Inorganica Chimica Acta, 23 (1977) 263–275

ICA Review

Di-Organocobalt Complexes of Macrocyclic Ligands and π-Acceptor Bidentate and Phosphine Ligands

MARK W. WITMAN and JAMES H. WEBER

Chemistry Department, University of New Hampshire, Parsons Hall, Durham, N.H. 03824, U.S.A.

Received November 6, 1976

Contents

1. Introduction
   A. Scope of the Review
   B. Origins of Organocobalt Chemistry
   C. Brief Summary of Mono-organocobalt Complexes
2. Synthesis of Di-organocobalt Complexes
   A. Complexes of Macrocyclic Ligands
   B. Complexes of Mono- and Bidentate π-acceptor Ligands
3. Characterization of Di-organocobalt Complexes
   A. X-ray Structures
   B. Nuclear Magnetic Resonance Studies
   C. Infrared Studies
4. Reactions of Di-organocobalt Complexes
   A. Substitution Reactions without Cobalt–Carbon Bond Cleavage
   B. Reactions with Light and Heat
   C. Insertion Reactions
   D. Reactions with Non-metallic Electrophiles
   E. Reactions with Metallic Electrophiles
5. References

1. Introduction

A. Scope of the Review

This review emphasizes cobalt complexes containing two σ-bonded carbon donor ligands. The first class of complexes to be discussed contain quadridentate ligands (chel) which form complexes of the type RR′Co(chel). (R and R′ are a variety of identical or different σ-bonded alkyl or aryl groups.) A second class of di-organocobalt complexes discussed in this review includes the dialkyl and diaryl complexes which contain π-acceptor ligands, such as triphenylphosphine, 2,2′-bipyridine, 1,10-phenanthroline, and acetylacetonate. These compounds are for the most part *cis*-octahedral complexes, although other geometries are known. We will emphasize the synthesis, structure, spectroscopic properties, and reactions of the complexes which were not covered in earlier reviews of organocobalt chemistry [1, 2]. For the most part we excluded complexes containing carbonyl ligands and π-donor ligands as well as those of the form R_2Co.

We will simplify and clarify the discussion of di-organocobalt complexes by prefacing it with introductory material. It includes the origin of organocobalt chemistry and a brief summary of the synthesis and reactivity of mono-organocobalt complexes.

B. Origins of Organocobalt Chemistry

Compounds with metal–carbon bonds have been known for many years and it is now clearly recognized that the formation of bonds to carbon is a general and characteristic property of all of the d-group transition metals. The development of organocobalt chemistry in particular can be traced to the isolation and characterization of the naturally-occurring cobalt corrinoid 5′-deoxyadenosylcobalamin. The unique feature of this compound is the cobalt–carbon bond, and its presence was unambiguously confirmed by an X-ray analysis carried out in 1961 [3].

The realization that the porphyrin-like corrin ring was an important factor in the stabilization of the cobalt–carbon bond, led to speculation that other organocobalt complexes could be prepared by employing analogous quadridentate ligands. The success of this thinking is best illustrated by two reviews [1, 2] which summarize the nearly 1,000 organocobalt complexes that have been prepared, and by the fact that many of the properties of the naturally-occurring cobalamins are indeed manifested by a variety of synthetic cobalt chelates. A particularly significant parallel is the ability of the synthetic ligands to stabilize a redox series of Co(III), Co(II) and Co(I) oxidation states [4–6]. This factor appears to be of fundamental importance in the making and breaking of cobalt–carbon bonds.

The synthetic organocobalt complexes which will be discussed here can be categorized according to the number of σ-bonded organoligands. Both mono- and di-organocobalt complexes are known. The former category has been well-studied and is the main focus of the previous reviews [1, 2]. Examples of di-organocobalt complexes are fewer in number, and relatively little is known concerning their reactivity.

In view of the similarity of the two categories of organocobalt complexes, however, it is desirable first to survey some fundamental properties of mono-organocobalt complexes. We will discuss in a general way the formation and cleavage of the cobalt–

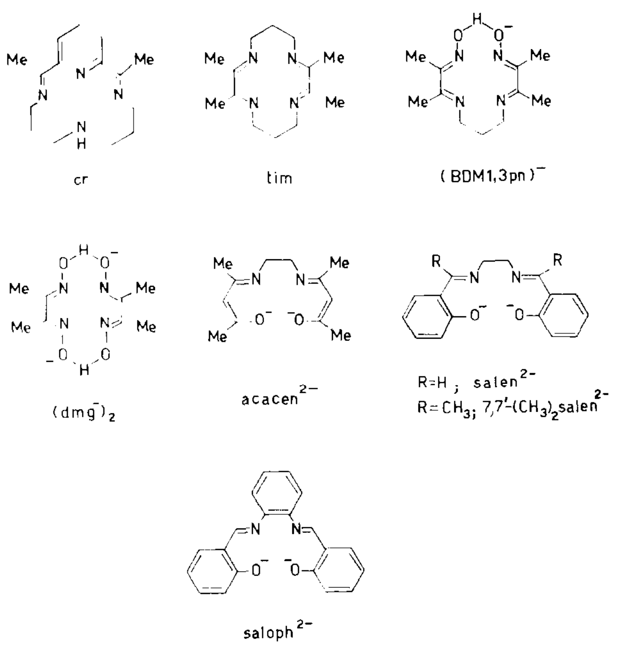


Fig. 1. Structures of chelating ligands that form mono-organocobalt complexes.

carbon bond. An emphasis will be placed on those reactions which have some bearing on the future discussion of the di-organocobalt complexes. The reader should consult the previously mentioned reviews [1, 2] or the treatise by Pratt [7] for specific examples of reactions or additional information concerning the properties of the mono-organocobalt complexes.

C. Brief Summary of Mono-organocobalt Complexes Synthesis

Fig. 1. shows a variety of macrocyclic and non-cyclic quadridentate ligands that stabilize mono-organocobalt bonds [8]. All of these chelating ligands (chel) contain, when complexed, 5- and 6-membered chelate rings. As can be seen, the donor atoms of these ligands are predominantly N_4 or N_2O_2, and all are members of a conjugated system with the exception of cr in which one nitrogen is tetrahedral. Complexes of the type RCo(chel)B (R = alkyl, aryl; B = H_2O, pyridine, phosphines, *etc.* or absent) are most often six-coordinate with a pseudo-octahedral configuration, or in some cases five-coordinate with a square pyramidal configuration. In both geometries the four equatorial positions are occupied by the donor atoms of the chelating ligands.

According to the usual conventions the oxidation state of cobalt in most organocobalt complexes is 3+ while the organic ligand is regarded as anionic (*i.e.*, R^-). We will often omit the cobalt oxidation number when it is 3+, but will usually denote other cobalt oxidation numbers. We also will use chel of 2− charge to designate the ligands of Fig. 1 in mono-organocobalt complexes. By means of these designations three limiting processes can be considered to lead to the formation of cobalt–carbon bonds: (1) reactions of Co(I) complexes with electrophiles, (2) reactions of Co(III) complexes with nucleophiles, and (3) reactions of Co(II) complexes with free radicals.

The reactions of Co(I) complexes with electrophilic agents is the most widely used route to organocobalt chelates. The Co(I) complexes are very powerful nucleophiles [9], and they undergo rapid oxidative addition reactions with a variety of electrophiles. This method of synthesis often involves the reduction of the appropriate Co(III) or Co(II) starting material *in situ* using reducing agents such as sodium borohydride or sodium amalgam, followed by the addition of any one of a number of alkylating agents such as alkyl halides or dialkyl sulfates (Eqn. 1, 2).

$$Co^{III}(chel)^+ + 2e^- \longrightarrow Co^{I}(chel)^- \qquad (1)$$

$$Co^{I}(chel)^- \xrightarrow{RX} RCo^{III}(chel) + X^- \qquad (2)$$

R = alkyl, allyl, benzyl, fluoroalkyl, *etc.*
$X = Cl^-, Br^-, I^-, 1/2\ SO_4^{2-}$, *etc.*

An alternative method of generating the $Co^{I}(chel)^-$ nucleophiles is the electrochemical reduction of $Co^{III}(chel)$ using controlled potential electrolysis [10]. This method provides a clean route to $Co^{I}(chel)^-$ and has the advantage of selectivity over the more commonly employed chemical methods since the reduction of the cobalt species to Co^0 or the reduction of the ligand can be avoided.

The use of $Co^{I}(chel)^-$ nucleophiles in the synthesis of mono-alkylcobalt chelates has been very successful and is used to synthesize complexes like $RCo(BDMI,3pn)^+$ (R = CH_3, C_2H_5, n-C_3H_7 and n-C_4H_9) [11] and RCo(salen) (R = CH_3, C_2H_5, and n-C_3H_7; and various ligand modifications) [12].

Organocobalt chelates can also be prepared by reacting Co(III) complexes directly with nucleophilic agents such as organolithium or Grignard reagents exemplified by Eqn. 3 [13].

$$Co^{III}(BDMI,3pn)Br_2 + RMgX \longrightarrow$$
$$\xrightarrow{H_2O} [RCo^{III}(BDMI,3pn)H_2O]^+ \qquad (3)$$

This method is of general applicability and has considerable utility as a route to organocobalt chelates. Generally an excess of RMgX or RLi is employed in order to account for the reaction of these reagents with acidic protons which are found on some of the chelating ligands.

The third general method of forming cobalt–carbon bonds involves the reaction of Co(II) chelates with organic radicals. For instance, Schrauzer *et al.* [14] synthesized methylcobalamin by the photolysis of $CH_3Co(dmg)_2py$ under nitrogen in the presence of the cobalt(II) derivative of vitamin B_{12}. Presumably the reaction involves the homolytic cleavage of the cobalt–carbon bond followed by the reaction of the methyl radical with the Co(II) complex (eqn. 4),

$$CH_3\cdot + Co^{II}(chel) \longrightarrow CH_3Co^{III}(chel) \qquad (4)$$

since radicals are known to be produced by the photolysis and thermolysis of methylcobalt complexes. Halpern and Phelan [15] synthesized $RCo(dmg)_2B$ complexes according to Eqn. 5 (B = py, PPh_3, *etc.*; RX = $C_6H_5CH_2I$, $C_6H_5CH_2Br$, *etc.*).

$$2Co^{II}(dmg)_2B + RX \longrightarrow RCo^{III}(dmg)_2B + XCo^{III}(dmg)_2B \qquad (5)$$

In a kinetics study they concluded that Eqn. 5 goes by a free radical mechanism. An interesting alkylcobalt synthesis based on the free radical reactions of hydrazines is also known [16].

Reactions

Cleavage of the cobalt–carbon bond of the mono-organocobalt complexes can occur by homolytic or heterolytic processes. Homolytic fission often occurs upon irradiation of the complexes with light and leads to Co(II) complexes and an organic radical (Eqn. 6). The radical may subsequently react by one

$$RCo^{III}(chel) \xrightarrow{h\nu} Co^{II}(chel) + R\cdot \qquad (6a)$$

$$R\cdot \longrightarrow RH, RR, etc. \qquad (6b)$$

of several routes: (1) abstract a hydrogen atom from the ligand or solvent to form RH, (2) dimerize to form RR, or (3) lose a hydrogen atom to form an alkene. Heterolytic cleavage can be induced by the reaction of the complexes with electrophiles (Eqn. 7) or nucleophiles (Eqn. 8). Electrophilic attack results

$$RCo^{III}(chel) + E^+ \longrightarrow [Co^{III}(chel)]^+ + RE \qquad (7)$$

$E^+ = Hg^{2+}, I_2, ICl,$ *etc.*

$$RCo^{III}(chel) + Nu^- \begin{cases} \nearrow NuCo^{III}(chel) + RH \\ \searrow [Co^{I}(chel)]^- + RNu \end{cases} \qquad (8)$$

$Nu^- = RS^-, CN^-,$ *etc.*

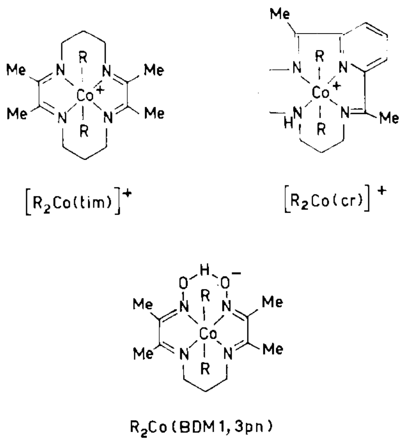
in the formation of Co(III) complexes and carbanions, while nucleophilic attack results in the same products, or in some cases Co(I) complexes and carbonium ions. Often the intermediate reaction products can not be detected because they either undergo further reaction, or because the cleavage is concerted with attack of the reagent. In these cases evidence about the mechanism of the cobalt–carbon bond cleavage comes from kinetic measurements or the identification of the ultimate reaction products.

Individual complexes show surprising differences in their pattern of reactivity with respect to cobalt–carbon bond cleavage. The course and rates of these reactions depend not only on the nature of the organic ligand and attacking agent (if any), but also on the nature of the chelating ligand which plays an important role in the polarization of the cobalt–carbon bond. For example the order of chelating ligand donor power is acacen > salen > $(dmg)_2$ > BDM1,3pn [17–20]. As a consequence the RCo(acacen) complexes are more likely than $[RCo(BDM1,3pn)]^+$ complexes to form carbanion intermediates, while the latter complexes tend to form carbonium ion intermediates.

2. *Synthesis of Di-organocobalt Complexes*

A. Complexes of Macrocyclic Ligands

There are many more mono-organocobalt than di-organocobalt complexes of the quadridentate ligands in Fig. 1. This is primarily due to the relatively few quadridentate ligands known to form stable complexes of the type *trans*-RR'Co(chel). In fact, of the chelating ligands shown in Fig. 1, only BDM1,3pn, tim, and cr form di-organocobalt complexes (Fig. 2). Complexes of the type RR'Co(BDM1, 3pn) (R = R' = CH_3, $C_6H_5CH_2$) represent the first isolated examples [21], although Farmery and Busch [22] reported the isolation of $[(CH_3)_2Co(tim)]^+$ and $[(CH_3)_2Co(cr)]^+$ a short time later. Additional *trans*-dialkyl, -diaryl and -alkyl–aryl complexes of these same ligands have been prepared, and their syntheses will now be discussed.


$[R_2Co(tim)]^+$ $[R_2Co(cr)]^+$

$R_2Co(BDM1,3pn)$

Fig. 2. Structures of di-organocobalt complexes of macrocyclic ligands.

A survey of the literature reveals that two general procedures have been employed in the synthesis of the RR'Co(chel) complexes. They are: (1) the reaction of Co(I) complexes with electrophiles, and (2) the reaction of Co(III) complexes with nucleophiles. In contrast to the mono-organocobalt chelates no syntheses of $\mathrm{RR'Co(chel)}$ by reactions of free radicals have been reported.

The formation of *trans*-dialkylcobalt complexes by method 1 implies the existence of intermediate nucleophiles of the type $\mathrm{RCo^{I}(chel)}$. These intermediates can either be generated *in situ* or in some cases isolated in an oxygen-free atmosphere. The subsequent reaction of these species with alkyl halides affords the di-organometallic compounds.

Costa *et al.* [21, 23, 24] synthesized complexes of the type $\mathrm{RR'Co(BDM1,3pn)}$ ($\mathrm{R = R' = CH_3}$ or $\mathrm{C_6H_5CH_2}$; $\mathrm{R = CH_3}$, $\mathrm{R' = C_6H_5}$) using variations of this method. The reaction of $\mathrm{Co(BDM1,3pn)I_2}$ with sodium borohydride in methanol in the presence of excess methyl iodide or benzyl chloride gave $\mathrm{(CH_3)_2Co(BDM1,3pn)}$ or $\mathrm{(C_6H_5CH_2)_2Co(BDM1,3pn)}$, together with the mono-substituted derivatives $\mathrm{RCo(BDM1,3pn)I}$ (Eqn. 9). Recently we have improved this synthesis by starting with $\mathrm{[Co^{III}(BDM1,3pn)(H_2O)_2]^{2+}}$ [25].

$$\mathrm{Co^{III}(BDM1,3pn)I_2 + 2RX \xrightarrow{NaBH_4} R_2Co^{III}(BDM1,3pn)} \qquad (9)$$

The dimethyl and dibenzyl complexes were also prepared by the carbon monoxide reduction of the corresponding mono-substituted derivatives [21, 23]. The reaction of $\mathrm{CH_3Co(BDM1,3pn)I}$ or $\mathrm{C_6H_5CH_2Co(BDM1,3pn)I}$ with CO in basic aqueous tetrahydrofuran (THF) gave a green solution. This color is characteristic of RCo(I) complexes [22, 26] and is presumably $\mathrm{[RCo^{I}(BDM1,3pn)]^-}$. The di-organocobalt complexes are formed upon addition of the appropriate alkyl halide (Eqn. 10).

$$\mathrm{RCo^{III}(BDM1,3pn)I + CO \xrightarrow[H_2O/THF]{NaOH} [RCo^{I}(BDM1,3pn)]^- \xrightarrow{RX} R_2Co^{III}(BDM1,3pn)} \qquad (10)$$

The existence of the assumed $\mathrm{[RCo^{I}(BDM1,3pn)]^-}$ intermediates is proven by the formation of unsymmetrical di-organocobalt complexes. For example, the mixed methyl–phenyl and benzyl–phenyl derivatives were prepared by the CO reduction of $\mathrm{C_6H_5Co(BDM1,3pn)I}$ in the presence of methyl iodide or benzyl chloride [21, 23] (Eqn. 11). The methyl–phenyl complex was also prepared by employing sodium amalgam as the reducing agent in anhydrous THF followed by the addition of methyl bromide [21]. (Eqn. 12).

$$\mathrm{RCo^{III}(BDM1,3pn)I + CO \xrightarrow[H_2O/THF]{NaOH} [RCo^{I}(BDM1,3pn)] \xrightarrow{R'X} RR'Co^{III}(BDM1,3pn)} \qquad (11)$$

$\mathrm{R = C_6H_5}$, $\mathrm{R' = C_6H_5CH_2}$ or $\mathrm{CH_3}$

$$\mathrm{C_6H_5Co^{III}(BDM1,3pn)I + Na(Hg) \xrightarrow{THF} [C_6H_5Co^{I}(BDM1,3pn)]^- \xrightarrow{CH_3Br} (C_6H_5)(CH_3)Co^{III}BDM1,3pn)} \qquad (12)$$

Schrauzer, Seck and Beckham [17] synthesized $\mathrm{(CH_3)_2Co(BDM1,3pn)}$ by reacting the free ligand with cobalt(II) acetate tetrahydrate in methanol followed by $\mathrm{NaBH_4}$ reduction in the presence of excess methyl iodide. After a reaction time of approximately 20 minutes in methanol, the solution was diluted with water in order to precipitate the neutral product. This *in situ* preparation has the advantage of not requiring the isolation of a $\mathrm{Co(BDM1,3pn)X_2}$ precursor, however it is of little use in the syntheses of the unsymmetrical derivatives.

Farmery and Busch [22] synthesized compounds of the type $\mathrm{[RR'Co(cr)]^+Y^-}$ and $\mathrm{[RR'Co(tim)]^+Y^-}$ ($\mathrm{R = R' = CH_3}$ or $\mathrm{C_6H_5CH_2}$; $\mathrm{R = CH_3}$, $\mathrm{R' = C_6H_5CH_2}$; $\mathrm{Y^- = BPh_4^-, PF_6^-}$) by the reactions of isolated $\mathrm{RCo^{I}(cr)}$ and $\mathrm{RCo^{I}(tim)}$ complexes with the appropriate alkyl halides. The *trans*-dialkylcobalt complexes were obtained as bright red or orange–brown crystals upon addition of $\mathrm{BPh_4^-}$ or $\mathrm{PF_6^-}$. Other examples of complexes synthesized by this method include $\mathrm{[(C_2H_5)_2Co(cr)]^+}$ and $\mathrm{[(n\text{-}C_3H_7)_2Co(cr)]^+}$ [27]. These reactions are significant not only because they represent another route to *trans-dialkylcobalt* chelates, but also because they confirm that the previously postulated $\mathrm{RCo^{I}(chel)}$ complexes are indeed intermediates in their synthesis.

The second general method of preparing $\mathrm{RR'Co(chel)}$ complexes is the reaction of Co(III) complexes with Grignard reagents (method 2) [21, 23]. For example, treatment of a suspension of $\mathrm{Co(BDM1,3pn)I_2}$ or $\mathrm{Co(BDM1,3pn)Br_2}$ in anhydrous THF with excess RMgX ($\mathrm{R = CH_3}$, $\mathrm{C_6H_5}$ or $\mathrm{C_6H_5CH_2}$) at -80 °C resulted in orange solutions. Subsequent hydrolysis and concentration of these solutions resulted in the corresponding di-organocobalt derivatives $\mathrm{(CH_3)_2Co(BDM1,3pn)}$, $\mathrm{(C_6H_5)_2Co(BDM1,3pn)}$ and $\mathrm{(C_6H_5CH_2)_2Co(BDM1,3pn)}$ (Eqn. 13).

$$\mathrm{Co^{III}(BDM1,3pn)I_2 + 2\,RMgX \xrightarrow{THF, -80^{\circ}C} R_2Co^{III}(BDM1,3pn)} \qquad (13)$$

Presumably the *trans*-diphenyl complexes of tim and cr could be prepared in this manner, but their synthesis has not been reported as of this writing. Other *trans*-diaryl complexes of the type $(p\text{-}\mathrm{FC_6H_4})_2\mathrm{Co(BDM1,3pn)}$, $(m\text{-}\mathrm{FC_6H_4})_2\mathrm{Co(BDM1,3pn)}$, $(p\text{-}\mathrm{FC_6H_4})\mathrm{(CH_3)Co(BDM1,3pn)}$, and $(m\text{-}\mathrm{FC_6H_4})\mathrm{(CH_3)Co(BDM1,3pn)}$ have been reported, but the method of preparation was not discussed [28].

The transfer of alkyl groups from one organocobalt complex to another represents a special case of method 2. Both the $[RCo^{I}(BDMl,3pn)]^-$ anion and $(CH_3)_2Co(BDMl,3pn)$ have been used as alkylating agents. For example, when the dimethyl derivative is reacted in methanol or aqueous THF with an equimolar amount of $[C_6H_5Co(BDMl,3pn)H_2O]^+$, the mixed methyl–phenyl derivative is obtained [52] (Eqn. 14).

$$(CH_3)_2Co(BDMl,3pn) + [C_6H_5Co(BDMl,3pn)H_2O]^+ \xrightarrow{MeOH} [CH_3Co(BDMl,3pn)]^+ + (CH_3)(C_6H_5)Co(BDMl,3pn) \quad (14)$$

Similarly, the electrochemical reduction of $[RCo(BDMl,3pn)H_2O]^+$ in air-free aprotic solvents yields the corresponding $[RCo^{I}(BDMl,3pn)]^-$ anions, which behave as alkylating agents toward the mono-alkyl Co(III) starting complexes [26]. When R = methyl or ethyl, the *trans*-dialkylcobalt complexes $(CH_3)_2Co(BDMl,3pn)$ and $(C_2H_5)_2Co(BDMl,3pn)$ are isolated (Eqn. (15).

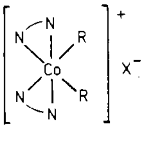
$$[RCo^{III}(BDMl,3pn)H_2O]^+ + 2e^- \longrightarrow [RCo^{I}(BDMl,3pn)]^- \quad (15a)$$

$$[RCo^{I}(BDMl,3pn)]^- + [RCo^{III}(BDMl,3pn)H_2O]^+ \longrightarrow R_2Co^{III}(BDMl,3pn) + Co^{I}(BDMl,3pn) \quad (15b)$$

This reaction has been interpreted in terms of a carbanion transfer from the Co(I) to the Co(III) complex, but a carbonium ion transfer from the Co(III) to the Co(I) complex cannot be ruled out.

B. Complexes of Mono- and Bidentate π-Acceptor Ligands

In contrast to the di-organocobalt complexes containing macrocyclic ligands, *cis*-dialkyl complexes are not generally synthesized by the oxidative addition of alkyl halides to Co(I) nucleophiles. However, Mestroni and co-workers [29] prepared a series of stable dialkyl cobalt complexes of 2,2′-bipyridine (bipy) and 1,10-phenanthroline (phen) using this method. The sodium borohydride reduction of methanolic solutions of $CoCl_2{\cdot}6H_2O$ in the presence of bipy or phen and alkyl halides gave the complexes of structures Ia to If after adding the appropriate anion (Eqn. 16) in which chel represents bipy or phen.



Ia R = $C_6H_5CH_2$, X = I^-, chel = bipy
Ib R = $C_6H_5CH_2$, X = ClO_4^-, chel = bipy
Ic R = $C_6H_5CH_2$, X = PF_6^-, chel = bipy
Id R = CH_3, X = ClO_4^-, chel = bipy
Ie R = C_2H_5, X = ClO_4^- chel = bipy
If R = $C_6H_5CH_2$, X = I^-, chel = phen

$$CoCl_2{\cdot}6H_2O + 2chel \xrightarrow[RX]{NaBH_4} cis\text{-}[R_2Co^{III}(chel)_2]^+ \quad (16)$$

The majority of the known non-macrocyclic dialkyl and diarylcobalt complexes have been synthesized using Grignard or organolithium reagents. This method was successfully employed by Chatt and Shaw [30] in the synthesis of diarylcobalt(II) complexes of the type *trans*-$R_2Co^{II}(PEt_2Ph)_2$ (R = mesityl, 2-biphenylyl, 2-methyl-1-naphthyl, pentachlorophenyl). In general, these organometallic complexes were prepared by the reaction of the appropriate Grignard reagent or organolithium reagent with a phosphine metal halide complex in benzene (Eqn. 17). In most cases the organolithium reagents resulted in poorer yields. The preparation of similar alkylcobalt(II) derivatives was attempted by the same methods but no dialkyl compounds were isolated.

$$CoBr_2(PEt_2Ph)_2 + 2RMgBr \xrightarrow{PhH} trans\text{-}R_2Co^{II}(PEt_2Ph)_2 + 2MgBr_2 \quad (17)$$

Yamazaki and Hagihara [31] subsequently reported that dialkylcobalt(II) complexes of h^5-cyclopentadienyl and tertiary phosphines could be prepared by the Grignard method. Stable σ-bonded dialkyl complexes of the type $(h^5\text{-}C_5H_5)(C_6H_5CH_2)_2Co(PPh_3)$ and $(h^5\text{-}C_5H_5)(CH_3)_2Co(PPh_3)$ were obtained by treatment of a slurry of the iodide, $(h^5\text{-}C_5H_5)Co(I)_2(PPh_3)$, with benzylmagnesium chloride or methylmagnesium bromide in benzene (Eqn. 18).

$$(h^5\text{-}C_5H_5)Co(I)_2(PPh_3) + 2RMgX \longrightarrow (h^5\text{-}C_5H_5)R_2Co(PPh_3) \quad (18)$$

The orange–red complexes were isolated in about 60% yield after hydrolysis of the mixture with water. The corresponding monoalkyl products, $(h^5\text{-}C_5H_5)RCo^{I}(PPh_3)$, were also isolated, and presumably account for the low yields of the dialkyl complexes. The mixed methyl–benzyl complex was prepared by the reaction of $(h^5\text{-}C_5H_5)(CH_3)Co(I)(PPh_3)$ with benzylmagnesium chloride (Eqn. 19).

$$(h^5\text{-}C_5H_5)(CH_3)Co(I)(PPh_3) + C_6H_5CH_2MgBr \longrightarrow (h^5\text{-}C_5H_5)(CH_3)(C_6H_5CH_2)Co(PPh_3) \quad (19)$$

King [32] also reported the synthesis of the dimethyl complex by the Grignard method.

Dimethyl cobalt(II) complexes using a series of substituted pyridines as stabilizing ligands were formed *in situ* by the reaction of $CoCl_2(py)_2$ with methylmagnesium bromide in benzene [33]. However, all efforts to isolate the products resulted in their decomposition. The complexes were characterized by electron paramagnetic resonance spectroscopy at −130 °C but no details were given.

The stable phosphine complex bis(tri-n-butylphosphine)bis(pentafluorophenyl)cobalt(II), $(C_6F_5)_2Co(PBu_3)_2$ was obtained by the reaction of pentafluorobenzenemagnesium bromide and cobalt(II) bromide in THF, followed by the addition of tri-n-butylphosphine [34] (Eqn. 20).

$$CoBr_2 + 2C_6F_5MgBr \xrightarrow{THF} \xrightarrow{PBu_3} (C_6F_5)Co(PBu_3)_2 \qquad (20)$$

Two recent papers by Klein and Karsch describe the synthesis of novel trimethylcobalt(III) [35], dimethylcobalt(III) [35], and dimethylcobalt(II) [36] complexes of trimethylphosphine. The trimethylcobalt(III) complex, trimethyltris(trimethylphosphine)cobalt(III) is of particular interest since it represents the first example of a stable trialkylcobalt complex. It is included in the di-organocobalt review because it readily undergoes reactions with compounds containing acidic hydrogens yielding the corresponding dimethylcobalt(III) derivatives and methane.

The synthesis of $(CH_3)_3Co(PMe_3)_3$ involves the reaction in ether at -70 °C of $Co(acac)_3$, three equivalents of methyllithium, and an excess of trimethylphosphine [35]. After slowly warming the solution to 20 °C the product is precipitated with pentane (Eqn. 21). The structure of $(CH_3)_3Co(PMe_3)_3$ will be discussed below.

$$Co(acac)_3 + 3LiCH_3 \xrightarrow[Et_2O]{PMe_3} (CH_3)_3Co(PMe_3)_3 + Li(acac) \qquad (21)$$

The dimethylcobalt(III) complexes of the type $(CH_3)_2Co(PMe_3)_3X$ ($X = Cl^-$, $^-OC_6H_5$, $^-C{\equiv}CC_6H_5$) were prepared by the reaction of the trimethyl complex with HCl, phenol, and phenylacetylene [35] (Eqn. 22).

$$(CH_3)_3Co(PMe_3)_3 + HCl \longrightarrow (CH_3)_2Co(PMe_3)_3Cl + CH_4 \qquad (22a)$$

$$(CH_3)_3Co(PMe_3)_3 + C_6H_5OH \longrightarrow (CH_3)_2Co(PMe_3)_3(OC_6H_5) + CH_4 \qquad (22b)$$

$$(CH_3)_3Co(PMe_3)_3 + HC{\equiv}CC_6H_5 \longrightarrow (CH_3)_2Co(PMe_3)_3(C{\equiv}CC_6H_5) + CH_4 \qquad (22c)$$

Additional dimethylcobalt complexes were obtained by the displacement of Cl^- from $(CH_3)_2Co(PMe_3)_3Cl$ by Br^- and I^- (Eqn. 23).

$$(CH_3)_2Co(PMe_3)_3Cl + NaBr \xrightarrow{THF} (CH_3)_2Co(PMe_3)_3Br + NaCl \qquad (23a)$$

$$(CH_3)_2Co(PMe_3)_3Cl + NaI \xrightarrow{THF} (CH_3)_2Co(PMe_3)_3I + NaCl \qquad (23b)$$

The five-coordinate dimethylcobalt(II) complex dimethyltris(trimethylphosphine)cobalt(II), $(CH_3)_2Co(PMe_3)_3$, was prepared under anaerobic conditions in ether (-70 °C) from cobalt(II) chloride and methyllithium in the presence of an excess of trimethylphosphine [36] (Eqn. 24).

$$CoCl_2 + 2CH_3Li \xrightarrow[PMe_3]{Et_2O, -70°C} (CH_3)_2Co(PMe_3)_3 \qquad (24)$$

The reactions of organoaluminum compounds with tris(acetylacetonato)cobalt(III)($Co(acac)_3$) in the presence of π-acceptor ligands provides a very convenient route to the preparation of *cis*-dialkyl cobalt complexes. It is assumed that these alkylation reactions proceed through stepwise exchange reactions of the acac ligands of $Co(acac)_3$ with the alkyl groups of the alkylaluminum compounds resulting in intermediate complexes having both alkyl and acac ligands. For example, diethylbis(2,2′-bipyridine)cobalt(II), $(C_2H_5)_2Co^{II}(bipy)_2$, was prepared in 85% yield by the reaction of $Co(acac)_3$, bipy, and diethylaluminum monoethoxide in ether at -10 °C [37]. The authors assumed a *trans*-complex, but that is unlikely in view of more recent results (see below).

A similar reaction of $Co(acac)_3$ with diethylaluminum monoethoxide in the presence of tetrakis(diphenylphosphinomethyl)methane, $C(CH_2PPh_2)_4$, results in the formation of an air sensitive *cis*-diethylcobalt complex [38] (Eqn. 25).

$$2C(CH_2PPh_2)_4 + 2Co(acac)_3 + 3(C_2H_5)_2Al(OC_2H_5) \longrightarrow 2(C_2H_5)_2HCo(C(CH_2PPh_2)_4) + 2C_2H_4 + + 3Al(acac)_2(OC_2H_5) \qquad (25)$$

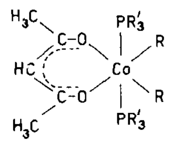
Finally, recent papers [39] describe the synthesis and properties of a series of trivalent *cis*-dialkylcobalt complexes with acac and a variety of tertiary phosphine ligands. These complexes were also prepared by mixing $Co(acac)_3$, a tertiary phosphine, and the appropriate dialkylaluminum monoethoxide reactants in ether (Eqn. 26).

$$Co(acac)_3 + R_2Al(OC_2H_5) + PR_3' \xrightarrow{Et_2O} R_2Co^{III}(acac)(PR_3')_2 \qquad (26)$$

The scope of the reaction is shown in structure II. The proof of the geometrical isomer shown will be discussed below.

3. Characterization of Di-Organocobalt Complexes

The structures and physical properties of the di-organocobalt compounds have been established in most cases utilizing the usual techniques of X-ray analysis, NMR and IR spectroscopy, chemical analysis



IIa R = CH_3, PR'_3 = PEt_3
IIb R = CH_3, PR'_3 = $PPhMe_2$
IIc R = C_2H_5, PR'_3 = $PPhMe_2$
IId R = n-C_3H_7, PR'_3 = $PPhMe_2$
IIe R = i-C_4H_9, PR'_3 = $PPhMe_2$
IIf R = CH_3, PR'_3 = PPh_2Me
IIg R = CH_3, PR'_3 = PBu_3
IIh R = CD_3CH_2, PR'_3 = $PPhMe_2$

and magnetic susceptibility measurements. The characterization of the di-organocobalt complexes of macrocyclic and non-macrocyclic ligands will be discussed in this section.

A. X-ray Structures

The crystal and molecular structure of the dimethyl compound $(CH_3)_2Co(BDMl,3pn)$ was determined by X-ray analysis [40]. The results confirm the *trans* configuration of the methyl groups, and a distorted octahedral geometry about the cobalt atom. In analogy to the mono-organocobalt chelates, the four nitrogen atoms of the macrocyclic ligand occupy the equatorial positions and are coplanar within experimental error. The cobalt atom is displaced only 0.029 Å from the plane defined by the four nitrogen atoms. The six-membered ring containing the cobalt atom, imine nitrogens, and trimethylene bridge has a flattened chair conformation. The mean value of the four C–CH_3 bond lengths (1.506 Å) is in agreement with the expected value. However, the shorter than expected N–C (1.31 Å) and C–C (1.45 Å) bond lengths indicate extensive π-delocalization in the two five-membered rings. These N–C and C–C bond lengths compare to mean N–C and C–C bond lengths of 1.29 Å and 1.47 Å, respectively, in $RCo(dmg)_2$ complexes [41].

The two axial cobalt–carbon bond lengths in $(CH_3)_2Co(BDMl,3pn)$ are equal and have a mean value of 2.047 Å. These values are typical of other methyl cobalt chelates and are only slightly longer than the value of 1.99 Å found for the corresponding monomethyl complex $[CH_3Co(BDMl,3pn)H_2O]^+$ [42]. The N–Co–CH_3 bond angles of 89.7° indicate a nearly perpendicular orientation of the axial methyl groups with respect to the macrocyclic ligand plane.

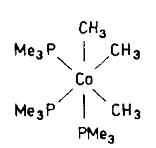
The molecular structure of a di-organo phosphine complex was also determined by X-ray analysis. Owsten and Rowe [43] confirmed the previously assumed [30] *trans*-square planar geometry of dimesitylbis(diethylphenylphosphine)cobalt(II), $((CH_3)_3C_6H_2)_2Co(PEt_2Ph)_2$, which was based on dipole moment and magnetic susceptibility measurements. The planes of the mesityl groups are perpendicular to the plane of the complex, a consequence of the *ortho*-methyl substituents. The square planar geometry is relatively unusual in complexes of Co(II) with monodentate ligands; it is presumably a consequence of the large ligand field strength of the phosphines, and steric factors which force a planar configuration of the ligands.

B. Nuclear Magnetic Resonance Studies

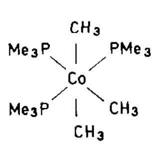
The majority of the di-organocobalt compounds are diamagnetic Co(III) complexes, and as a consequence useful NMR spectra have been obtained. The ^1H, ^{31}P, and ^{19}F spectra have been used to characterize the structure of the complexes. We will discuss some of the more interesting results below.

The ^1H NMR spectra of $(CH_3)_2Co(BDMl,3pn)$ and $(CH_3)(C_6H_5)Co(BDMl,3pn)$ in $CDCl_3$ [44], and of $[(CH_3)_2Co(tim)]BPh_4$ and $[(CH_3)_2Co(cr)]BPh_4$ in $(CD_3)_2SO$ [22] have been reported. The spectra confirm the presence of two axial organo groups attached to cobalt. The high field position of these methyl groups (0.06 to 0.36 ppm vs. TMS) is common for dimethylcobalt complexes and reflects the well-known electron donating capability of CH_3^- [45, 46], and thus the buildup of charge density on cobalt. This effect is further demonstrated in the series of complexes of the type $(CH_3)(X)Co(BDMl,3pn)$ (X = I, *m*-FC_6H_4, *p*-FC_6H_4, C_6H_5, and CH_3) [44], where the axial methyl chemical shift moves to higher field in the order I (0.71 ppm) < *m*-FC_6H_4 (0.38 ppm) < *p*-FC_6H_4 (0.36 ppm) < C_6H_5 (0.35 ppm) < CH_3 (0.06 ppm). The superior σ-donor power of CH_3^- found in this study is in agreement with a similar investigation of the ^{19}F NMR spectra of *para*- and *meta*-substituted $[(FC_6H_4)Co(BDMl,3pn)X]$ complexes (X = CH_3, FC_6H_4, and I) [28].

Klein and Karsch [35] demonstrated the usefulness of ^{31}P NMR spectra in the determination of the structure of $(CH_3)_3Co(PMe_3)_3$ (structure III). Both



IIIa, facial



IIIb, meridional

the facial and meridional isomers are possible. The facial isomer (IIIa) has three equivalent phosphorous atoms, and should therefore produce only one peak in the ^{31}P NMR spectrum. The meridional isomer (IIIb) has two equivalent phosphorous atoms and a different third phosphorous atom. This isomer should give rise to a doublet and a triplet of 2:1 intensity. The spectrum actually observed consisted of a doublet and an upfield triplet of 2:1 intensity ratio, thus confirming the meridional structure IIIb. Unfortunately, the paramagnetic five-coordinate complex $(CH_3)_2Co^{II}(PMe_3)_3$ could not be characterized by ^{31}P or ^{1}H NMR [36].

The ^{1}H and ^{31}P NMR spectra of the previously discussed dialkylcobalt complexes, $R_2Co(acac)(PR'_3)_2$ (structures IIa to IIh), confirm that these compounds have an octahedral configuration with the two cobalt-bonded alkyl groups *cis* to each other and the PR'_3 *trans* to each other [39]. The methyl protons of acac are magnetically equivalent and appear as a singlet from −80 to +20 °C. The protons in the two cobalt-bonded methyl groups are also equivalent and appear as a triplet at low temperature due to coupling with ^{31}P, but appear as a singlet at higher temperatures due to the dissociation of PR'_3. The ^{31}P NMR spectra of these complexes indicate that the two equivalent phosphorous nuclei undergo exchange at room temperature since the singlet observed at −70 °C broadens considerably as the temperature is raised.

C. Infrared Studies

Infrared spectroscopy has not yet been utilized extensively in the characterization of the di-organocobalt complexes. However, the frequencies $\nu((Co-CH_3)$ and $\delta_s(Co-CH_3)$ have been reported for several dimethyl complexes [35, 36, 39]. Although correlation of the existing data is difficult due to the different matrices used, several trends are apparent. For example, the $\nu(Co-CH_3)$ and $\delta_s(Co-CH_3)$ frequencies are found in the regions 460–479 cm^{-1} and 1157–1161 cm^{-1}, respectively, for the series of complexes $(CH_3)_2Co(PMe_3)_2X$ ($X = CH_3$, Cl, Br, I) [35]. The order of increasing frequency $CH_3 < I < Br < Cl$ was observed for $\nu(Co-CH_3)$. Other dialkyl complexes of the type $R_2Co(acac)(PR'_3)_2$ show $\nu(Co-C)$ bands at a slightly higher frequency (570–585 cm^{-1}) [39].

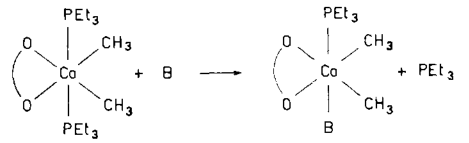
4. Reactions of Di-organocobalt Complexes

In contrast to the reactivity studies of the mono-organocobalt compounds, very little is known about the reactivity of the di-organocobalt complexes. Generally, reactions occur with cleavage of a cobalt–carbon bond, however simple substitution reactions involving other ligands are also known. The discussion of reactions will be classified according to (1) substitution reactions without cobalt–carbon bond cleavage, (2) reactions with light and heat, (3) insertion reactions, (4) cobalt–carbon bond cleavage by non-metallic electrophiles, and (5) cobalt–carbon bond cleavage by metallic electrophiles.

A. Substitution Reactions without Cobalt–Carbon Bond Cleavage

A few of the di-organocobalt compounds without macrocyclic ligands undergo a variety of substitution reactions which do not affect their cobalt–carbon bonds. These reactions are unknown for the di-organo derivatives of the quadridentate ligands BDMI,3pn, tim, and cr. This is a consequence of the chelate effect, and of strong π-electron interactions between the metal ion and the imine and oxime nitrogens.

Ikariya and Yamamoto [39] observed that one of the tertiary phosphine ligands in $(CH_3)_2Co(acac)(PR'_3)_2$ (structure II) could be replaced by pyridine or 4-picoline to give $(CH_3)_2Co(acac)(PR'_3)(py)$ and $(CH_3)_2Co(acac)(PR'_3)(4\text{-pic})$, respectively. Eqn. 27 exemplifies the reactions in which



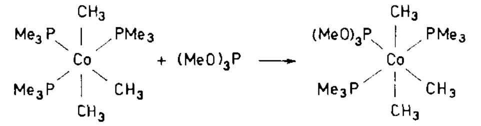
(27)

B is py or 4-pic and PR'_3 is PEt_3 (structure IIa). The two phosphine ligands were also replaced by the bidentate ligand (bipy) to give $R_2Co(acac)(bipy)$ (Eqn. 28). The authors do not describe the necessary

$$R_2Co(acac)(PR'_3)_2 + bipy \longrightarrow R_2Co(acac)(bipy) \qquad (28)$$

rearrangement of the reactant of Eqn. 27 to accommodate bidentate bipy. The substitution reaction of Eqn. 27 is in agreement with the variable temperature ^{31}P NMR spectra of the complex; the data indicate that rapid phosphine exchange occurs at room temperature [39].

Other complexes containing phosphine ligands react similarly. The dimethyl complex $(CH_3)_2Co(PMe_3)_3Cl$ reacts with excess NaX ($X = Br^-, I^-$) to yield the corresponding bromide and iodide complexes. This reaction (Eqn. 23) was discussed earlier with respect to its synthetic utility [35]. In addition, trimethylphosphite selectively replaces the trimethylphosphine ligand which is *trans* to a CH_3 group, in its reaction with $(CH_3)_3Co(PMe_3)_3$ (structure IIIb) (Eqn 29). The stereospecificity of this reaction



(29)

presumably reflects the well-known ground state *trans*-labilizing influence of CH_3 and the greater lability to nucleophiles of $Co-PMe_3$ than $Co-CH_3$ bonds.

B. Reactions with Light and Heat

In analogy to the mono-organocobalt complexes cobalt–carbon bond cleavage of di-organocobalt complexes containing macrocyclic ligands can be induced photochemically or thermally in both the solid state and in solution. The light sensitivity of

$[(CH_3)_2Co(tim)]^+$ and $[(CH_3)_2Co(cr)]^+$ in solution has been observed, but details are unknown [22]. In contrast the photo- and thermal-lability of $(CH_3)_2Co(BDMl,3pn)$ was studied in detail [47].

The anaerobic photolysis of $(CH_3)_2Co(BDMl,3pn)$ is faster in i-C_3H_7OH ($t_{1/2}$ = 16.0 min) than in C_2H_5OH ($t_{1/2}$ = 34.5 min). These relative rates parallel the ease of abstraction of the α-proton from the alcohol and are explainable on that basis. Mass spectral analysis of the alkane formed during the anaerobic photolysis of $(CD_3)_2Co(BDMl,3pn)$ corroborates the conclusion of a free radical process because the only observed alkane product is CD_3H. The anaerobic photolysis products, CH_4 and $Co^I(BDMl,3pn)$, can be explained by the processes in Eqn. 30. In Eqn. 30b the unstable $CH_3Co^{II}(BDMl,3pn)$ disproportionates to the cobalt(I) analog and the starting dimethyl complex which reacts further with light (Eqn. 30a).

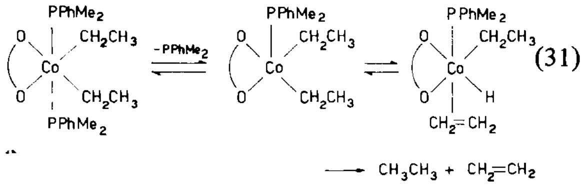
$$(CH_3)_2Co^{III}(BDMl,3pn) \xrightarrow{h\nu, N_2} CH_3Co^{II}(BDMl,3pn) + CH_4 \qquad (30a)$$

$$2CH_3Co^{II}(BDMl,3pn) \longrightarrow (CH_3)_2Co^{III}(BDMl,3pn) + Co^I(BDMl,3pn) \qquad (30b)$$

Photolysis of $(CH_3)_2Co(BDMl,3pn)$ in the presence of oxygen and bromide ion yields CH_4 and $Co(BDMl,3pn)Br_2$.

Several papers have been published on the thermal decomposition reactions of dialkylcobalt complexes of bidentate and phosphine ligands, and mechanisms involving both the homolytic scission of cobalt–carbon σ-bonds and the β-elimination of cobalt hydrides have been proposed [38, 39]. The latter course has been established for the *cis*-diethyl complex $(C_2H_5)_2Co(acac)(PPhMe_2)_2$ [39] (structure IIc) and $H(C_2H_5)_2Co((PCH_2PPh_2)_4C)$ [38]. On heating these complexes in the solid state ethylene and ethane are formed in a 1:1 ratio. The observation that n-butane is not formed in these reactions precludes the possibility that ethane and ethylene are formed by the disproportionation of free ethyl radicals since the rate constant for the coupling of ethyl radicals is six times greater than that for their disproportionation [48].

Further evidence supporting the contention that ethyl radicals are not intermediates was provided from experiments using $(CD_3CH_2)_2Co(acac)(PPhMe_2)_2$ (structure IIh) [39]. The formation of $CH_2{=}CD_2$ and CH_2DCD_3 in a 1:1 molar ratio upon heating is compatible with a mechanism involving the β-elimination of a cobalt hydride and concomitant formation of 1 equivalent of ethylene. The initial step is followed by the reduction of a second cobalt–alkyl bond by the hydride to yield 1 equivalent of ethane. In addition, the solution thermolysis of $(CD_3CH_2)_2Co(acac)(PPhMe_2)_2$ (structure IIh) gave appreciable quantities of *cis*- and *trans*-$C_2H_2D_2$, C_2HD_3 and C_2H_3D. These products are the result of a H–D scrambling process, and can be accounted for by the reversible elimination, ethylene-insertion process shown in Eqn. 31.



(31)

C. Insertion Reactions

Relatively few insertion reactions involving the Co–C bond of di-organocobalt complexes are known. Solutions of $(CH_3)_2Co(PMe_3)_3$ absorb carbon monoxide at 20 °C to form acetone and diamagnetic Co(0) dimers of the composition $[Co(CO)_2(PMe_3)_2]_2$ [36]. The formation of intermediate σ-acetyl cobalt(II) complexes followed by the reductive elimination of acetone was assumed (Eqn. 32).

$$(CH_3)_2Co^{II}(PMe_3)_3 \xrightarrow[-PMe_3]{-78^\circ C, CO} (CH_3CO)Co^I(CO)_2(PMe_3)_2 + [Co^0(CO)_2(PMe_3)_2]_2 + (CH_3)_2CO \qquad (32a)$$

$$(CH_3CO)Co^I(CO)_2(PMe_3)_2 \xrightarrow{20^\circ C} [Co^0(CO)_2(PMe_3)_2]_2 + (CH_3)_2CO \qquad (32b)$$

The same dimethyl complex reacts with NO at low temperature to form $(CH_3)_2Co(NO)(PMe_3)_2$ which rearranges via NO insertion into a Co–C σ-bond to give $[CH_3Co(CH_3NO)(PMe_3)_2]_2$ at 15 °C (Eqn. 33).

$$(CH_3)_2Co(PMe_3)_3 + NO \xrightarrow{-30^\circ C} (CH_3)_2Co(NO)(PMe_3)_2 + PMe_3 \qquad (33a)$$

$$2(CH_3)_2Co(NO)(PMe_3)_2 \xrightarrow{15^\circ C} [CH_3Co(CH_3NO)(PMe_3)_2]_2 \qquad (33b)$$

NMR spectra of the dimer suggest a structure containing two bridging CH_3NO groups.

The dialkyl complexes $R_2Co(acac)(PR'_3)_2$ (structure II) react with carbon monoxide to yield the corresponding dialkyl ketones and $Co^I(acac)(CO)_2(PR'_3)$ [39] (Eqn. 34). Carbon monoxide insertion into one

$$R_2Co^{III}(acac)(PR'_3)_2 \xrightarrow[-PR'_3]{CO} R_2Co(acac)(CO)(PR'_3) \xrightarrow{CO} R(RCO)Co(acac)(CO)(PR'_3) \xrightarrow{CO} Co^I(acac)(CO)_2(PR'_3) + R_2CO \qquad (34)$$

of the alkylcobalt bonds followed by reductive elimination of the ketone was assumed.

Finally, in support of the foregoing conclusions the trimethylcomplex $(CH_3)_3Co(PMe_3)_3$ reacts with 4 equivalents of carbon monoxide to form the stable acetyl cobalt(I) complex $(CH_3CO)Co^{I}(CO)_2(PMe_3)_2$ and acetone [35] (Eqn. 35).

$$(CH_3)_3Co(PMe_3)_3 + 4CO \xrightarrow{-PMe_3} (CH_3CO)Co(CO)_2(PMe_3)_2 + (CH_3)_2CO \quad (35)$$

D. Reactions with Non-metallic Electrophiles

Electrophilic reagents that induce cleavage of cobalt–carbon bonds in di-organocobalt complexes include halogen molecules, protonic acids, and a variety of metal ions. In this section we will discuss the halogens and the protonic acids electrophiles; we will describe metal ion electrophiles in the next section.

The reactions of halogens with RR'Co(BDMl,3pn) (R = R' = CH_3, C_6H_5; RR' = $(CH_3)(C_6H_5)$, $(C_2H_5)(C_6H_5)$) in $CHCl_3$ have been discussed [49]. The dealkylation (or dearylation) reactions of these complexes with I_2 are interesting since the reactions occur with two different stoichiometries depending upon the I_2/complex molar ratio. These 1:1 and 2:1 reactions, exemplified by the dimethyl derivative, are shown in Eqns. 36 and 37, respectively.

$$(CH_3)_2Co(BDMl,3pn) + I_2 \longrightarrow CH_3Co(BDMl,3pn)I + CH_3I \quad (36)$$

$$(CH_3)_2Co(BDMl,3pn) + 2I_2 \longrightarrow Co(BDMl,3pn)I_2 + 2CH_3I \quad (37)$$

Information about the mechanism of these reactions was obtained using the polar ICl molecule in place of I_2. When RR'Co(BDMl,3pn) (R = R' = CH_3, C_6H_5; RR' = $(CH_3)(C_6H_5)$, $(C_2H_5)(C_6H_5)$) was treated with ICl in the molar ratio ICl/complex = 1, the products shown in Eqn. 38 were observed.

$$RR'Co(BDMl,3pn) + ICl \longrightarrow RI + R'Co(BDMl,3pn)Cl \quad (38)$$

The exclusive formation of RI in preference to RCl was interpreted in terms of an electrophilic attack at carbon by the electropositive I^+ species. Furthermore, the reactions of $R(C_6H_5)Co(BDMl,3pn)$ (R = CH_3, C_2H_5) with ICl show that the alkyl group is more reactive than phenyl (Eqn. 39).

$$R(C_6H_5)Co(BDMl,3pn) + ICl \longrightarrow (C_6H_5)Co(BDMl,3pn)Cl + RI \quad (39)$$

The preference for the alkyl substituent in the reactions of the unsymmetrical complexes was not expected since similar reactions involving the unsymmetrical organomercurials and iodine gave the opposite result [50]. In addition, this behavior appears to be in contrast to kinetic data for the reactions of $R_2Co(BDMl,3pn)$ with $C_6H_5Hg^+$ [27] and $[RCo(BDMl,3pn)]^+$ with Hg^{2+} [51], where the phenyl derivatives react faster than the methyl derivatives. This anomaly has not been explained satisfactorily and more data is needed.

The manner in which divalent dialkylcobalt complexes react with halogens appears to be governed in some respects by the coordination number of the complex, and the nature of the non-alkyl ligands. For example, the five-coordinate complexes $(CH_3)_2Co^{II}(PMe_3)_3$ are rapidly oxidized by iodine or bromine to give the corresponding dimethylcobalt(III) halides (Eqn. 40), without cleavage of a cobalt–carbon bond [36]. The octahedral complex $(C_2H_5)_2Co^{II}(bipy)_2$, in contrast, reacts with iodine to give the corresponding iodocomplex, and, presumably, ethyl iodide [37] (Eqn. 41).

$$2(CH_3)_2Co^{II}(PMe_3)_3 + X_2 \longrightarrow 2(CH_3)_2Co^{III}X(PMe_3)_3 \quad (40)$$

$$(C_2H_5)_2Co^{II}(bipy)_2 + 2I_2 \longrightarrow Co^{II}(bipy)_2I_2 \quad (41)$$

Nearly all of the di-organocobalt complexes discussed in this review are susceptible to electrophilic attack by H_3O^+. These reactions invariably lead to cleavage of at least one cobalt–carbon bond, in contrast to the essentially unreactive mono-organocobalt chelates. The increased reactivity observed for the di-organocobalt compounds is presumably a manifestation of the increased electron density on cobalt which activates the alkyl ligands for electrophilic attack.

Costa and co-workers [52, 53] first reported the reaction of $(CH_3)_2Co(BDMl,3pn)$ with H_3O^+. The products CH_4 and $[CH_3Co(BDMl,3pn)]^+$ were identified, but no information regarding the stoichiometry or rate of this reaction was reported. Subsequent titration data [25, 54] indicate that the reaction occurs with the indicated 1:1 stoichiometry (Eqn. 42) and proceeds to completion.

$$(CH_3)_2Co(BDMl,3pn) + H_3O^+ \longrightarrow CH_4 + [CH_3Co(BDMl,3pn)(H_2O)]^+ \quad (42)$$

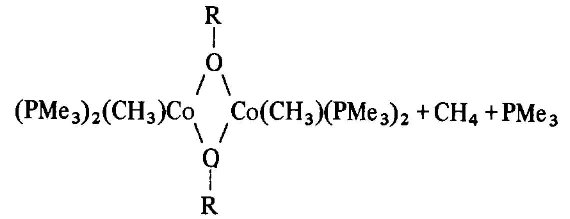
Kinetic studies [25, 27] on the reaction of $(CH_3)_2Co(BDMl,3pn)$ with excess H_3O^+ show a first-order dependence on the concentration of the dimethyl complex and $[H_3O^+]$. The second-order rate constants show a small solvent dependence and are greater than those determined for $[(CH_3)_2Co(tim)]^+$ by a factor of about 15. The slower rate observed for the positively charged $[(CH_3)_2Co(tim)]^+$ complex compared to the neutral $(CH_3)_2Co(BDMl,3pn)$ complex reflects the expected electrostatic repulsion between the two positively-charged reactants.

Klein and Karsch [36] reported that weakly acidic alcohols ROH (R = CH_3, C_6H_5) cleave both cobalt–carbon bonds of $(CH_3)_2{}^{II}Co(PMe_3)_3$ with the liberation of two equivalents of methane (Eqn. 43).

$$(CH_3)_2Co^{II}(PMe_3)_3 + 2ROH \longrightarrow 2CH_4 + Co(OR)_2 + 3PMe_3 \qquad (43)$$

These reactions presumably occur in a step-wise fashion since the 1:1 reaction resulted in isolable monomethyl complexes of the composition $[(CH_3)Co(PMe_3)_2OR]_2$ (Eqn. 44).

$$2(CH_3)_2Co(PMe_3)_3 + 2ROH \longrightarrow$$



$$(PMe_3)_2(CH_3)Co(OR)_2Co(CH_3)(PMe_3)_2 + CH_4 + PMe_3$$

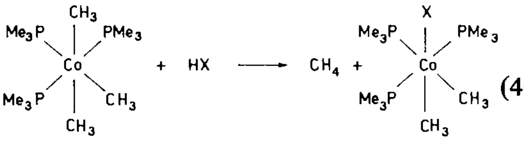
(44)

These intermediates are unstable in solutions containing excess ROH however, and decompose further yielding the products shown in Eqn. 43. An exception is the 1:1 reaction of $(CH_3)_2Co(PMe_3)_3$ with Hacac which gives the more stable $(CH_3)Co(acac)(PMe_3)_2$ compound (Eqn. 45).

$$(CH_3)_2Co(PMe_3)_2 + Hacac \longrightarrow (CH_3)Co(acac)(PMe_3)_2 + CH_4 + PMe_3 \qquad (45)$$

The divalent complex $(C_2H_5)_2Co^{II}(bipy)_2$ also reacts with weak acids such as water and alcohol to cleave both cobalt–carbon bonds [37].

The trimethyl complex $(CH_3)_3Co(PMe_3)_3$ (structure IIIb) reacts with acids to yield from 1 to 3 equivalents of methane [35]. Treatment of this complex with a variety of protic acids in the molar ratio acid/complex = 1 results in the loss of one of the *trans* methyl groups, and leads to the formation of dimethylcobalt(III) complexes (Eqn. 46).



(46)

$(X = Cl^-, C_6H_5O^-, C_6H_5C{\equiv}C^-)$

The remaining methyl groups react further with excess acid to form an additional two equivalents of methane. The enhanced reactivity of *trans* methyl groups seen in the 1:1 reactions is once again entirely consistent with the well known *trans* labilizing influence of CH_3.

E. Reactions with Metallic Electrophiles

In contrast to the mono-organocobalt compounds, the reactions of metal electrophiles with di-organocobalt complexes remain relatively unstudied. Two papers describe the alkyl and aryl transfer reactions of $R_2Co(BDM1,3pn)$, $[R_2Co(tim)]^+$ and $[R_2Co(cr)]^+$ with Hg^{2+} and $C_6H_5Hg^+$ [27, 55]. One group [55] studied the reactions of $(CH_3)_2Co(BDM1,3pn)$ with $HgCl_2$ in acetonitrile. In the presence of excess Hg^{2+} a two step reaction was observed which resulted in the transfer of both methyl groups to mercury (Eqns. 47 and 48). In the presence of excess complex a third reaction was observed (Eqn. 49).

$$(CH_3)_2Co(BDM1,3pn) + Hg^{2+} \xrightarrow{\text{fast}} [CH_3Co(BDM1,3pn)]^+ + CH_3Hg^+ \qquad (47)$$

$$[CH_3Co(BDM1,3pn)]^+ + Hg^{2+} \xrightarrow{\text{slow}} Co^{III}(BDM1,3pn)^{2+} + CH_3Hg^+ \qquad (48)$$

$$(CH_3)_2Co(BDM1,3pn) + CH_3Hg^+ \longrightarrow [CH_3Co(BDM1,3pn)]^+ + (CH_3)_2Hg \qquad (49)$$

Reaction 49 also occurs with $C_6H_5Hg^+$ and with $(C_6H_5)_2Co(BDM1,3pn)$ or $(C_6H_5CH_2)_2Co(BDM1,3pn)$ as donors.

Espenson *et al.* [27] published the results of a kinetic study on the reactions of $R_2Co(BDM1,3pn)$, $(R_2Co(tim)]^+$ and $[R_2Co(cr)]^+$ with $C_6H_5Hg^+$ (R = CH_3, C_2H_5, C_6H_5, n-C_3H_7). These reactions were very fast in 1:1 THF–H_2O, and in fact when R = C_6H_5, C_2H_5 and n-C_3H_7 the reactions were too rapid for the stopped-flow technique.

For $(CH_3)_2Co(BDM1,3pn)$, $[(CH_3)_2Co(tim)]^+$ and $[(CH_3)_2Co(cr)]^+$ the reactions with $C_6H_5Hg^+$ follow a second-order rate expression supporting a mechanism in which there is a direct transfer of a methyl carbanion in a transition state formed by the biomolecular interaction of the dimethyl complex and $C_6H_5Hg^+$. The second-order rate constants followed the order: $(CH_3)_2Co(BDM1,3pn)$ (2×10^6 M^{-1} sec^{-1}) > $[(CH_3)_2Co(cr)]^+$ (2.1×10^5 M^{-1} sec^{-1}) > $[(CH_3)_2Co(tim)]^+$ (1.3×10^5 M^{-1} sec^{-1}). The slower rates observed for $[(CH_3)_2Co(tim)]^+$ and $[(CH_3)_2Co(cr)]^+$ relative to $(CH_3)_2Co(BDM1,3pn)$ are consistent with their positive charge, and therefore lower reactivity toward electrophilic reagents.

Witman and Weber [54] studied the reactivity and kinetics of the reactions of $(CH_3)_2Co(BDM1,3pn)$ with Zn^{2+}, Cd^{2+}, and Pb^{2+}. In the presence of a 1:1 complex/M^{2+} ratio or excess metal ion (M^{2+}) the products shown in Eqn. 50 are observed.

$$(CH_3)_2Co(BDM1,3pn) + M^{2+} \longrightarrow [CH_3Co(BDM1,3pn)]^+ + CH_3M^+ \qquad (50)$$

The unstable CH_3M^+ products slowly decompose by reacting with the i-C_3H_7OH solvent (Eqn. 51).

$$CH_3M^+ + i\text{-}C_3H_7OH \longrightarrow CH_4 + M(i\text{-}OC_3H_7)^+ \qquad (51)$$

The kinetics of the very fast reactions with excess Cd^{2+} and Zn^{2+} were studied and the mechanism determined (Eqn. 52).

$$\mathrm{(CH_3)_2Co(BDMl,3pn) + M^{2+} \overset{K}{\rightleftharpoons} M^{2+}\cdot(CH_3)_2Co(BDMl,3pn)} \qquad (52a)$$

$$\mathrm{M^{2+}\cdot(CH_3)_2Co(BDMl,3pn) \xrightarrow[solvent]{k_1} [CH_3Co(BDMl,3pn)(solv)]^+ + CH_3M^+} \qquad (52b)$$

The kinetic data for M^{2+} (K, k_1) are: Zn^{2+} (3.8×10^3 M^{-1}, 3.8×10^2 sec^{-1}) and Cd^{2+} (10.6×10^3 M^{-1}, 4.0×10^2 sec^{-1}).

The reactions of excess $(CH_3)_2Co(BDMl,3pn)$ with Zn^{2+}, Cd^{2+}, and Pb^{2+} are in agreement with Eqn. 53 [56]. The very reactive $(CH_3)_2M$ is decomposed by the i-C_3H_7OH solvent with the formation of methane. The chemistry of Eqn. 53 was demonstrated by a variety of techniques including spectrophotometric titration, rates of $(CH_3)_2Co(BDMl,3pn)$ decomposition, and the rates of CH_4 evolution from the decomposition of $(CH_3)_2M$.

$$\mathrm{(CH_3)_2Co(BDMl,3pn) + M^{2+} \xrightarrow{fast} [CH_3Co(BDMl,3pn)]^+ + CH_3M^+} \qquad (53a)$$

$$\mathrm{(CH_3)_2Co(BDMl,3pn) + CH_3M^+ \xrightarrow{slow} [CH_3Co(BDMl,3pn)]^+ + (CH_3)_2M} \qquad (53b)$$

Additional examples of reactions of di-organocobalt complexes with metal electrophiles include the reactions of $(CH_3)_2Co(BDMl,3pn)$ with Ag^+ to form Ag^0 and C_2H_6 [25, 33]. A recent example is the reaction of $(CH_3)_2Co(acac)(PPhMe_2)_2$ (structure IIb) with Hg^{2+} to form $(CH_3)_2Hg$ [39].

Costa and co-workers [53] first reported the reactions of methyl transfer from $(CH_3)_2Co(BDMl,3pn)$ to $[Co^{III}(chel)(H_2O)_2]^+$ (chel = acacen, salen, saloph, and $7,7'$-$(CH_3)_2$salen) (Eqn. 54).

$$\mathrm{(CH_3)_2Co(BDMl,3pn) + [Co^{III}(chel)(H_2O)_2]^+ \longrightarrow [CH_3Co(BDMl,3pn)]^+ + CH_3Co(chel)H_2O} \qquad (54)$$

These reactions are analogous to the methyl-transfer reactions to Hg^{2+} and RHg^+ described above since they also occur by an $S_{E}2$ mechanism. Other dialkyl complexes show that this behavior includes $[(CH_3)_2Co(tim)]^+$ and $[(CH_3)_2Co(Cr)]^+$ [27]. The fact that the same second-order rate constants are observed for the reactions of the latter two complexes with a given diaquo-cobalt chelate suggests that the rate of methyl transfer is controlled by the rate of Co–H_2O substitution in the $[Co(chel)(H_2O)_2]^+$ complexes.

References

1 J. M. Pratt and P. J. Craig, *Adv. Organometal. Chem.*, *11*, 331 (1973).
2 D. Dodd and M. D. Johnson, *J. Organometal. Chem.*, *52*, 1 (1973).
3 P. G. Lenhert and D. C. Hodgkin, *Nature*, *192*, 937 (1961).
4 G. Costa, *Coord. Chem. Rev.*, *8*, 63 (1972).
5 G. Costa, A. Puxeddu and E. Reisenhofer, *Coll. Czech. Chem. Comm.*, *36*, 1065 (1971).
6 A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani and G. Tauzher, *Inorg. Chim. Acta Rev.*, *4*, 41 (1970).
7 J. M. Pratt, "Inorganic Chemistry of Vitamin B_{12}", Academic Press, N.Y. (1972).
8 chel: $(dmg)_2$, bis(dimethylglyoximato); sal_2en, (bis-(salicylaldehyde)1,2-ethane); BDMl,3pn), 2,3,9,10-tetramethyl-1,4,8,11-tetra-aza-undeca-1,3,8,10-tetraen-11-ol-1-olato; saloph, (N,N'-o-phenylenebis(salicylideneiminato); tim, 2,3,9,10-tetramethyl-1,4,8,11-tetra-azacyclotetradeca-1,3,8,10-tetraene; cr, 2,12-dimethyl-3,7,-11,17-tetraazabicyclo(11·3·11)-heptadeca-1,(17),2,11,-13,15-pentaene; acacen, N,N'ethylene-bis(acetylacetoneiminato); $7,7'$-$(CH_3)_2$salen,N,N'ethylenebis(7,7'-dimethylsalicylideneiminato); and others. Axial ligands will often be omitted to simplify the discussion.
9 G. N. Schrauzer and E. Deutsch, *J. Am. Chem. Soc.*, *91*, 3341 (1969).
10 H. A. O. Hill, J. M. Pratt, M. P. O'Riordan, F. R. Williams and R. J. P. Williams, *J. Chem. Soc. A*, 1859 (1971).
11 V. E. Magnuson and J. H. Weber, *J. Organometal. Chem.*, *92*, 233 (1975).
12 R. M. McAllister and J. H. Weber, *J. Organometal. Chem.*, 77, 91 (1974).
13 G. Costa, G. Mestroni and E. de Savorgnani, *Inorg. Chim. Acta*, *3*, 323 (1969).
14 G. N. Schrauzer, J. W. Sibert and R. J. Windgassen, *J. Am. Chem. Soc.*, *90*, 6681 (1968).
15 J. Halpern and P. F. Phelan, *J. Am. Chem. Soc.*, *94*, 1881 (1972).
16 V. L. Goedkin, S.-M. Peng and Y-a. Park, *J. Am. Chem. Soc.*, *96*, 284 (1974).
17 G. M. Schrauzer, J. A. Seck and T. M. Beckham, *Bioinorg. Chem.*, *2*, 211 (1973).
18 G. N. Schrauzer and E. A. Stadlbauer, *Bioinorg. Chem.*, *3*, 353 (1974).
19 G. Costa, A. Puxeddu and E. Reisenhofer, *J. Chem. Soc. Dalton*, 1519 (1972).
20 J. H. Espenson, W. R. Bushey and M. E. Chmielewski, *Inorg. Chem.*, *14*, 1302 (1975).
21 G. Costa, G. Mestroni, T. Licari and E. Mestroni, *Inorg. Nucl. Chem. Lett.*, *5*, 561 (1969).
22 K. Farmery and D. H. Busch, *Chem. Commun.*, 1091 (1970).
23 G. Costa, G. Mestroni and G. Tauzher, *J. Chem. Soc. Dalton*, 450 (1972).
24 G. Costa, G. Mestroni, G. Pellizer, G. Tauzher and T. Licari, *Inorg. Nucl. Chem. Lett.*, *5*, 515 (1969).
25 M. W. Witman, *Ph.D. Dissertation*, University of New Hampshire, 1976.
26 G. Costa, A. Puxeddu and E. Reisenhofer, *Chem. Commun.*, 993 (1971).
27 J. H. Espenson, H. L. Fritz, R. A. Heckman and C. Nicolini, *Inorg. Chem.*, *15*, 906 (1976).
28 H. A. O. Hill, K. G. Morallee, F. Cernivez and G. Pellizer, *J. Am. Chem. Soc.*, *94*, 277 (1972).
29 G. Mestroni, A. Camus and E. Mestroni, *J. Organometal. Chem.*, *24*, 775 (1970).
30 J. Chatt and B. L. Shaw, *J. Chem. Soc.*, 285 (1961).
31 H. Yamazaki and N. Hagihara, *Bull. Chem. Soc. Jap.*, *38*, 2212 (1965).
32 R. B. King, *Inorg. Chem.*, *5*, 82 (1966).
33 K. Matsuzaki and T. Yasukawa, *J. Phys. Chem.*, *71*, 1160 (1967).

34 C. F. Smith and C. Tamborski, *J. Organometal. Chem.*, *32*, 257 (1971).
35 H.-F. Klein and H. H. Karsch, *Chem. Ber.*, *108*, 956 (1975).
36 H.-F. Klein and H. H. Karsch, *Chem. Ber.*, *109*, 1435 (1976).
37 T. Saito, Y. Uchida, A. Misono, A. Yamamoto, K. Morifuji and S. Ikeda, *J. Organometal. Chem.*, *6*, 572 (1966).
38 J. Ellerman and W. H. Gruber, *Angew. Chem. Int. Ed.*, *7*, 129 (1968).
39 T. Ikariya and A. Yamamoto, *Chem. Lett.*, 85 (1976); *J. Organometal. Chem.*, *116*, 239 (1976).
40 M. Calligaris, *J. Chem. Soc. Dalton*, 1628 (1974).
41 P. G. Lenhert, *Chem. Commun.*, 980 (1967).
42 S. Brückner, M. Calligaris, G. Nardin and L. Randaccio, *Inorg. Chim. Acta*, *3*, 278 (1969).
43 P. G. Owsten and J. M. Rowe, *J. Chem. Soc.*, 3411 (1963).
44 G. Pellizer, G. R. Tauszik, G. Tauzher and G. Costa, *Inorg. Chim. Acta*, *7*, 60 (1973).
45 D. P. Rillema, J. Endicott and J. Barber, *J. Am. Chem. Soc.*, *95*, 6987 (1973).
46 P. G. Swetik and D. G. Brown, *J. Electroanal. Chem. Interfac. Chem.*, *51*, 433 (1974).
47 M. W. Witman and J. H. Weber, *Inorg. Nucl. Chem. Lett.*, *11*, 591 (1975).
48 R. A. Sheldon and J. K. Kochi, *J. Am. Chem. Soc.*, *92*, 4395 (1970).
49 R. Dreos, G. Tauzher, N. Marsich and G. Costa, *J. Organometal. Chem.*, *92*, 227 (1975).
50 F. R. Jensen and B. Rickborn, "Electrophilic Substitution of Organomercurials", McGraw–Hill, New York (1968) p. 82.
51 G. Tauzher, R. Dreos, G. Costa and M. Green, *J. Organometal. Chem.*, *81*, 107 (1974).
52 G. Mestroni, C. Cocevar and G. Costa, *Gazz. Chim. Ital.*, *103*, 273 (1973).
53 G. Costa, G. Mestroni and C. Cocevar, *Chem. Commun.*, 706 (1971).
54 M. W. Witman and J. H. Weber, *Inorg. Chem.*, *15*, 2375 (1976).
55 G. Mestroni, G. Zassinovich, A. Camus and G. Costa, *Transition Met. Chem.*, *1*, 32 (1975).
56 M. W. Witman and J. H. Weber, submitted for publication.