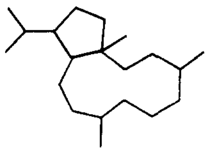
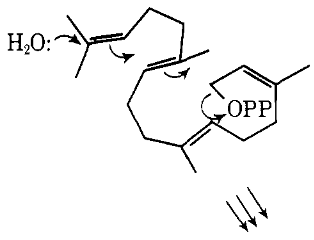
configuration of **1**. The bridgehead methyl at C(1) has the β configuration, all other substituents are α. In general bond distances and angles agree with generally accepted values and there are no abnormally short intermolecular contacts.

Work in progress indicates that we have isolated several compounds having the same new carbon skeleton, which we wish to name the dollabellane skeleton **4**. Thus the acetate **1** is (1*S**, 2*E*, 4R*, 7E, 10S*, 11R*, 12R*)-10-acetoxy-18-hydroxy-2,7-dollabelladiene.[7] The dollabellane skeleton could be formed by cyclization of geranylgeraniol pyrophosphate as shown.



4



1

The compounds isolated from the digestive glands of mollusks have invariably been traced to a dietary source. This has not been possible in the present study, since *Dollabella* is a nocturnal feeder and there are no reports of its dietary preferences.

Acknowledgments. We wish to thank J. R. Lance for identifying the preserved materials. This research was supported by a grant from the National Science Foundation (GB-37227).

Supplementary Material Available: Fractional coordinates (Table I), important bond distances (Table II), important bond angles (Table III), and observed and calculated structure factors (Table IV) (11 pages). Ordering information is given on any current masthead page.

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Reductive Elimination Reactions

Sir:

Within the set of important class reactions in coordination and catalytic chemistry[1] is the symmetric pair of "oxidative addition" and "reductive elimination". Mechanistic complexity within this pair of reactions has been clearly indicated by recent studies.[2-4] Through reactions of $HCo[P(OCH_3)_3]_4$[5] and $CH_3Co[P(OCH_3)_3]_4$[5] with H^+ and CH_3^+, we have obtained a series of $Y_2Co[P(OCH_3)_3]_4^+$ complexes which provide further information on intimate mechanism in reductive elimination. A valuable and general synthetic procedure has been developed from the elimination reactions.

The cis complex[6] $H_2Co[P(OCH_3)_3]_4^+$ was readily generated by protonation of $HCo[P(OCH_3)_3]_4$ with a nonmineral acid[5,8] and isolated in high yields as $H_2Co[P(OCH_3)_3]_4^+PF_6^-$.[9,10] In solution at 25°, the dihydride[11] slowly evolved hydrogen to form $Co[P(OCH_3)_3]_5^+$.[12] Exposure of solutions[13,14] of the dihydride cation to deuterium gave an equilibrium[13b] mixture of $D_2Co[P(OCH_3)_3]_4^+$ and H_2 in ~24 h; no HD was detected.[15] Hence a conventional equilibrium (eq 1)

$$H_2Co[P(OCH_3)_3]_4^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} H_2 + Co[P(OCH_3)_3]_4^+ \quad (1)$$

must be extant with the H_2 elimination step strictly intramolecular. An analogous exchange was observed in acetonitrile although a small amount of HD was produced due to a deprotonation step (eq 2) that occurs slowly in donor solvents.[15]

$$S + H_2Co[P(OCH_3)_3]_4^+ \overset{\text{slow}}{\rightleftharpoons} SH^+ + HCo[P(OCH_3)_3]_4 \quad (2)$$

Kinetic studies of the reaction of the dihydride with trimethyl phosphite (eq 3)

$$H_2Co[P(OCH_3)_3]_4^+ + (P(OCH_3)_3 \rightarrow H_2 + Co[P(OCH_3)_3]_5^+ \quad (3)$$

and the isolation of solid $Co[P(OCH_3)_3]_4^+PF_6^-$ and of labile adducts of $Co[P(OCH_3)_3]_4^+$ further delineate the solution chemistry of the dihydride and the clean character of this reversible reductive elimination step. Reaction rate for the phosphite reaction (eq 3) with the dihydride in dichloromethane solution was, under pseudo-first-order conditions, essentially insensitive to reactant ratio. Reaction order in phosphite was established by the initial rates method, and the data were fully consistent with a steady state condition for the intermediate complex formed in eq 1, followed by reaction 4

$$Co[P(OCH_3)_3]_4^+ + P(OCH_3)_3 \xrightarrow{k_4} Co[P(OCH_3)_3]_5^+ \quad (4)$$

where the very stable $Co[P(OCH_3)_3]_5^+$ complex was formed with the condition of $-d\{H_2Co[P(OCH_3)_3]_4^+\}/dt = k_1k_4\{H_2Co[P(OCH_3)_3]_4^+\}[P(OCH_3)_3]/(k_{-1}[H_2] + k_4\cdot[P(OCH_3)_3])$ at 30 °C with $k_1 = 4.2 \times 10^{-5}\ s^{-1}$. Reaction rate was substantially higher in coordinating solvents indicating that the further equilibrium reaction (eq 5)

$$Co[P(OCH_3)_3]_4^+ + S \rightleftharpoons SCo[P(OCH_3)_3]_4^+ \quad (5)$$

must be considered in such solvents (vide infra). The slow decomposition of the dihydride in the absence of added phosphite results from reaction 4 with free phosphite derived from the dissociative reaction (eq 6).

$$H_2Co[P(OCH_3)_3]_4^+ \rightleftharpoons H_2Co[P(OCH_3)_3]_3^+ + P(OCH_3)_3 \quad (6)$$

An estimate of the ligand dissociation rate, for dihydride, based on ^1H DNMR spectra[16] in the +20 to 70° range, is about 10^2 s^{-1} at 70°.

Methylation of $HCo[P(OCH_3)_3]_4$ or protonation[17] of $CH_3Co[P(OCH_3)_3]_4$ quantitatively (eq 7) yielded methane; the major cobalt products[12] identified were $Co[P(OCH_3)_3]_5^+$ and cobalt metal.

$$CH_3(H)Co[P(OCH_3)_3]_4^+ \rightarrow CH_4 + Co[P(OCH_3)_3]_4^+ \quad (7)$$

Methane elimination was very fast even at −78°; the methylhydrido cobalt complex was too unstable for isolation or spectral characterization. Protonation of $CH_3Co[P(OCH_3)_3]_4$ in a deuterated solvent gave only CH_4 and protonation of $CD_3Co[P(OCH_3)_3]_4$ gave only CD_3H. Hence this elimination reaction is clean and fully intramolecular in character; there can be no long-lived radical intermediates.

Intermediacy of $Co[P(OCH_3)_3]_4^+$ was demonstrated by trapping reactions as in the reaction of $CH_3Co[P(OCH_3)_3]_4$ with NH_4PF_6 at 0° which gave methane and $Co[P(OCH_3)_3]_4(NH_3)^+PF_6^-$.[18,19] Similarly, protonation of the methyl complex in the presence of olefins and acetylenes gave high yields of isolable $Co[P(OCH_3)_3]_4L^+$ complexes.[20] Hence, the reductive elimination reaction in this $CH_3(H)Co^+$ complex has broad synthetic value which we have also extended to $CoL_3L_2^+$ complexes by protonation of η^3-$C_3H_5Co[P(OCH_3)_3]_3$[5] in the presence of four-electron donors like butadiene (butadiene produced the fluxional η^4-$C_4H_6Co[P(OCH_3)_3]_3^+$ caion[21]).

Isolation of $Co[P(OCH_3)_3]_4^+$ as a blue solid salt was achieved by an indirect procedure[22] (eq 8).

$$CH_3Co[P(OCH_3)_3]_4 \xrightarrow[-78°]{H^+-C_3H_6} Co[P(OCH_3)_3]_4(C_3H_6)^+PF_6^- \xrightarrow[\text{vacuum}]{25°} Co[P(OCH_3)_3]_4^+\ PF_6^- \quad (8)$$

Direct reaction[23] of the blue salt with hydrogen and with donor ligands[24] was quantitative to give $H_2Co[P(OCH_3)_3]_4^+PF_6^-$ and $Co[P(OCH_3)_3]_4L^+PF_6^-$, respectively. On dissolution of the blue salt in non- or weakly coordinating solvents,[25] a relatively rapid redox and redistribution reaction occurred with the formation of $Co[P(OCH_3)_3]_5^+$, cobalt metal, and presumably[12] $Co[P(OCH_3)_3]_6^{3+}$.

In reductive elimination for cis dihydrido- and methylhydridometal complexes, it would appear that rates will invariably be higher for the latter type of complex. In our cobalt system, the methane elimination unlike the dihydrogen elimination was irreversible (reversibility in this type of system would be an uncommon phenomenon) but this alone does not account for rate differences between the two cobalt complexes since k_1 (eq 1) for the dihydride is several orders of magnitude smaller than the rate of methane elimination in $CH_3(H)Co[P(OCH_3)_3]_4^+$. Interestingly, $C_3H_5(H)Co[P(OCH_3)_3]_3^+$ is more stable than $CH_3(H)Co[P(OCH)_3)_3]_4^+$, a point of significance since $C_3H_5(H)_2Co[P(OCH_3)_3]_3$ is an intermediate in the catalytic hydrogenation of arenes with $C_3H_5Co[P(OCH_3)_3]_3$.[26,27]

Alkylation of $CH_3Co[P(OCH_3)_3]_4$ has been effected with $(CH_3)_3O^+PF_6^-$ in a variety of solvents. The alkylation step was slow; a precise determination of reaction rate has been precluded by the lack of a good oxonium salt solvent inert to reactants and products in the alkylation reaction although dimethyl carbonate seemed unreactive. The dimethylcobalt complex, $(CH_3)_2Co[P(OCH_3)_3]_4^+$, was too unstable for conventional isolation, and reductive elimination occurred in this complex at a rate intermediate between the two examples discussed above.[28] Methane was irreversibly produced and little deuterium incorporation in the methane was observed when the alkylation reaction was effected in deuterated solvents. Reaction of $(CH_3)_3O^+$ with $CD_3Co[P(OCH_3)_3]_4$ in dichloromethane produced CH_3D, CD_3H, CH_4, and CD_4; no CH_2D_2 was detected.[29] CH_4 and CD_4 were produced probably because the alkylation step was reversible. Thus, as in the reductive elimination reaction in the H_2Co^+ and $CH_3(H)Co^+$ cations, the elimination step in the dimethyl cation appears to be intramolecular. The expected product in reductive elimination of methane from $(CH_3)_2Co[P(OCH_3)_3]_4^+$ is the cationic carbene $CH_2Co[P(OCH_3)_3]_4^+$. We have evidence, from the decomposition of $(CH_3)_2Co[P(OCH_3)_3]_4^+$ in a CD_2Cl_2 medium, of a possible carbene–solvent reaction. The major hydrocarbon product was CH_4 but small amounts of C_2H_6 and $CH_2{=}CD_2$ were detected. Attempts to isolate the putative carbene complex from the reaction mixture have been unsuccessful and no characteristic "carbene" reactions with other substrates have been demonstrated.

Disparity in the rates for the two cases of methane elimination may reflect a multistep methane elimination step in the dimethylcobalt cation which could consist of reactions 9-11,

$$(CH_3)_2Co[P(OCH_3)_3]_4^+ \rightleftharpoons (CH_3)_2Co[P(OCH_3)_3]_3^+ + P(OCH_3)_3 \quad (9)$$

$$(CH_3)_2Co[P(OCH_3)_3]_3^+ \rightleftharpoons (CH_2)(H)(CH_3)Co[P(OCH_3)_3]_3^+ \quad (10)$$

$$(CH_2)(H)(CH_3)Co[P(OCH_3)_3]_3^+ \xrightarrow{\text{fast}} CH_4 + \{CH_2Co[P(OCH_3)_3]_3^+\} \quad (11)$$

whereas the elimination step in the methylhydridocobalt cation is probably "concerted". Equilibrium 9 probably lies largely to the right.[28]

We note the significance of this general class[30] of compounds not only for mechanistic studies of the reductive elimination step but also for an extensive evaluation of the steric,[31] charge,[32] and electronic factors that influence the thermodynamic and kinetic parameters of the elimination step. Thus, in the $Y_2ML_4^z$ class, L may be varied extensively within the cobalt and iron[30] groups. A systematic study of this class of complexes is in progress as well as of allylmetal protonation and alkylation reactions that should yield important information about metal complexes often postulated as reaction intermediates especially in olefin isomerization.

Acknowledgment. We gratefully acknowledge support of this research by the National Science Foundation.

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(4) (a) A different ordering of reductive elimination rates for $Y_2Os(CO)_4$ complexes was reported by Evans and Norton[3b] but mechanistic features of the cobalt and osmium systems differ quite sharply. (b) $(CH_3)_2Fe[(C_6H_5)_2PCH_2CH_2P(C_6H_5)_2]_2$ decomposes with liberation of CH_4, C_2H_6, and C_2H_4 to form a postulated iron carbene complex. Substantial ethane formation differentiates the iron from our cobalt system. T. Ikariya and A. Yamamoto, *J. Chem. Soc., Chem. Commun.*, 720 (1974). (c) Concerted reductive elimination of phenyl groups (to give biphenyl) is presumed for $(C_6H_5)_2Pt(PR_3)_2$ complexes on solid state pyrolysis; P. S. Braterman, R. J. Cross, and G. B. Young, *ibid.*, 627 (1975). (d) Cis-reductive elimination of ethane is observed for $(CH_3)_3AuP(C_6H_5)_3$; (A. Tamaki, S. A. Magennis, and J. K. Kochi, *J. Am. Chem. Soc.*, **96,** 6140 (1974)) and for $Pt(CH_3)_3L_3^+$ (H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **12,** 362 (1973)). (e) More general discussions or reviews of reductive elimination reactions involving alkylmetal complexes are: M. C. Baird, *J. Organomet. Chem.*, **64,** 289

(1974); P. S. Braterman and R. J. Cross, *J. Chem. Soc., Dalton Trans.*, 657 (1972); and P. S. Braterman and R. J. Cross, *Chem. Soc. Rev.*, **2**, 271 (1973).

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(6) In solution, the complex yields a proton NMR spectrum fully consistent with a cis stereochemistry.[5] However, since there is a very slight asymmetry in the Co–H mutliplet, a very small amount of the trans may be present. Cis–trans interconversion should be very fast in the solution state.[5,7] Thus, although experiments show a cis dihydride to be formed in the reverse of reaction 1, this does not prove that a concerted cis oxidative addition prevails.

(7) P. Meakin, E. L. Muetterties, and J. P. Jesson, *J. Am. Chem. Soc.*, **95**, 75 (1973).

(8) Mineral acids decompose the complex.

(9) An analogous hydride, $H_2Co[P(OC_2H_5)_3]_4^+$, was obtained from the HCo-$[P(OC_2H_5)_3]_4$.

(10) The dihydrides were fully characterized by NMR and elemental analysis.

(11) In vacuum, thermolysis of the salt begins above ~150° as signaled by a measurable rate of hydrogen evolution.

(12) Another cobalt species must be formed (stoichiometry considerations). This species is probably $Co[P(OCH_3)_3]_6^{3+}$ but characterization data are not as yet unequivocal. The overall reaction would be: $9Co[P(OCH_3)_3]_4^+ \rightarrow 6Co[P(OCH_3)_3]_5^+ + 2Co^0 + Co[P(OCH_3)_3]_6^{3+}$. The trigonal bipyramidal $Co[P(OCH_3)_3]_5^+$ is in a virtual thermodynamic sink and invariably forms in these reductive eliminations. For this reason, extended studies to $Y_2CoL_4^+$ systems with $L = P(CH_3)_3$ or $P(O\text{-}i\text{-}C_3H_7)_3$ may simplify mechanistic studies because of the expected stability of these CoL_4^+ cations.

(13) Reaction conditions were 25° and ~700 mm D_2 pressure in dichloromethane solution.

(14) (a) The H_2–D_2 exchange reaction is substantially faster than the slow "decomposition" of $H_2Co[P(OCH_3)_3]_4^+$ through the intermediate Co-$[P(OCH_3)_3]_4^+$ to $Co[P(OCH_3)_3]_5^+$, $Co[P(OCH_3)_3]_6^{3+}$, and Co^0. (b) Coordinated deuterium was favored.

(15) Proton exchange between $H_2Co[P(OCH_3)_3]_4^+$ and $HCo[P(OCH_3)_3]_4$ is moderately fast in solution especially if the solvent is capable of solvating the proton.

(16) The multiline ^1H spectrum of the cis dihydride broadens to a single resonance as temperature increases and then the single resonance sharpens on further temperature increase to 70° (thermal decomposition at 80° and above is of sufficient consequence that spectral studies above this temperature were not feasible). There was no evidence of the expected fast exchange *intramolecular* limiting spectrum of a binominal quintet. Fast dissociation of phosphite ligands in this upper temperature range is consistent with the DNMR data.

(17) Protonation of the methyl complex is a substantially faster step than the complimentary alkylation [typically $(CH_3)_3O^+PF_6^-$ was used] of the hydride, an observation consistent with the relatively congested cobalt coordination sphere in these complexes (close approach of H^+ to cobalt should be less hindered than that of CH_3^+ in for example $(CH_3)_3O^+$).

(18) Elemental analysis and NMR characterization. AB_3 ^{31}P spectrum.

(19) This ammonia complex reacted with H_2 and with $P(OCH_3)_3$ to form H_2Co-$[P(OCH_3)_3]_4^+$ and $Co[P(OCH_3)_3]_5^+$, respectively. The first step in these reactions is dissociation of the ammonia ligand.

(20) These included ethylene, propylene, 1-hexene, and diphenylacetylene. The acetylene complex was more stable than the ethylene complex; both these complexes showed the expected A_2B_2 ^{31}P NMR spectrum.

(21) This complex gave a low temperature AB_2 ^{31}P pattern which is that expected for a square pyramidal form with an apical phosphite ligand (analogous to that established for the isoelectronic η^4-$C_4H_6Fe(CO)_3$).

(22) The yellow propylene complex was prepared and isolated as a PF_6^- salt at −78°. Evacuation of this salt at 25° led to complete propylene removal to give the blue $Co[P(OCH_3)_3]_4^+PF_6^-$ salt.

(23) Reaction of the solid at 25°

(24) NH_3, $P(OCH_3)_3$, and C_2H_4.

(25) In dichloromethane, the green solution of the complex rapidly precipitated Co^0. Acetonitrile formed a red, weak complex with $Co(P(OCH_3)_3]_4^+$. This complexation stabilized such solutions; decomposition occurred over a several hour period.

(26) F. J. Hirsekorn, M. C. Rakowski, and E. L. Muetterties, *J. Am. Chem. Soc.*, **97**, 237 (1975).

(27) $C_3H_5CoH_2[P(OCH_3)_3]_3$ in the absence of a reducible substrate slowly eliminates propylene. The stability of this intermediate is ~1–2 orders of magnitude greater than that of $C_3H_5(H)Co[P(OCH_3)_3]_3^+$.

(28) Methane formation was never quantitative. For example, in dichloromethane the yield of methane was about 70–75% with a 1:1 stoichiometry. Reactivity of the cobalt intermediate complex towards the solvent may partly account for this result. Extensive dissociation of $(CH_3)_2Co[P(OCH_3)_3]_4^+$ to $(CH_3)_2Co[P(OCH_3)_3]_3^+$ is expected on steric grounds. Liberated phosphite ligand should then react rapidly with the oxonium salt. In fact, a higher yield of methane was obtained when the ratio of oxonium salt to CH_3Co-$[P(OCH_3)_3]_4$ was raised to 2:1.

(29) Analysis based on high resolution mass spectral data. We are indebted to Dr. J. Henion for obtaining these data.

(30) D. H. Gerlach, W. G. Peet, and E. L. Muetterties, *J. Am. Chem. Soc.*, **94**, 4545 (1972).

(31) Steric factors may also tend to favor the elimination step in cobalt vis a vis iron since the metal radius is smaller in the former.

(32) For evidence that charge plays an important role see R. Ettore, *Inorg. Nucl. Chem. Lett.*, **5**, 45 (1969).

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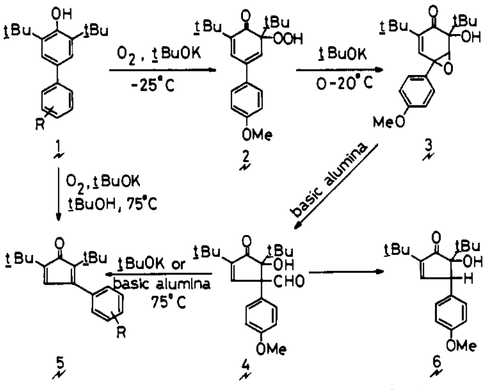
Mechanism of the Formation of Cyclopentadienone Derivatives from 4-Aryl-2,6-di-*tert*-butylphenols by Base-Catalyzed Oxygenation

Sir:

Recently it has been shown that 4-aryl-2,6-di-*tert*-butylphenols (**1**) are easily oxygenated in the presence of *t*-BuOK in *t*-BuOH to give antiaromatic 3-aryl-2,5-di-*tert*-butylcyclopentadienones (**5**) in good yields.[1] The reaction provides a novel and convenient method for the synthesis of such antiaromatic compounds.[2] We now wish to report the mechanism of this interesting reaction, clarified with the aim of isolation of intermediates employing **1** (R = 4-OMe) which quantitatively gives the cyclopentadienone **5** (R = 4-OMe).

It has been found that modification of the reaction conditions makes it possible to isolate the intermediates. Thus, oxygen was bubbled through a solution of **1** (R = 4-OMe) (15 mmol) in *t*-BuOH/petroleum ether (1:1) (100 ml) containing *t*-BuOK (75 mmol) at −25 °C for 40 min. Acidification of the reaction mixture with aqueous NH_4Cl solution and evaporation of the solvent afforded hydroperoxide **2** in 85% yield: yellow needles; mp 99–101°; ir (KBr) 3340 (OOH), 1665 cm^{-1} (C=O); NMR ($CDCl_3$) δ 1.03 (9, H, s, *t*-Bu), 1.28 (9 H, s, *t*-Bu), 3.84 (3 H, s, OMe), 6.61 (1 H, d, vinyl H, J = 2.8 Hz), 7.05 (1 H, d, vinyl H, J = 2.8 Hz), 6.7–7.6 (4 H, m, ArH), 9.00 (1 H, s, OOH, exchangeable with D_2O).[3] Treatment of this hydroperoxide with *t*-BuOK in *t*-BuOH at 75 °C quantitatively gave **5** (R = 4-OMe), while the treatment at room temperature resulted in the formation of **3** and **5** (R = 4-OMe) in 75 and 25% yields, respectively. The ratio of **3** to **5** (R = 4-OMe) depends on the reaction temperature: the higher temperature causes the higher yield of **5** (R = 4-OMe).[1] As was shown by separate experiments,[1] the cyclopentadienones **5** are formed in high yields upon heating the epoxy-*o*-quinols of type **3** with *t*-BuOK in *t*-BuOH at 75 °C. It is, therefore, obvious that the formation of **5** (R = 4-OMe) on the oxygenation of **1** (R = 4-OMe) proceeds by a mechanism involving these intermediates. All attempts to isolate any intermediate between **3** and **5** (R = 4-OMe) in this reagent system were unsuccessful. However, adsorption of **3** on activated basic alumina (activity I) in CH_2Cl_2 followed by elution with MeOH afforded isomeric ring contracted product **4** in 50% yield: colorless needles; mp 158–160°; ir (KBr) 3460 (OH), 1730 (CHO), 1710 cm^{-1} (ring C=O); NMR ($CDCl_3$): δ 0.63 (9 H, s, *t*-Bu), 1.33 (9 H, s, *t*-Bu), 3.39 (1 H, s, OH, exchangeable with D_2O), 3.85 (3 H, s, OMe, 7.24 (1 H, s, vinyl H), 6.9–7.4 (4 H, m, ArH), 9.17 (1 H, s, CHO); together with **5** (R = 4-OMe) (25%). In addition, treatment of **3** with the same basic alumina in *t*-BuOH at 75 °C quantitatively afforded **5** (R = 4-OMe). The compound **4** was also obtained by treatment of **3** with silica gel or CF_3COOH at room temperature. Taking account of the conclusions by Hart et al.[8] for the acid-catalyzed

Scheme I



R: 4-OMe, 3-OMe, 2-OMe, 4-Me, 3-Me, 2-Me, 4-Cl, H