vapor pressure equation[19] and boiling point[19] were 4.25×10^4 mm. and 378.89°K. The $P_E + P_A$ sum was 20.19 cc. mole^{-1}. The mean value of the dipole moment of methoxysilane is 1.166 D., the estimated standard deviation of this mean being ±0.0004 D.

The mean of the least-squares values of $P_E + P_A$ for disiloxane is 27.68 cc. mole^{-1}. The electronic polarization, P_E, estimated from the bond refraction values,[21] 3.17 and 1.80, for Si–H and Si–O is 22.62 cc. mole^{-1}, which gives P_A = 5.06 cc. mole^{-1}. For methoxysilane, the group and bond refraction values, Si–O–CH_3 = 8.284[2b] and Si–H = 3.17,[21] gave P_E = 17.79 cc. mole^{-1}, so that P_A = 2.40 cc. mole^{-1}.

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[21] A. I. Vogel, W. T. Cresswell, and J. Leicester, *J. Phys. Chem.*, **58**, 174 (1954).

CONTRIBUTION FROM THE RESEARCH LABORATORIES,
ETHYL CORPORATION, FERNDALE 20, DETROIT MICHIGAN

he Addition of Dicyclopentadienylrhenium Hydride to Some Acetylenes

BY MICHAEL DUBECK AND RAYMOND A. SCHELL

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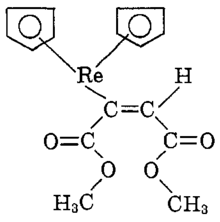
Dicyclopentadienylrhenium hydride reacts with dimethylacetylene dicarboxylate to form a dicyclopentadienylrhenium-substituted dimethyl maleate. Methyl propiolate reacts similarly to yield a dicyclopentadienylrhenium-substituted acrylate. The maleate–rhenium complex can be readily isomerized to the fumarate form with platinum. Hydrogenation of the maleate over platinum produces a cyclopentylcyclopentadienylrhenium-substituted dimethyl fumarate.

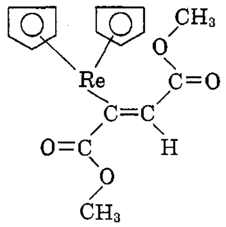
In contrast to a number of studies on the reactions of transition metal carbonyls and their derivatives with acetylenes,[1,2] the behavior of the transition metal cyclopentadienyls has received little published attention. Of the latter class of compounds, only dicyclopentadienylnickel is known to yield stable products with acetylenes.[3] Our present studies in this area of transition metal derivatives not containing carbonyls show that dicyclopentadienylrhenium hydride reacts with some acetylenes to form novel products.

Results

Dicyclopentadienylrhenium hydride reacts almost instantaneously with dimethylacetylene dicarboxylate in tetrahydrofuran at room temperature. The reaction will also occur in other solvents, such as diethyl ether, but at a reduced rate. The resulting product has been assigned a structure corresponding to a dicyclopentadienylrhenium-substituted dimethyl maleate (I). Treatment of the maleate-type complex with platinum in benzene at 70° readily transforms it into the corresponding geometric isomer II. Although both complexes possess very similar infrared spectra, II is bright red in color as opposed to a dark amber-red for I. Both complexes possess similar chemical properties, being unstable in air but inert toward water. However, solubilities in organic solvents differ markedly—I is quite soluble in diethyl ether, benzene, and methanol, whereas the isomer II exhibits only slight solubility in ether and is moderately soluble in benzene and methanol. As is characteristic of dicyclopentadienylrhenium hydride, the complexes I and II behave as bases. They can be extracted from organic solvents, such as benzene or diethyl ether, with 10% aqueous sulfuric acid and are reliberated into the organic phase by neutralizing the acid.



I

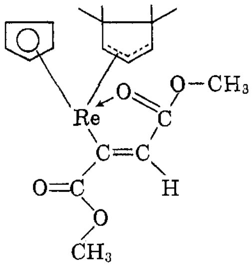


II

In an attempt to determine the stability of these materials to strong acid, a solution of I in 10% aqueous sulfuric acid was allowed to stand for 18 hr. The acid was then neutralized and I was extracted from the aqueous phase and crystallized from diethyl ether, with a recovery of approximately 50%. This observation illustrates the remarkable inertness of this particular rhenium–carbon σ-bond to protolytic attack.

Hydrogenation of I over platinum in ethanol at atmospheric pressure and room temperature yields an extremely dark red diamagnetic complex for which structure III is assigned and which corresponds to a cyclopentenylcyclopentadienylrhenium-substituted dimethyl fumarate. A strong coordinate bond exists between the *cis* carbonyl group and rhenium.

Compound III exhibits oxidative instability similar



III

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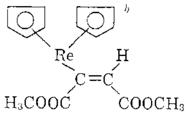
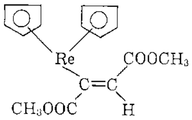
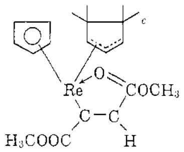
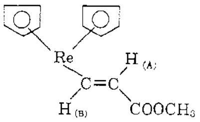
[1] M. A. Bennett, *Chem. Rev.*, **62**, 611 (1962).

[2] P. M. Treichel, E. Pitcher, and F. G. A. Stone, *Inorg. Chem.*, **1**, 511 (1962).

[3] M. Dubeck, *J. Am. Chem. Soc.*, **82**, 502 (1960); *ibid.*, **82**, 6193 (1960).

TABLE I

NUCLEAR MAGNETIC RESONANCE ABSORPTIONS OF THE ADDUCT COMPLEXES

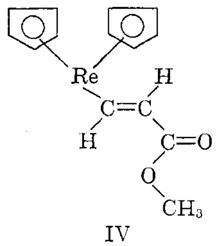
Complex	τ[a] (benzene)	τ (deuterio-chloroform)	Relative intensity	Hydrogen assignment
 [b]	6.28 s	6.47 s	6	Methoxyl
	5.52 s	5.68 s	10	Cyclopentadienyl
	3.52 s	3.27 s	1	Vinyl
	6.34 s		3	Methoxyl
	6.08 s		3	Methoxyl
	5.65 s		10	Cyclopentadienyl
	3.06 s		1	Vinyl
 [c]	6.70 s		3	Methoxyl
	5.37 s		3	Methoxyl
	5.34 s		5	Cyclopentadienyl
	3.43 s		1	Vinyl
		6.41 s	3	Methoxyl
		5.28 s	10	Cyclopentadienyl
		3.96 d, J = 16 c.p.s.	1	Vinyl $H_{(A)}$
		−0.32 d, J = 16 c.p.s.	1	Vinyl $H_{(B)}$

[a] The chemical shifts were determined with a 60-Mc. Varian 4300 spectrometer (s, singlet; d, doublet). Tetramethylsilane was employed as an internal standard only in the case of deuteriochloroform. [b] The n.m.r. of this complex in 5% aqueous sulfuric acid revealed a metal hydride singlet at 10.6 p.p.m. upfield from the internal standard, sodium 3(trimethylsilyl)-1-propane sulfonate. This signal is of equal intensity to the lone olefinic proton at −6.66 p.p.m. downfield from the standard. [c] Complex multiplets attributed to the cyclopentenyl ring are present at τ 5.10, 5.74, 7.05, 7.21, 7.51, and 8.73.

to that of I and II and is stable to water. Compound III does not exhibit basic properties and cannot be extracted from organic solutions with 10% sulfuric acid. The solubility of III in organic solvents is widespread, as it is quite soluble in petroleum ether, benzene, carbon disulfide, alcohols, diethyl ether, and acetone. The complex possesses the unique property of imparting a deep amber color to solutions in organic media, even in relatively high dilution.

Attempted hydrogenation of I in acetic acid over platinum failed to produce complex III because of excessive decomposition. However the experiments proved valuable in that dimethyl succinate, dimethyl fumarate, and dimethyl maleate were detected in the reaction mixtures. These fragments support our proposed structures which clearly illustrate the absence of any carbon–carbon bond formation between the reactants.

Methyl propiolate forms an adduct with dicyclopentadienylrhenium hydride in a manner analogous to the acetylenic diester. The reaction is best performed in ethanol at room temperature using stoichiometric quantities of the reactants. Structurally, the product is a β-substituted dicyclopentadienylrhenium methyl acrylate, IV. Its properties are similar to that of I in that it is oxidatively unstable, possesses similar solubility characteristics, and is basic, being readily soluble in aqueous sulfuric acid. In contrast to complex I, however, the methyl propiolate adduct cannot be hydrogenated or isomerized over platinum and is recovered unchanged under conditions that promote reaction in the case of the diester adduct.



IV

Although dicyclopentadienylrhenium hydride readily forms adducts with the acetylenic esters, it is inert toward acetylene and 3-hexyne at room temperature. At elevated temperatures in the region of 70–150°, acetylene forms resinous materials with the rhenium complex. The rhenium hydride derivative will not react with the olefinic esters, dimethyl maleate and dimethyl fumarate.

The nuclear magnetic resonance spectra for all of the rhenium complexes, which presently provide the principal basis for the structural assignments, are summarized in Table I.

Discussion

The addition of dicyclopentadienylrhenium hydride to the acetylene bond occurs in a *cis* manner to yield the structures of the primary adducts I and IV. Even in the absence of supporting structure proofs, which will be discussed, a *cis* addition could be inferred from the nature of the reactants and the mild conditions under which reaction occurs. The rhenium hydride linkage is a thermally stable one both in solution and as a pure melt. Under the conditions of reaction with the acetylenic esters and the isolation of only one adduct product, it is highly unlikely that an ionic or a free radical type of addition occurs which could yield the *trans* addition product II as the kinetically controlled primary adduct. A more probable mechanism would be one involving a simple four-center transition complex in which the spatial arrangement of the four groups about the original acetylenic linkage approximates that designated by structures I and IV.

The structural assignments for each of the four new rhenium complexes, and consequently the validity of the proposed *cis* addition, are based primarily on nuclear magnetic resonance (n.m.r.) data. Although n.m.r. on the initial adduct, I, cannot distinguish between the ester groups being disposed *cis* or *trans*, the easy interconversion of this adduct into its geometric isomer II allows a reasonable assignment by comparing the n.m.r. spectra of the two isomers. As shown in Table I, the chemical shifts of the ten cyclopentadienyl and one lone vinyl type hydrogens are essentially the same for the initial adduct and its isomerized form. However, the methoxy hydrogens of the initial adduct in benzene display a single absorption at τ 6.47, whereas the isomerized material possesses two shifts for the methoxy hydrogens at τ 6.34 and 6.08. Of the two compounds, the methoxy hydrogens in the *cis* adduct (I) are in a more similar environment than those in structure II designated for the isomerized product. Therefore, the assignment of structure I to the initial adduct, which shows only one methoxy hydrogen shift, and of structure II to its geometric isomer, with two distinct chemical shifts for these hydrogens, seems the most plausible. Additional evidence that ester groups disposed *trans* do indeed exhibit two chemical shifts for the methoxy hydrogens is provided by structural considerations of the product formed on hydrogenation of the initial adduct. This hydrogenated adduct, which has been assigned the structure III, possesses two chemical shifts for each of the *trans* methyl ester groups at τ 6.70 and 6.37.

The transformation of the adduct I upon catalytic hydrogenation into the structure III is adequately supported by the chemical and physical properties of the new complex. The most contrasting chemical property of this hydrogenated complex, in comparison to materials I, II, and IV, is that it is not a base and cannot be extracted from organic solution with 10% aqueous sulfuric acid. This suggests that the coordination sphere about rhenium is completely saturated with respect to ligands and, therefore, rhenium cannot be protonated in a manner similar to I, II, and IV. That such saturation is accomplished by coordination with an ester carbonyl, as shown in III, is borne out by the observation that the hydrogenated complex possesses only a single carbonyl absorption in the infrared spectrum at 1690 cm.$^{-1}$, whereas compounds I and II display doublets at about 1685 and 1710 cm.$^{-1}$. The lost carbonyl frequency appears to be shifted to the region of 1550 cm.$^{-1}$ since this absorption is broadened in III as compared to the sharp singlets exhibited by I and II at 1590 and 1575 cm.$^{-1}$, respectively.

An examination of the n.m.r. spectum of this new complex III clearly shows that one of the cyclopentadienyl rings has been hydrogenated. The intensity of the singlet at τ 5.34, attributed to cyclopentadienyl hydrogens, is reduced to a relative value of 5 in comparison to intensities of 3 for each of the methoxy hydrogens at τ 6.48 and 6.17. A lone vinyl type hydrogen is still present at τ 3.27, attesting to the fact that the ester double bond is intact. The remaining hydrogens are scattered throughout the spectrum in the form of complex multiplets and are due to the partially hydrogenated ring. Based on the elemental composition of the complex and the uptake of hydrogen, this ring must be a cyclopentenyl ring. Due to the complex nature of the n.m.r. absorptions, attempts were not made to identify the hydrogens on the hydrogenated ring. The loss of two coordination electrons from the sphere of rhenium by the conversion of a cyclopentadienyl into a cyclopentenyl ring is compensated by coordination with an ester carbonyl that is disposed *cis* relative to rhenium. Such an arrangement of the ester group indicates that isomerization takes place during some stage of the reduction of I.

On the basis of the results obtained with dimethylacetylene dicarboxylate, it can be concluded that the dicyclopentadienylrhenium hydride–methyl propiolate adduct is also a product resulting from a *cis* addition. Two products are possible with a *cis* addition, as it can occur to place rhenium α to the ester group or β as shown in structure IV. The assignment of IV to the isolated product is adequately supported by its nuclear magnetic spectrum (Table I). As in the case of the initial adduct, the ten cyclopentadienyl protons exhibit a single shift at τ 5.38 while the methoxy hydrogens give a signal at τ 6.41. The two olefinic hydrogen shifts, however, provide the basis for the proposed structure, as the wide separation of the shifts coupled with a 16-c.p.s. splitting is only consistent with a *trans* disposition. To fulfill such a requirement, the rhenium hydride *cis* addition must proceed in a manner that places rhenium β to the ester carbonyl. Infrared absorptions, which could provide additional evidence in support of the structural proposal, are too complex for an unambiguous interpretation.

Experimental

All manipulations were carried out under an atmosphere of prepurified nitrogen. The solvents employed were rendered anhydrous with appropriate procedures, distilled, and stored under nitrogen. Dicyclopentadienylrhenium hydride was prepared using the method described by Green, Pratt, and Wilkinson.[4]

Reaction of Dimethylacetylene Dicarboxylate with Dicyclopentadienylrhenium Hydride.—Dimethylacetylene dicarboxylate, 0.85 g. (0.006 mole), was added dropwise to a stirred solution of 2.0 g. (0.006 mole) of dicyclopentadienylrhenium hydride in 60 ml. of tetrahydrofuran. During the addition of the acetylenic ester, the reaction solution changed color instantaneously from an initial yellow, which is characteristic of the rhenium complex, to a deep red. After letting the reaction solution stand at room temperature for an additional 1 hr., all tetrahydrofuran was removed from the reaction system and the residue was extracted with diethyl ether. The extract was then filtered, concentrated, and cooled in the region of −20° until crystallization was induced.

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[4] M. L. H. Green, L. Pratt, and G. Wilkinson, *J. Chem. Soc.*, 3916 (1958).

Following additional crystallization, the product I came down in the form of dark red rhombic crystals, m.p. 107–108°. Yields in the order of 70% have been obtained.

Anal. Calcd. for $C_{16}H_{17}O_4Re$: C, 41.8; H, 3.69; Re, 40.5; mol. wt., 460. Found: C, 42.4; H, 3.89; Re, 40.8; mol. wt., 481 (isopiestic). Principal infrared absorptions, cm.$^{-1}$ (KBr pellet): 3150 m, 3000 m, 2930 m, 1710 s, 1785 s, 1590 s, 1440 m, 1430 s, 1390 m, 1335 s, 1220–1140 s (br), 1095 s, 1058 m, 1025 s, 1010 s, 995 m, 975 m, 955 s, 945 s, 892 s, 865 s, 832 s, 825 s, 812 m, 785 s.

Isomerization of Adduct I.—Freshly reduced platinum (60 mg.) was added to 420 mg. of complex I dissolved in approximately 20 ml. of benzene. This mixture, together with a magnetic stirring bar, was sealed in a glass ampoule. The mixture was heated at 75° for 17 hr., while maintaining rapid stirring. It was then filtered, the filtrate was reduced to dryness under reduced pressure, and the residue was crystallized twice from methanol to yield 407 mg. (95% yield) of blood-red rhombic crystals, m.p. 151–152°.

Anal. Calcd. for $C_{16}H_{19}O_4Re$: C, 41.8; H, 3.69. Found: C, 42.0; H, 3.91. Principal infrared absorptions, cm.$^{-1}$ (KBr pellet): 3120 m, 3000 m, 2940 m, 1700 s, 1675 s, 1575 s, 1440 m, 1420 s, 1385 s, 1345 s, 1290 s, 1240 m, 1200–1110 s (br), 1090 s, 1050 m, 1010 s, 995 s, 980 s, 935 s, 880 m, 862 s, 825 s, 815 s, 788 s, 772 m, 735 m, 708 m.

Hydrogenation of Adduct I.—The complex (460 mg., 1.0 × 10^{-3} mole) was dissolved in 30 ml. of anhydrous ethanol and hydrogenated over 70 mg. of platinum at 26° and atmospheric pressure. Following a 5.5-hr. reaction period the stirring was discontinued, and the reaction mixture was allowed to stand in the apparatus for an additional 16 hr. It was then filtered, and the filtrate was concentrated and cooled at −30° until crystallization was induced. Successive recrystallization from diethyl ether and ethanol enabled the isolation of 240 mg. (53%) of very dark red, needle-like crystals, m.p. 132–133°.

Anal. Calcd. for $C_{16}H_{18}O_4Re$: C, 41.7; H, 4.13. Found: C, 42.3; H, 4.28. Principal infrared absorptions, cm.$^{-1}$ (KBr pellet): 3140 m, 3000 m, 2950 m, 2930 m, 2860 m, 1690 s, 1550 s, 1480 m, 1450 s, 1420 s, 1370 s, 1320 m, 1255 m, 1220–1170 s (b), 1135 m, 1095 m, 1055 m, 1020 s, 990 m, 945 m, 906 m, 890 m, 892 m, 882 m, 865 m, 815 s, 795 m, 695 m.

β-Dicyclopentadienylrhenium Methyl Acrylate.—The titled adduct formed from dicyclopentadienylrhenium hydride and methyl propiolate is best prepared in the manner described for complex I, but with ethanol as the reaction medium. Recrystallization from methanol results in the isolation of orange-brown plates (40% yield), m.p. 161–162°.

Anal. Calcd. for $C_{14}H_{15}ReO_2$: C, 41.9; H, 3.77. Found: C, 42.5; H, 3.99. Principal infrared absorptions, cm.$^{-1}$ (KBr pellet): 3150 m, 2930 m, 1610 vs, 1430 s, 1390 s, 1350 m, 1345 m, 1245 s, 1215 m, 1150 vs (b), 1105 s, 1065 s, 1030 s, 970 s, 910 m, 865 m, 840 s, 835 s, 818 s, 725 s.

Attempts to either hydrogenate or isomerize IV under conditions found suitable for adduct I were unsuccessful as the complex was recovered unchanged from the reaction mixtures.

Acknowledgment.—This study was partially supported by the United States Atomic Energy Commission under Contract No. AT(11-1)-999. We are indebted to Dr. A. H. Filbey for his aid and encouragement throughout the course of this work and to Prof. N. LeBel, Wayne State University, for the n.m.r. spectra.

CONTRIBUTION FROM DAYTON LABORATORY,
MONSANTO RESEARCH CORPORATION, DAYTON, OHIO

The Formation of P–N and P–N–P Bonds by Elimination of Phenol in a Basic Condensation[1]

BY MORRIS L. NIELSEN

Received July 13, 1964

Displacement of phenol from a phenyl ester of phosphoric acid or a phosphoramidic acid by anions of certain amines or phosphoramidates in the presence of a base results in the formation of P–N and P–N–P bonds. From $(C_6H_5O)_3PO$ and $NaNH-C_6H_5$ there was obtained $(C_6H_5O)_2P(O)NHC_6H_5$; with $NaN(C_6H_5)_2$, the product was $(C_6H_5O)_2P(O)N(C_6H_5)_2$. From $(C_6H_5O)_3PO$ and sodium amide, however, the product was $(C_6H_5O)_2P(O)NHP(O)(OC_8H_5)_2$. From $(C_6H_5O)_2P(O)NH_2$, by self-condensation, was obtained both $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)NH_2$ and $(C_6H_5O)_2(O)NHP(O)(OC_6H_5)NHP(O)(OC_6H_5)-NH_2$. From $(C_6H_5O)_3PO$ and $(C_6H_5O)_2P(O)NH_2$ the principal product was $(C_6H_5O)_2P(O)NHP(O)(OC_6H_5)NHP(O)-(OC_6H_5)_2$. The last three compounds have not been reported before. The properties of these compounds and their metal and amine derivatives are described.

Introduction

A familiar reaction for the formation of P–N bonds is the displacement of halogen on phosphorus by ammonia, azides, hydrazine, or amines. For example

$$(C_6H_5O)P(O)Cl + 2NH_3 \longrightarrow (C_6H_5O)_2P(O)NH_2 + NH_4Cl$$

Displacement of halogen by an amide in the presence of a base has, according to Debo,[2] yielded P–N–P bonds.

$$(C_2H_5O)_2P(O)Cl + (C_2H_5O)_2P(O)NHC_2H_5 + NaH \longrightarrow (C_2H_5O)_2P(O)N(C_2H_5)P(O)(OC_2H_5)_2 + NaCl + H_2$$

The present work arose from an attempt to prepare a P–N bond by displacement of phenol by amide in a reaction which would have been analogous to the hydrolysis of an ester.

$$(C_6H_5O)_2P(O)OC_6H_5 + OH^- \longrightarrow (C_6H_5O)_2P(O)O^- + C_6H_5OH$$

$$(C_6H_5O)_2P(O)OC_6H_5 + NH_2^- \longrightarrow (C_6H_5O)_2P(O)NH^- + C_6H_5OH$$

When triphenyl phosphate and sodium amide were heated together in toluene, however, there was ob-

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[1] Presented in part at the 147th National Meeting of the American Chemical Society, Philadelphia, Pa., April, 1964.

[2] A. Debo, German Patent 1,041,044 (to Chemische Fabrik Joh. A. Benckiser G.m.b.H., Oct. 16, 1958); *Chem. Abstr.*, **53**, 24,397*e*.