Alkyls and Aryls of Transition Metals. Part IV.* **51**. Cobalt(II) and Iron(II) Derivatives.

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The preparation and properties of stable organometallic complexes of the types trans- $[MR_2(PR'_3)_2]$ (M = Co, Fe; R, R' = organic radicals) are described. The groups R are ortho-substituted aryl groups where the substituents are somewhat bulky. These are the first planar complexes of cobalt(II) and iron(II) having only monodentate ligands. Their configurations were established by their magnetic and electric dipole moments. Possible reasons for the unusual configurations and stabilities of these organometallic derivatives are discussed.

VERY few stable alkyl or aryl derivatives of cobalt or iron are known although several unstable compounds have been described. With cobalt these include the very unstable $[CoMe(CO)_4]$ (ref. 1) and some ill-defined α - and β -naphthylcobalt derivatives.^{2,3} Some acetylides of the types $K_4[Co(C \equiv CR)_6]$ and $K_3[Co(C \equiv CR)_6]$ have also been described.⁴

Stable iron derivatives of the type $[FeR(\pi-C_5H_5)(CO)_2]$ (R = alkyl or aryl) have been prepared,⁵ and iron also gives unstable acetylides of the types $K_{4}[Fe(C=CR)_{6}]$ and K₃[Fe(C≡CR)₆].4,6

After the preparation of very stable alkyls, aryls, and ethynyls of platinum(II) of the types $[PtXRL_2]$ and $[PtR_2L_2]$ (R = alkyl, aryl, or substituted ethynyl; L = tertiary phosphine, arsine, or sulphide),^{7,8} and of aryl- and ethynyl-nickel(II) complexes⁹ $[NiXR(PR'_{3})_{2}]$ and $[NiR_{2}(PR'_{3})_{2}]$ (where R = ortho-substituted arylor substituted ethynyl radical) we have now prepared similar compounds of cobalt(II) and a compound of iron(II). These complexes are only of the type trans- $[MR_2(PR'_3)_2]$ (M = Co, Fe; R = orthosubstituted aryl group) and are less stable than the corresponding nickel complexes. In a given series of aryl complexes $[MR_2(PR'_{a})_2]$ the stabilities fall off markedly in the order of M, nickel > cobalt > iron. In general these organometallic complexes were prepared in a similar way to their nickel(II) analogues, by reaction of a Grignard reagent or lithium compound with a tertiary phosphine-metal halide complex. The products were hydrolysed (usually with dilute halogen acid); the desired complex was then precipitated or could be isolated from the organic layer:

$$[CoBr_2(PEt_2Ph)_2] + 2MgBrR \longrightarrow [CoR_2(PEt_2Ph)_2] + 2MgBr_2 \qquad (1)$$

$$[FeCl_2(PEt_2Ph)_4] + 2MgBrR \longrightarrow [FeR_2(PEt_2Ph)_2] + 2MgClBr + 2PEt_2Ph \quad . \quad . \quad (2)$$

Attempted Preparation of Alkylcobalt(II) and Cobalt Acetylide Derivatives.—Addition of $[CoBr_2(PEt_2Ph)_2]$ to ethereal methylmagnesium bromide at -65° gave an olive-green solution which on warming to -40° rapidly became dark brown. The product of this reaction was very unstable and no methylcobalt derivative could be isolated. Using methyl-lithium instead of the Grignard reagent gave similar results.

Treatment of bis(tertiary phosphine)cobaltous halides with (1) phenylethynylmagnesium bromide in ether or (2) lithium phenylacetylide in ether gave dark brown or reddishbrown amorphous products from which no cobalt-phenylacetylide complex could be

- ¹ Hieber, Vohler, and Braun, Z. Naturforsch., 1958, 13b, 192.
- ² Ingles and Polya, J., 1949, 2280.

- ³ Briggs and Polya, J., 1951, 1615.
 ⁴ Nast, Angew. Chem., 1960, 72, 26.
 ⁵ Piper and Wilkinson, J. Inorg. Nuclear Chem., 1956, 3, 104.
- ⁶ Nast and Urban, Z. anorg. Chem., 1956, 287, 17.
- ⁷ Chatt and Shaw, J., 1959, 705.
 ⁸ Chatt and Shaw, J., 1959, 4020.
 ⁹ Chatt and Shaw, J., 1960, 1718.

^{*} Part III, J., 1960, 1718.

isolated. Neither could one be isolated on use of sodium phenylacetylide in liquid ammonia.

Arylcobalt(II) Derivatives.—Addition of the turquoise-blue complex [CoBr₂(PEt₂Ph)₂] to mesitylmagnesium bromide at -30° resulted in the rapid formation of an olive-green reaction mixture which slowly became reddish-brown. The intermediate olive-green substance was probably [CoBr(mesityl)(PEt₂Ph)₂] but this compound appears to be very labile and soluble and attempts to isolate it were unsuccessful. From the final reddishbrown mixture the golden-yellow trans-[Co(mesityl)₂(PEt₂Ph)₂] was readily isolated in ca. 80% yield. This compound was stable in cold benzene solution, especially in the absence of air, but it decomposed rapidly in hot benzene. A poorer yield was obtained by the action of mesityl-lithium on [CoBr₂(PEt₂Ph)₂]. Other aryl groups giving stable arylcobalt derivatives were 2-biphenylyl, 2-methyl-1-naphthyl, and pentachlorophenyl. The pentachlorophenyl complex was most stable: thus $[Co(C_6Cl_5)_2(PEt_2Ph)_2]$ did not decompose below 220° and was moderately stable in boiling benzene. The other arylcobalt complexes decomposed completely below 150° and also in hot benzene. The diarylcobalt complexes of the type [Co(aryl)₂(PEt₂Ph)₂] have very small or zero dipole moments, indicating a trans-planar configuration.

The phenyl, o-tolyl, o-chlorophenyl, o-bromophenyl, α -naphthyl, and 9-anthryl groups all appeared to give similar cobalt complexes which, however, decomposed on attempted isolation. Diethylphenylphosphine, of the phosphines tried, gave the most readily crystallisable and stable arylcobalt derivatives; the corresponding triethylphosphine-arylcobalt complexes were less stable.

One would expect these planar diarylcobalt(II) complexes to have one unpaired electron. Magnetic-susceptibility measurements on the solid compounds at 20° indicated magnetic moments of 2·3-2·7 B.M. These values are consistent with a planar cobalt(II) complex with one unpaired electron, since such complexes appear to have a large orbital contribution to the magnetic moment. For example, Figgis and Nyholm 10 found the magnetic moments of some planar cobalt(II) complexes with chelate ligands to be as high as 2.9 B.M.

Attempts to prepare Monoarylcobalt(II) Complexes.—As mentioned above, the addition of [CoBr₂(PEt₂Ph)₂] to solutions of arylmagnesium bromides first gave very unstable olivegreen complexes, probably $[CoBr(aryl)(PEt_2Ph)_2]$, which could not be isolated. In the nickel series analogous monoarylnickel complexes were readily prepared from diarylnickel complexes by fission with dry hydrogen chloride (1 mol.), but attempts to obtain monoarylcobalt complexes in this way were not successful. On addition of dry hydrogen chloride (1 mol.) to a solution of trans- $[Co(mesity])_{2}(PEt_{2}Ph)_{2}]$ the solution became olivegreen but, on isolation, unchanged starting material (ca. 50% recovery) and a bluish-green, very labile product strongly smelling of diethylphenylphosphine, were obtained: the second product was probably impure [CoCl₂(PEt₂Ph)₂].

Aryliron(II) Complexes.—Since bis(pentachlorophenyl)bis(diethylphenylphosphine) cobalt(II) was so stable it seemed possible that an analogous iron(II) complex might be stable. The necessary starting materials, e.g., [FeX₂(PEt₂Ph)₂], are unknown although analogous triphenylphosphine complexes $[FeX_2(PPh_3)_2]$ have been described briefly.^{11,12} When anhydrous ferrous chloride and diethylphenylphosphine (>4 mol.) were boiled together in benzene the ferrous chloride gradually dissolved to give a colourless solution, possibly containing the octahedral complex [FeCl₂(PEt₂Ph)₄]. Removal of the solvent gave the complex as very soluble colourless crystals which rapidly became green in air. Addition of the crude benzene solution of this ferrous chloride-diethylphenylphosphine complex to a solution of pentachlorophenylmagnesium chloride gave the golden-yellow complex $[Fe(C_6Cl_5)_2(PEt_2Ph)_2]$. This iron complex was much less stable than the analogous cobalt complex and was partially decomposed after being dissolved in benzene at 25° for

Figgis and Nyholm, J., 1954, 12; 1959, 338.
 Hieber and Floss, Z. anorg. Chem., 1957, 291, 314.
 Naldini, Internat. Conference Pure Appl. Chem., Munich, 1959.

several minutes. This made a determination of the dipole moment difficult. The compound was shown by an X-ray powder diagram to be isomorphous with the corresponding cobalt complex and therefore of *trans*-planar configuration. The magnetic moment of 3.6 B.M. is consistent with the planar arrangement of ligands and two unpaired electrons.

Adding the crude ferrous chloride-diethylphenylphosphine complex to a solution of mesitylmagnesium bromide at -40° caused a bright orange precipitate to be formed, probably [Fe(mesityl)₂(PEt₂Ph)₂]. This complex decomposed very rapidly on attempted isolation.

Factors affecting the Stability of Aryl-cobalt(II) and -iron(II) Derivatives.—Four-coordinate cobalt(II) and iron(II) complexes with monodentate ligands, e.g., $[MX_2(PR_3)_2]$ $(M = Co, Fe; X = halogen; PR_3 = tertiary phosphine)$ usually have high magnetic moments and are considered to be tetrahedral. The diaryl-cobalt(II) and -iron(II) complexes are probably forced into a planar configuration by a combination of electronic (or ligand field) and steric effects. Both tertiary phosphines and aryl groups have large ligand field strengths ^{13,14} and if these are sufficiently great the planar configuration with the electronic arrangements shown in the Figure would be thermodynamically more stable than the tetrahedral arrangement where the ligand field stabilisation energy (L.F.S.E.) will be small. The tetrahedral iron complexes would have the high-spin arrangement (A) because the ligand field splitting is unlikely to be sufficient to give the low-spin arrangement (B) in tetrahedral complexes of metals of the first transition series.





The high L.F.S.E. is perhaps the main factor contributing to the stability of organometallic complexes such as described in this series of papers. The large ligand fields ensure a large energy difference (ΔE) between the highest filled electronic energy level and lowest vacant level, as required by our hypothesis to explain the stability of organometallic complexes.^{7,9}

If a large ligand splitting were the only factor, all complexes of the type $[MR_2(PR'_3)_2]$ (M = Fe or Co) should be stable, but only those containing aryl groups with two orthosubstituents or one bulky ortho-substituent are stable. As described when discussing the corresponding nickel compounds,⁹ these ortho-substituents prevent rotation of the aryl groups about the metal-carbon bond. Thus the aryl groups are fixed with their planes approximately perpendicular to that of the complex and interact specially with the d_{xy} orbitals by π -bonding, so reducing still further the energy level of d_{xy} and increasing ΔE . This, however, does not appear to be sufficient to account for the stabilities of the iron

¹⁴ Chatt and Hayter, $J_{.,}$ 1961, in the press.

¹³ Chatt, Gamlen, and Orgel, J., 1959, 1047.

and cobalt complexes, because even one small *ortho*-substituent will prevent rotation but does not give a stable complex; *e.g.*, $[Co(o-tolyl)_2(PEt_2Ph)_2]$ is not stable.

The ortho-groups also hinder attack at the metal atom by reagents or solvents.⁹ In the nickel series a small ortho-substituent, as in the o-tolyl complexes, was sufficient to give isolatable derivatives. In the cobalt series a bulky ortho-substituent or two smaller ortho-substituents were necessary. These will undoubtedly be more effective in hindering attack at the metal atom and they will also tend to stabilise the square planar arrangement of ligands relative to the tetrahedral, owing to the steric repulsions of the ortho-substituents. We cannot tell which effect is the more important.

Any formation of the tetrahedral complexes with small L.F.S.E. and ΔE would lead to dissociation of the complex and since the detached alkyl or aryl ligands, unlike most ligands, are not stable entities, this would lead to complete decomposition of the complex. This we consider to be the reason for our inability to prepare the complexes *trans*-[CoX(dio-substituted aryl)(PEt₂Ph)₂], where the bulky organic ligand of high ligand field strength has been replaced by a relatively small halogen, X, of low strength, so reducing the stability of the planar configuration relative to the tetrahedral. In nickel complexes of d^8 electronic configuration, which favours the planar arrangement of ligands, complexes of type *trans*-[NiX(o-substituted aryl)(PEt₂Ph)₂] are stable. In the cobalt series with the d^7 electronic configuration, which is more favourable to a tetrahedral arrangement of ligands, compounds of the above type are unstable.

In the iron(II) complexes with a d^6 electronic configuration the planar arrangement of monodentate ligands is even less likely, and all the factors mentioned above must enter into the stabilisation of trans-[Fe(C₆Cl₅)₂(PEt₂Ph)₂]. The electronegative chlorine atoms must make an additional important contribution by withdrawing electrons from the metal atom into the aromatic system, so increasing π -bonding and ΔE .

The marked fall in stability along the series trans-[M(di-o-substituted aryl)₂(PEt₂Ph)₂] (M = Ni > Co > Fe) may be explained by the progressive reduction, one at a time, in the number of electrons in low-energy orbitals, and corresponding reduction in L.F.S.E. It is unlikely that manganese(II) will form analogous complexes, but chromium(II), which in a planar complex would have four unpaired electrons in low-energy orbitals and a large quantum-mechanical exchange energy, may do so.

The organometallic complexes of iron(II) are particularly interesting because they show that completion of the stable co-ordination shell (octahedral for d^6 complexes) is not essential for stable transition-metal-carbon bonds, and a considerable electron deficiency (in this case, 4 electrons) can be tolerated. The essential features appear to be (a) steric shielding of the metal to hinder attack by solvents or reagents, and (b) a large ΔE to prevent dissociation. The large ΔE demands ligands of a large ligand field strength and a rectilinear arrangement of ligands as in square-planar or octahedral complexes as opposed to tetrahedral complexes.

Chromium(III), which forms complexes such as $[Cr(CH_2Ph)(H_2O)_5]^{2+}$, is an apparent exception to this.¹⁵ However, so large a ΔE is not necessary here because the three non-bonding *d*-orbitals (d_{ϵ}) are singly occupied, and so promotion to an antibonding orbital (d_{γ}) will not be assisted by interelectronic repulsions.

A further point of interest in this series of compounds is the effect of the organic radicals on the attachment of the tertiary phosphine ligands to the metal atom. The compounds $[MCl_2(PR_3)_2]$ (M = Ni, Co) are sufficiently unstable to smell of the phosphine. The organic derivatives have no smell. Evidently the organic groups with their large ligand field splittings so increase L.F.S.E. that the whole complex tightens, stabilising the attachment of phosphorus as well as that of carbon to the metal. In the case of iron(II) this is even more marked; *trans*-[Fe(C₆Cl₅)₂(PEt₂Ph)₂] has no smell, but [FeCl₂(PEt₂Ph)_x] (x = 2 or 4) was too labile to be isolated in the presence of air.

¹⁵ Anet and Leblanc, J. Amer. Chem. Soc., 1957, 79, 2649.

EXPERIMENTAL

M. p.s were determined on a Kofler hot-stage and are corrected. Magnetic moments were measured on the solid compound at 20° .

The tertiary phosphine-cobalt halide complexes were prepared by adding the appropriate phosphine (2 mol.) to a solution of the cobalt halide in ethanol; the complex separated at once or on cooling to $0^{\circ.16}$ In this way were prepared *dibromobis(triethylphosphine)cobalt*(II), bluish-green prisms, m. p. 134—136° (decomp.) (Found: C, 31·6; H, 7·15. $C_{12}H_{30}Br_2COP_2$ requires C, 31·5; H, 6·65%), μ 4·5 B.M.; *dichlorobis(diethylphenylphosphine)cobalt*(II), blue needles, m. p. 71—73° (Found: C, 51·95; H, 6·55. $C_{20}H_{30}Cl_2COP_2$ requires C, 51·8; H, 6·55%); *dibromobis-(diethylphenylphosphine)cobalt*(II), blue needles, m. p. 71—73° (Found: C, 51·95; H, 6·55. $C_{20}H_{30}Cl_2COP_2$ requires C, 51·8; H, 6·55%); *dibromobis-(diethylphenylphosphine)cobalt*(II), bluish-green prisms, m. p. 80—82° (Found: C, 43·6; H, 5·55. $C_{20}H_{30}Br_2COP_2$ requires C, 43·6; H, 5·5%), μ 4·5 B.M.; *dibromobis(ethyldiphenylphosphine)-cobalt*(II), greenish-blue prisms, m. p. 186—196° (decomp.) (Found: C, 52·2; H, 4·7. $C_{28}H_{30}Br_2COP_2$ requires C, 51·95; H, 4·65%); *dichlorobis(triphenylphosphine)cobalt*(II), blue prisms, m. p. 247—251° (decomp.) (Found: C, 66·15; H, 4·85. $C_{36}H_{30}Br_2COP_2$ requires C, 66·05; H, 4·6%), μ 4·3 B.M.; *dibromobis(triphenylphosphine)cobalt*(II), bluish-green prisms, m. p. 234—239° (Found: C, 57·95; H, 4·15. $C_{36}H_{30}Br_2COP_2$ requires C, 58·15; H, 4·05%); *di-iodobis(triphenylphosphine)cobalt*(II), dark brown prisms, m. p. 209—214° (decomp.) (Found: C, 50·92; H, 3·6. $C_{36}H_{30}CoI_2P_2$ requires C, 51·65; H, 3·6%), μ 4·6 B.M.

Preparation of Arylcobalt(II) Complexes.—trans-Dimesitylbis(diethylphenylphosphine)cobalt(II) [Co(mesityl)₂(PEt₂Ph)₂]. (1) Grignard method. A solution of dibromobis(diethylphenylphosphine)cobalt (6.00 g.) in benzene (50 c.c.) was added at -30° to a solution of mesitylmagnesium bromide, prepared from magnesium (0.96 g.), 2-bromomesitylene (5.9 c.c.), and tetrahydrofuran (20 c.c.). The mixture was allowed to warm and stirred for 40 min. at 20°, then it was cooled to -30° and hydrolysed by dilute hydrochloric acid. Benzene (80 c.c.) was added and the organic layer separated, washed with water, and dried (MgSO₄). Evaporation of the solvent and addition of ethanol gave dimesitylbis(diethylphenylphosphine)cobalt(II) as lemonyellow plates (5.25 g.), m. p. 119—124° (decomp.) (from benzene–ethanol) (Found: C, 72.9, 72.9; H, 8.2, 8.7. C₃₈H₅₂CoP₂ requires C, 72.5; H, 8.3%), μ 2.5 B.M.

(2) Mesityl-lithium method. A 0·14N-solution of mesityl-lithium in ether (25 c.c.) was added to one of dibromobis(diethylphenylphosphine)cobalt(II) (0·90 g.) in benzene (20 c.c.). After $\frac{3}{4}$ hr. the mixture was cooled to $ca. -30^{\circ}$ and water was added. The crude product isolated from the organic layer was recrystallised from benzene-methanol-ethanol, to give the desired dimesitylcobalt complex (0·61 g.), identical with that described above.

trans-Dimesitylbis(triethylphosphine)cobalt(II). This was similarly prepared in 15% yield from mesitylmagnesium bromide and trans-dibromobis(triethylphosphine)cobalt(II). It formed yellow needles, m. p. $113-116^{\circ}$ (decomp.), from benzene-ethanol. This compound was very unstable and analytical figures were erratic.

trans - $Di - (2 - biphenylyl)bis(diethylphenylphosphine)cobalt(II) [Co(2 - C₆H₄·C₆H₅)₂(PEt₂Ph)₂]. Dibromobis(diethylphenylphosphine)cobalt(II) (3.0 g.) in benzene (50 c.c.) was added at <math>-10^{\circ}$ to the Grignard reagent prepared from magnesium (0.48 g.), 2-bromobiphenyl (4.66 g.), and tetrahydrofuran (35 c.c.). The mixture was then stirred at 20° for $\frac{3}{4}$ hr., cooled to ca. -20° , and hydrolysed with dilute hydrobromic acid, and the precipitated solid filtered off and crystallised from benzene-methanol, to give trans-di-(2-biphenylyl)bis(diethylphenylphosphine)-cobalt(II) as yellow prisms (0.73 g.), m. p. 115—119° (decomp.) (Found: C, 75.95; H, 7.15. C₄₄H₄₈P₂Co requires C, 75.75; H, 6.95%), μ 2.6 B.M. A further quantity (0.46 g.) was isolated from the organic layer of the filtrate from the reaction product.

trans-Di-(2-methyl-1-naphthyl)bis(diethylphenylphosphine)cobalt(II) [Co(C₁₀H₆·CH₃)₂(PEt₂Ph)₂]. This complex was similarly prepared in 30% yield by using 1-bromo-2-methylnaphthalene to make the Grignard reagent. It was obtained as golden-yellow needles, m. p. 144–146° (much decomp.), from benzene-methanol (Found: C, 74·75; H, 7·25. C₄₂H₄₈CoP₂ requires C, 74·85; H, 7·15%), μ 2·7 B.M.

trans-Bis(pentachlorophenyl)bis(diethylphenylphosphine)cobalt(II) [Co(C₆Cl₅)₂(PEt₂Ph)₂]. A solution of pentachlorophenylmagnesium chloride was prepared from magnesium (0.48 g.; activated with benzyl chloride, 0.05 g.), tetrahydrofuran (25 c.c.), and hexachlorobenzene

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¹⁶ Jensen, Z. anorg. Chem., 1936, 229, 282.

(5.7 g.). This Grignard solution was cooled to *ca.* -10° , and dibromobis(diethylphenylphosphine)cobalt(II) (2.5 g.) and ether (15 c.c.) were added. The mixture was then stirred at 20° for 70 min., cooled to *ca.* -30° , and hydrolysed with dilute hydrochloric acid. The resultant precipitate was collected and recrystallised from benzene-methanol, to give transbis(pentachlorophenyl)bis(diethylphenylphosphine)cobalt(II) as lemon-yellow plates (2.43 g.), m. p. 224–228° (decomp.) (Found: C, 43.55; H, 3.55; Cl, 39.65. $C_{32}H_{30}Cl_{10}COP_2$ requires C, 43.2; H, 3.4; Cl, 39.85%), μ 2.3 B.M. A further quantity (0.3 g.) was isolated from the mother-liquors of the original reaction mixture.

Preparation of Bis(pentachlorophenyl)bis(diethylphenylphosphine)iron(II).—A solution of the phosphine-ferrous chloride complex was prepared by heating under reflux for 2 hr. a mixture of anhydrous ferrous chloride (0.72 g.), dry benzene (30 c.c.), and diethylphenylphosphine (2.37 g.), cooling, and filtering off the small amount of residue. This solution was then added dropwise at *ca*. -20° to a filtered Grignard reagent, prepared from magnesium (0.96 g.), hexachlorobenzene (11.4 g.), and tetrahydrofuran (30 c.c.). The resultant mixture was then stirred at 20° for 40 min., cooled to -30° , and hydrolysed with dilute hydrochloric acid. The precipitated solid was collected and recrystallised under nitrogen from benzene–ethanol, to give *bis(pentachlorophenyl)bis(diethylphenylphosphine)iron*(II) as golden-yellow prisms (0.13 g.), m. p. 135—142° (decomp.) (Found: C, 43.25; H, 3.55. $C_{32}H_{30}Cl_{10}FeP_2$ requires C, 43.35; H, 3.4%), μ 3.6 B.M.

Dipole moments of some diaryl-cobalt(II) and -iron(II) complexes in benzene at 25°.

μ(D)	
	~ 0
	~0 *
	$\sim 0 *$

* Calculated by using estimated values of densities and refractivities (see Part I of this series 7).

Determination of Dipole Moments.—These were determined as described in Parts I and II of this series; the measurements and estimated values (shown in parentheses) are recorded in the annexed Table, where the atom polarisation has been assumed to be 15% of the electron polarisation.

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