Journal of Organometallic Chemistry, 427 (1992) 349–353
Elsevier Sequoia S.A., Lausanne
JOM 22434

Photochemical reactions of $[(Ph_3P)_2ReH_7]$ and $[(Ph_2PCH_2CH_2PPh_2)ReH_7]$

Denise Baudry, Jean-Michel Cormier and Michel Ephritikhine
Service de Chimie Moléculaire, DSM, DRECAM, CNRS URA 331, CEA-CEN Saclay, 91191 Gif sur Yvette (France)

(Received July 26, 1991)

Abstract

$[(Ph_3P)_2ReH_7]$ (Ia) reacted in tetrahydrofuran with cyclopentadiene or cyclohexa-1,4-diene under UV irradiation to give $[(Ph_3P)(\eta\text{-}C_5H_5)ReH_4]$ (II), and a 1:2 mixture of $[(Ph_3P)_2(\eta\text{-}C_6H_6)ReH]$ and $[(Ph_3P)(\eta\text{-}C_6H_6)ReH_3]$ (III), respectively; III was isolated from the photochemical reaction of Ia with 3,3-dimethylbutene in benzene. When using $[(dppe)ReH_7]$ (Ib) (dppe = $Ph_2PCH_2CH_2PPh_2$) instead of Ia in these three reactions, no cyclopentadienyl compound was obtained, but $[(dppe)(\eta\text{-}C_6H_6)ReH]$ (IV) and $[(dppe)(\eta\text{-}C_6H_6)ReCH_2CH_2CMe_3]$ (V) were isolated; IV and V are precursors to arene and cyclohexadienylrhenium derivatives containing dppe.

Introduction

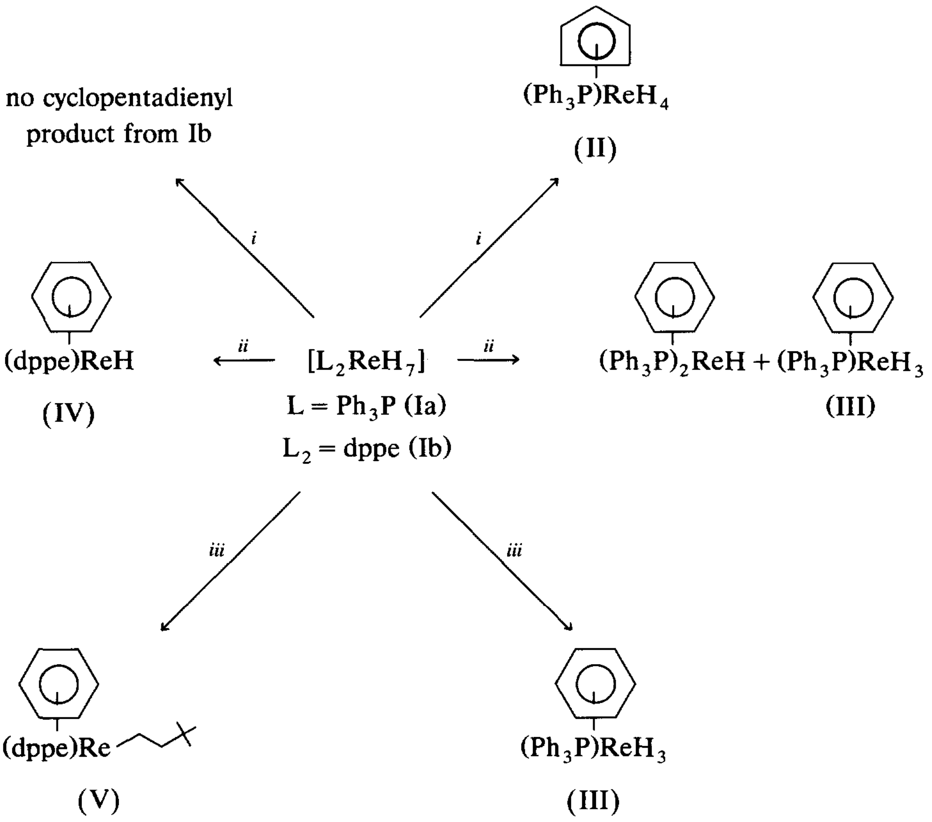
Bisphosphine rhenium heptahydrides such as $[(Ph_3P)_2ReH_7]$ (Ia) are unstable thermally and easily eliminate dihydrogen [1]. Reaction of Ia with cyclopentadiene or cyclohexadiene in tetrahydrofuran (THF) afforded the dienetrihydrido-compound $[(Ph_3P)_2(\eta\text{-}1,3\text{-diene})ReH_3]$ [2] and its treatment with 3,3-dimethylbutene in benzene gave the cyclohexadienyldihydrido-derivative $[(Ph_3P)_2(\eta\text{-}C_6H_7)ReH_2]$ [3]. Under the same conditions, the heptahydride $[(dppe)ReH_7]$ (Ib), (dppe = $Ph_2PCH_2CH_2PPh_2$) is remarkably inert; this different behaviour has not been explained. We have found that both Ia and Ib are activated by UV light to give products which depend markedly on the phosphine ligand; here we report the synthesis, characterization and some reactions of these compounds.

Results and discussion

Compound Ia was irradiated for 75 min (quartz vessel, 100 W Hg lamp) at 20°C in tetrahydrofuran (THF) in the presence of cyclopentadiene (Scheme 1); the

---

Correspondence to: Professor M. Ephritikhine, Service de Chimie Moleculaire, Bat. 125, CEA-CEN Saclay, 91191 Gif sur Yvette, France.



Scheme 1. Reagents and conditions. *i*: cyclopentadiene in THF; *ii*: 1,4-cyclohexadiene in THF; *iii*: 3,3-dimethylbutene in benzene. All reactions at 20°C under UV irradiation.

orange product $[(Ph_3P)(\eta\text{-}C_5H_5)ReH_4]$ (II) (30% yield), which has been characterized by its NMR spectrum, was previously obtained by photolysis of $[(Ph_3P)_3ReH_5]$ and cyclopentadiene in THF [4]. Similar treatment of Ia with cyclohexadiene afforded a mixture of $[(Ph_3P)_2(\eta\text{-}C_6H_6)ReH]$ [3] and $[(Ph_3P)(\eta\text{-}C_6H_6)ReH_3]$ (III) in the ratio 1:2. The arene rhenium trihydride complex III was the only organometallic compound formed by irradiation of Ia and 3,3-dimethylbutene in benzene, and was isolated as pale yellow crystals (50% yield). That the complexes $[(Ph_3P)_2(\eta\text{-}1,3\text{-diene})ReH_3]$ and $[(Ph_3P)_2(\eta\text{-}C_6H_7)ReH_2]$ are likely intermediates in these UV-induced reactions of Ia was indicated by irradiating them, which gave, in similar yield, the same products as obtained directly from Ia. It is noteworthy that photodissociation of a phosphine ligand is prefered over H_2 elimination in these photochemical processes [4].

When Ia was replaced by Ib, no cyclopentadienyl compound could be detected (Scheme 1, reaction i), whereas reactions ii and iii gave the yellow arene complexes IV and V. The formation of the alkyl compound V is reminiscent of the formation of $[(PhMe_2P)_2(\eta\text{-}C_6H_6)ReCH_2CH_2CMe_3]$ by photolysis of a benzene solution of $[(PhMe_2P)_3ReH_5]$ and *t*-butylethylene [4]. The chelating dppe ligand clearly favours H_2 elimination in the photochemical reactions of Ib.

Table 1

NMR spectra of the complexes [a]

Compound	Phosphine ligand	Arene or dienyl ligand	Hydride or alkyl ligand
$[(Ph_3P)(C_5H_5)ReH]$ (II)	7.3 (m, 15H)	4.45 (s, 5H)	−8.70 (d, 20, 4H)
$[(Ph_3P)(C_6H_6)ReH_3]$ (III)	7.80 and 7.15 (m, 15H)	4.60 (s, 6H)	−7.90 (d, 25, 3H)
$[(dppe)(C_6H_6)ReH]$ (IV)	7.3 (m, 20H) 2.7 and 2.4 (m, 4H)	4.15 (s, 6H)	−9.45 (t, 36, 1H)
$[(dppe)(C_6H_6)ReCH_2CH_2CMe_3]$ (V)	7.5 and 7.0 (m, 20H) 2.2 and 1.9 (m, 4H)	4.35 (s, 6H)	0.7 (m, 2H, β-CH_2), 0.60 (s, 9H, Me) 0.1 (m, 2H, α-CH_2)
$[(dppe)(C_6H_6)ReH_2][BF_4]$ (VI)	7.6 (m, 20H) 2.65 and 2.60 (m, 4H)	6.0 (s, 6H)	−9.60 (t, 40, 2H)
$[(dppe)(C_6H_7)ReH_2]$ (VII)	7.8 and 7.2 (m, 20H)	6.4 (t, 5, 1H, 3-H) 4.9 (t, 5, 2H, 2,4-H) 4.4 (m, 1H, 6 *exo*-H)	[b]
	2.9 and 2.1 (m, 7H, PCH_2 and 1,5-H and 6-*endo* H)		
$[(dppe)(C_6H_6)Re(CO)][BF_4]$ (VIII)	7.5 (m, 20H)	5.60 (s, 6H)	
$[(dppe)(C_6H_7)Re(CO)]$ (IX)	8.0 and 7.1 (m, 20H)	6.0 (t, 5, 1H, 3-H) 4.4 (t, 5, 2H, 2,4-H) 3.9 (m, 1H, 6 *exo*-H)	
	2.6 and 2.1 (m, 7H, PCH_2 and 1,5-H and 6-*endo* H)		

[a] At 25°C MHz (except III and VI which were measured at 200 MHz), in benzene-d_6 (except II and IV which were measured in dichloromethane-d_2, and VI and VIII in acetone-d_6). δ relative to TMS (multiplicity, *J* in Hz, intensity, assignment). [b] The hydride resonances are visible on the spectrum recorded at −20°C in dichloromethane-d_2: −4.18 (t, 40, 1H) and −14.5 (dt, 10 and 40, 1H).

Complexes IV and V are precursors of arene and cyclohexadienyl rhenium derivatives with the dppe ligand. The hydride IV was protonated by HBF_4 in diethylether to produce the colourless cationic dihydride $[(dppe)(\eta\text{-}C_6H_6)ReH_2][BF_4]$ (VI) (quantitative yield). The latter was transformed back into IV by treatment with NaOMe in methanol, and its reaction with $LiAlH_4$ afforded the yellow cyclohexadienyl complex $[(dppe)(\eta\text{-}C_6H_7)ReH_2]$ (VII) (70%). Protonation of V under CO led to the formation of the orange carbonyl compound $[(dppe)(\eta\text{-}C_6H_6)Re(CO)][BF_4]$ (VIII) (85%), which reacted with $LiAlH_4$ to give the yellow cyclohexadienyl derivative $[(dppe)(\eta\text{-}C_6H_7)Re(CO)]$ (IX) (70%).

The new complexes (with the exception of IV) have been characterized by their elemental analyses (C, H, P), their mass spectra and their ^1H NMR spectra (Table 1).

Experimental

Microanalyses were carried out by the Service Central d'Analyses du CNRS. The ^1H NMR spectra (Table 1) were recorded on Bruker WP-80/CW or WP-200/SY instruments. Chemical shifts are relative to tetramethylsilane. The IR spectra were recorded in nujol mulls on a Perkin-Elmer Infracord 137 instrument.

The mass spectra of cationic complexes were recorded on an AEI MS 80 instrument equipped with a fast atom bombardment source and those of the neutral complexes on an AEI MS-50 spectrometer (the masses are given for ^{187}Re). Photolyses were carried out in a quartz vessel by using a medium pressure Hg lamp (Hanau, 100 W for the triphenylphosphine complexes, 450 W for Ib).

All experiments were carried out under dinitrogen using standard Schlenk techniques. Evaporations were carried out under reduced pressure. Solvents were dried and deoxygenated by standard methods and distilled before use. $LiAlH_4$ (Prolabo), $HBF_4 \cdot Et_2O$ (Ega Chimie), 3,3-dimethylbutene and dienes (Fluka) were used without purification. Alumina (Merck) was grade II–III. $[(Ph_3P)_2ReH_7]$ [1,2], $[(dppe)ReH_7]$ [1], $[(Ph_3P)_2(C_6H_8)ReH_3]$ [2] and $[(Ph_3P)_2(C_6H_7)ReH_2]$ [3] were prepared by published methods.

$[(Ph_3P)(C_5H_5)ReH_4]$ (II)

A solution of Ia (400 mg) and cyclopentadiene (1 ml) in THF (90 ml) was irradiated at 20°C for 75 min. After evaporation of the solvent, II was extracted with methanol and characterized by its NMR spectrum [4]; it was formed in *ca.* 40% yield.

$[(Ph_3P)(C_6H_6)ReH_3]$ (III)

From Ia. A solution of Ia (400 mg) and 3,3-dimethylbutene (1.5 ml) in benzene (250 ml) was irradiated for 2 h. The solvent was evaporated and the residue was chromatographed on alumina: Ph_3P was eluted with a mixture of pentane and acetone (in proportions 99:1) and III by the mixture pentane–acetone 85:15. After evaporation, a yellow powder of III was obtained (148 mg, 50%); the analytical sample was prepared by recrystallization from the mixture pentane–acetone. Analysis. Found: C, 54.60; H, 4.65; P, 5.95. $C_{24}H_{24}PRe$ calcd.: C, 54.34; H, 4.53; P, 5.85%. IR: 2000, 1960 cm^{-1}. Mass spectrum: $m/e = 527$ $(M-3)$.

From $[(Ph_3P)_2(C_6H_7)ReH_2]$. A solution of the cyclohexadienyldihydrido-complex (400 mg) in benzene (90 ml) was irradiated for 1 h. The reaction mixture was treated as before and III was isolated in 60% yield.

From $[(Ph_3P)_2(C_6H_8)ReH_3]$. A solution of the dienetrihydrido-compound (200 mg) in THF or benzene (90 ml) was irradiated for 30 min. The reaction mixture was treated as before, leading to a mixture (70 mg) containing III (65%) and $[(Ph_3P)_2(C_6H_6)ReH]$ (35%), which was characterized by NMR [2].

$[(dppe)(C_6H_6)ReH]$ (IV)

A solution of Ib (400 mg) and cyclohexa-1,4-diene (2 ml) in THF (180 ml) was irradiated for 4 h. The solvent was evaporated and the residue was dissolved in diethyl ether (50 ml). Addition of $HBF_4 \cdot Et_2O$ (50 μl) led to the precipitation of VI. The brown solid was filtered off, washed with Et_2O, dried under vacuum, and dissolved in acetone. Addition of NaOMe (50 mg) in methanol (10 ml) gave a yellow solution which was evaporated to dryness. The residue was extracted with Et_2O and after evaporation, IV was obtained as a yellow oil.

$[(dppe)(C_6H_6)ReCH_2CH_2CMe_3]$ (V)

A solution of Ib (300 mg) and 3,3-dimethylbutene (2 ml) in benzene (180 ml) was irradiated for 2.5 h. The solvent was evaporated off and the residue was chromatographed on alumina. The yellow product was eluted with cyclohexane and, after evaporation, V was isolated as a yellow powder (120 mg, 31%). Yellow needles were obtained by recrystallization from acetone at −30°C. Analysis. Found: C, 60.81; H, 5.64; P, 8.33; $C_{38}H_{43}P_2Re$ calcd.: C, 60.96; H, 5.75; P, 8.29%. Mass spectrum: $m/e = 748$ (M).

[(dppe)(C_6H_6)ReH_2][BF_4] (VI)

$HBF_4 \cdot Et_2O$ (50 μl) was added to a solution of IV (100 mg) in diethyl ether (20 ml). Colourless microcrystals immediately deposited; these were filtered off, washed with Et_2O, and dried under vacuum (111 mg, 98%). Analysis. Found: C, 50.95; H, 4.47; P, 8.18; $C_{32}H_{32}BP_2F_4Re$ calcd.: C, 51.06; H, 4.25; P, 8.24%. IR: 1100, 875, 830, 745 and 705 cm^{-1}. Mass spectrum: $m/e = 663$ ($M - 89(BF_4 + H_2)$).

[(dppe)(C_6H_7)ReH_2] (VII)

$LiAlH_4$ (100 mg) was added to a solution of VI (100 mg) in diethyl ether (20 ml). The reaction mixture was stirred for 1h, hydrolyzed with a few drops of water, and filtered. The solvent was evaporated and the residue was extracted with CH_2Cl_2. After evaporation, the yellow product was recrystallized from acetone (60 mg, 68%). Analysis. Found: C, 57.78; H, 4.95; P, 9.28; $C_{32}H_{33}P_2Re$ calcd.: C, 57.65; H, 4.95; P, 9.31%. IR: 1920, 1870 cm^{-1}. Mass spectrum: $m/e = 663$ ($M - 3$).

[(dppe)(C_6H_6)Re(CO)][BF_4] (VIII)

Carbon monoxide was bubbled into a solution of V (65 mg) in Et_2O (20 ml) and $HBF_4 \cdot Et_2O$ (60 μl) was added into the solution. Yellow microcrystals immediately formed; these were filtered off, washed with Et_2O, dried under vacuum and recrystallized from an acetone-methanol mixture (1:10) at −30°C (58 mg, 85%). IR: 1910, 1100 cm^{-1}. Mass spectrum: $m/e = 691$ ($M - 87$ (BF_4)), 663 ($M - 115$ (BF_4 + CO)).

[(dppe)(C_6H_7)Re(CO)] (IX)

$LiAlH_4$ (60 mg) was added to a solution of VIII (60 mg) in diethyl ether (20 ml). The reaction mixture was stirred for 1 h, hydrolyzed with a few drops of water, and filtered. The solvent was evaporated off and the residue was extracted with CH_2Cl_2. After evaporation, the pale yellow product was recrystallized from acetone (37 mg, 70%). Analysis. Found: C, 57.23; H, 4.57; P, 9.00; $C_{33}H_{31}OP_2Re$ calcd.: C, 57.22; H, 4.48; P, 8.96%. Mass spectrum: $m/e = 692$ (M) and 664 ($M - 28$ (CO)).

Acknowledgments

The authors are grateful to Dr. H. Felkin for helpful discussions.

References

1 J. Chatt and R.S. Coffey, J. Chem. Soc. (A), (1969) 1963.

2 D. Baudry, M. Ephritikhine and H. Felkin, J. Organomet. Chem., 224 (1982) 363; W.D. Jones and J.A. Maguire, Organometallics, 4 (1985) 951.

3 D. Baudry, P. Boydell and M. Ephritikhine, J. Chem. Soc., Dalton Trans., (1986) 525.

4 M.A. Green, J.C. Hufman, K.G. Caulton, W.K. Rybak and J.J. Ziolkowski, J. Organomet. Chem., 218 (1981) C39.