_2H_5) IN BENZENE AND BENZENE-d_6 SOLUTIONS

Solvent	C_2H_4	C_2H_6	C_2DH_5
C_6H_6	60	40	
C_6D_6	58	42	<1

TABLE 4

PERCENTAGE COMPOSITION OF THE PHOTOLYSIS PRODUCTS OF $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(C_6H_4CH_3\text{-}p)$ IN BENZENE SOLUTION

Compound	Ratio (%)
4,4'-Dimethylbiphenyl	45
4-Methylbiphenyl	3
Biphenyl	18
Triphenylphosphine	34

the solvent was not a source of hydrogen in ethane formation. Moreover, no n-butane could be detected in any photolytic decomposition of $(\eta^5\text{-}C_5H_5)Ni(PPh_3)(C_2H_5)$, indicating that radical formation and subsequent coupling does not occur in this process.

Photolysis of $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(C_6H_5)$ and $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(C_6H_4CH_3\text{-}p)$ in benzene and benzene-d_6

Photochemical degradation of $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(C_6H_5)$ in benzene solution led to the formation of triphenylphosphine as well as biphenyl in low yield. In order to determine the source of the biphenyl, photolysis of the phenyl compound in benzene-d_6 was also investigated. Analysis of the product by mass spectrometry indicated its percentage composition to be biphenyl-d_0 (3%), biphenyl-d_5 (11%), and biphenyl-d_{10} (86%). Thus, the majority of the biphenyl obtained in this photolysis arises from the coupling of two solvent molecules, and only a small percentage from either inter-molecular dimerization or attack of phenyl radicals on the solvent to give biphenyl-d_5. Remarkably, biphenyl-d_{10} was also a significant product in the photolysis of $(\eta^5\text{-}C_5H_5)Fe(CO)_2(C_6H_5)$ in benzene-d_6 [10]. Further studies on related phenyl derivatives of the transition metals are in progress to better understand these results [18].

The photolysis of $(\eta^5\text{-}C_5H_5)(PPh_3)Ni(C_6H_4CH_3\text{-}p)$ in benzene solution led to the formation of four organic products, which were identified by gas chromatography and mass spectrometry. These products were shown to be 4,4'-dimethylbiphenyl, 4-methylbiphenyl, biphenyl and triphenylphosphine, which were formed in percentage ratios of 45%, 3%, 18%, and 34%, respectively (Table 4). Here again, combination of solvent molecules (to form biphenyl) appears to be a significant reaction pathway, although the major pathway involves a bimolecular process, leading to 4,4'-dimethylbiphenyl (Table 4). It is important to note that no detectable amount of toluene was formed under these photolytic conditions, in contrast to similar photolytic studies on $(\eta^5\text{-}C_5H_5)_2Ti(C_6H_4CH_3\text{-}p)_2$ [7].

Experimental section

All reactions were carried out in an argon atmosphere. The argon was dried with H_2SO_4 and P_2O_5 and trace amounts of oxygen were removed using BTS catalyst. Solvents were dried and freshly distilled under argon. Column chromatography was carried out under argon using Ventron-Alfa neutral grade alumina which had been deactivated with 5% water and degassed. Photolyses were conducted by means of a 450 W Hanovia photochemical lamp located in a quartz, water-cooled immersion well. This unit was placed ca. 7—10 cm from a Schlenk tube containing the solution to be photolyzed. Gas chromatographic analyses were performed on a Varian series 2400 gas equipped with a flame ionization detector. Gas samples were separated on a 6 ft Porapak Q column and spiked with known materials. The organic compounds were separated on a 5 ft 15% OV-101 column and the individual peaks were compared with known samples. Corrections were made for the response factor of each organic compound measured. Proton NMR spectra were recorded on a Varian A-60 spectrometer. Mass spectra were recorded on a Perkin-Elmer-Hitachi RMU GL instrument operating at ca. 20—30 eV to minimize fragmentation. Corrections for any fragmentation in the analysis of deuterated methanes obtained under photolytic conditions were made by comparisons with spectra of standard deuterated methanes analyzed under similar conditions. All spectra are the average of several runs. Toluene-free benzene was prepared by an overnight reflux with basic $KMnO_4$ followed by fractional distillation. The compounds $(\eta^5\text{-}C_5H_5)Ni(PPh_3)R$ (R = CH_3, C_2H_5, C_6H_5 and $C_6H_4CH_3\text{-}p$) were prepared by literature methods (13).

Preparation of cyclopentadienylthallium-d_5

A modification of a literature procedure [19] was used. A solution of sodium deuteroxide was prepared under argon from 11.5 g (0.5 mol) of sodium and 100 ml of D_2O (99.9% D) which was cooled in an ice bath. To this solution was added with stirring 3.3 g (0.05 mol) of freshly distilled cyclopentadiene, and stirring was continued for 14 h at ambient temperature. Thallium chloride (12.4 g, 0.05 mol) which had been previously dried in a vacuum over at 70°C was added to the above solution and the mixture was stirred for 5 h. The product was separated by filtration and sublimed at 95°C/10^{-3} mmHg. Mass spectroscopic analysis of the light yellow crystalline sublimate showed it to contain 84% C_5D_5Tl (*m/e* at 275 and 273, from ^{205}Tl and ^{203}Tl, respectively) and 16% C_5D_4HTl (*m/e* at 274 and 272). This ratio corresponds to 97% deuterated cyclopentadienylthallium from the overall ratio of deuterium to hydrogen content. The yield was 86%.

Preparation of nickelocene-d_{10}

Modification of several literature methods [20,21] were employed. In a 250 ml, 3-necked flask containing 50 ml of 1,2-dimethoxyethane and 2.40 g (0.04 mol) of nickel powder, 2.5 ml of bromine was added dropwise with stirring. When the reaction was completed, the solvent was removed under reduced pressure. A portion of this freshly prepared nickel bromide (2.185 g, 0.01 mol) and 5.48 g (0.02 mol) of C_5D_5Tl was mixed in 50 ml of benzene. After stirring for 6 h at 40°C, the green solution was filtered, the solvent was removed under reduced pressure, and a green solid was collected. The product was purified by sublimation at 80°C/10^{-2} mmHg. The yield was 45%.

Preparation of $(\eta^5\text{-}C_5D_5)(PPh_3)Ni(CH_3)$ and $(\eta^5\text{-}C_5D_5)(PPh_3)Ni(CD_3)$

These deuterated compounds were prepared via a disproportionation reaction between $(PPh_3)_2NiCl_2$ and nickelocene-d_{10}, followed by methylation of the resulting (η^5-C_5D_5)(PPh_3)NiCl intermediate by means of either CH_3Li or CD_3Li, respectively. Standard published procedures [13,14] were used in each case.

Photolysis of (η^5-C_5H_5)(PPh_3)Ni(CH_3) and deuterated analogs in benzene and benzene-d_6 solutions

A solution of 0.10 g (ca. 0.25 mmol) of the compound in 20 ml of benzene was irradiated in a Pyrex Schlenk tube for 12 h while stirring via a magnetic stirrer in an argon atmosphere, during which time the solution changed color from green to brown. The gas phase was analyzed by gas chromatography. The deuterium content of the methane and ethane was derived from mass spectroscopic data (Tables 1 and 2). Triphenylphosphine was always one of the photochemical degradation products. The photolyzed solution was passed through a column of alumina under argon and was eluted with hexane and ethyl ether. After removing the solvent under reduced pressure, the residue was sublimed and the triphenylphosphine was identified from its melting point (78—80°C) and mass spectrum, which contained a major peak for the parent ion at *m/e* 262. When solutions were chromatographed in air and the solid was sublimed, the product isolated was triphenylphosphine oxide, as evidenced by its melting point (156—157°C) as well as its mass spectrum (M^+, *m/e* 278). In most runs, a colored band could be eluted with benzene. After evaporation of the solvent, a brown residue was obtained which could not be further identified.

Photolysis of (η^5-C_5H_5)(PPh_3)Ni(C_2H_5) in benzene and benzene-d_6 solutions

A solution of 0.104 g (0.25 mmol) of the complex in 20 ml of benzene was photolyzed under similar conditions as for the methyl derivative. The gas phase was analyzed by gas chromatography, and the deuterium content of the products was derived from mass spectrometric data (Table 3).

Photolysis of (η^5-C_5H_5)(PPh_3)Ni(C_6H_5) in benzene and benzene-d_6 solutions

A solution of 0.116 g (0.25 mmol) of the complex in 20 ml of benzene was photolyzed as above for 24 h. The resulting solution was chromatographed over silica gel and eluted with 20 ml of benzene-hexane (1/1) followed by 20 ml of acetone. The solvents were removed at room temperature and the solid materials were identified by both gas chromatographic and mass spectrometric methods. The benzene-hexane solution contained biphenyl (12% yield) which showed peaks at *m/e* 154 and *m/e* 77, corresponding to [$C_{12}H_{10}^+$] and [$C_6H_5^+$] ions, respectively. When photolysis was carried out in benzene-d_6, the mass spectrum showed three peaks at *m/e* 164 (86%), *m/e* 159 (11%), and *m/e* 154 (3%), corresponding to the ions [$C_{12}D_{10}^+$], [$C_{12}D_5H_5^+$] and [$C_{12}H_{10}^+$], respectively. Triphenylphosphine was also identified by mass spectrometry as part of the material obtained from evaporation of the acetone solution.

Photolysis of (η^5-C_5H_5)(PPh_3)Ni($C_6H_4CH_3$-p) in benzene solution

A solution of this compound (0.119 g, 0.25 mmol) in 25 ml of toluene-free benzene was photolyzed as above for 18 h. The resulting solution was passed through a column of alumina, eluting with benzene, hexane, and finally with ethanol and ethyl ether. The green band eluted with benzene contained unreacted starting complex. The colorless bands eluted with hexane, ethanol and ethyl ether contained photolysis products and were combined. An insoluble residue remained on the column. The solvents were removed and the resulting solid was weighed, corresponding to 40% of the original complex. This mixture was dissolved in toluene-free benzene and analyzed. Each product was identified by both gas chromatography and mass spectrometry (Table 4).

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