PREPARATIONS AND REACTIONS OF ALKYLCOBALT COMPLEXES AND DIPHENYLACETYLENECOBALT COMPLEXES HAVING A π-CYCLOPENTADIENYL GROUP AS A LIGAND

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SUMMARY

Methyl- and benzyl-cobalt complexes of type π-$C_5H_5Co(L)RR'$ [L = Ph_3P, Ph_2CH_3P, and Ph_3As; R, R' = CH_3, $PhCH_2$, and I] were prepared from the reaction of π-$C_5H_5Co(L)I_2$ (I) with Grignard reagents.

The reaction of I (L = Ph_3P) with isopropylmagnesium bromide in the presence of diphenylacetylene afforded an acetylene complex, π-$C_5H_5Co(PPh_3)(PhC\equiv CPh)$ (VI), a cobaltacyclopentadiene complex, π-$C_5H_5Co(PPh_3)(PhC\equiv CPh)_2$ (VII), or a stilbenyl complex of divalent cobalt, π-$C_5H_5Co(PPh_3)(CPh=CHPh)$ (VIII), depending on the conditions applied.

The diphenylacetylene group in (VI) was readily replaced by fumaronitrile, dimethyl-fumarate and -maleate to give complexes of type π-$C_5H_5Co(PPh_3)(olefin)$. On the other hand, reactions of (VI) with substituted acetylenes resulted in the formation of cobaltacyclopentadiene complexes without loss of diphenylacetylene.

The reaction of (VII) with ethylene gave π-cyclopentadienyl-π-1,2,3,4-tetraphenylcyclohexadienecobalt (XV).

The structures of some of these new compounds are discussed briefly on the basis of their proton NMR spectra.

Many of the alkyltransition metal compounds so far isolated have tertiary phosphines, carbon monoxide, cyclopentadienyl radicals, etc., and also their proper combinations, as π-acceptor ligands. However, stable alkylnickel complexes had not been isolated (although tertiary phosphines had been used as a ligand[1]) previous to our report[2] on the preparation of stable alkylnickel complexes represented by the formula, π-$C_5H_5Ni(PR'_3)R$. The stabilities of these complexes decreased when tertiary phosphines were replaced by triphenylarsine and then triphenylstibine; the instability of the carbon monoxide analogue, π-$C_5H_5Ni(CO)CH_3$[3], was also known although the compound had not been well-characterized. These observations suggested the superiority of the combination of tertiary phosphine and the cyclopentadienyl radical to stabilize a sigma bonding in an alkyltransition metal compound.

In the present paper, we give details of the preparations and reactions of alkylcobalt complexes represented by the formula, π-$C_5H_5Co(L)R_2$, and of related diphenylacetylenecobalt complexes previously reported only briefly by us[4,5].

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TABLE 1

π-C$_5$H$_5$Co(L)RR'
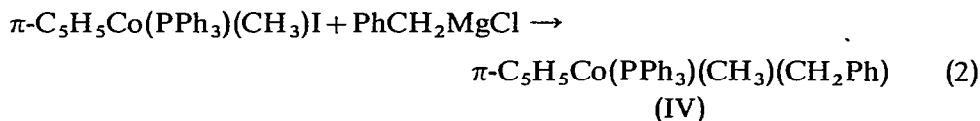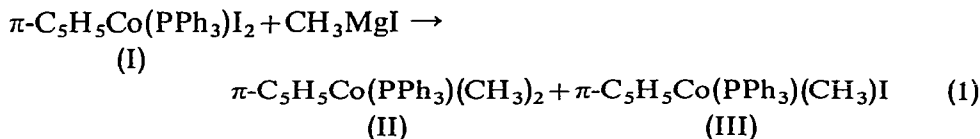
Compound[a]	Color	Yield (%)	M.p.[b] (°C)	Analyses (%) C Found (Calcd.)	H Found (Calcd.)	PMR[c] Band position (τ) and assignment
M(PPh$_3$)(CH$_3$)$_2$	red	54	142–143	71.80 (72.11)	6.42 (6.30)	2.7 (br. s, C$_6$H$_5$); 5.59 (s, C$_5$H$_5$); 9.94 (d, J(PH) = 6 cps; CH$_3$)[e].
M(PPh$_3$)(CH$_3$)I	brown	13	112	54.35 (54.57)	4.41 (4.39)	
M(PPh$_3$)(CH$_3$)(CH$_2$Ph)	red	51	112–113	76.07 (75.60)	6.13 (6.14)	2.3~3.2 (P-C$_6$H$_5$ and C-C$_6$H$_5$); 5.72 (s, C$_5$H$_5$); 6.75 and 8.30 (br. t, J(HH) and J(PH)≈7 cps; CH$_2$); 9.17 (d, J(PH)≈6 cps; CH$_3$)[f].
M(PPh$_3$)(CH$_2$Ph)$_2$	red	68	102	77.96 (78.16)	6.03 (6.03)	2.5~3.2 (P-C$_6$H$_5$ and C-C$_6$H$_5$); 5.67 (s, C$_5$H$_5$); 6.85 and 7.15 (br. t, J(HH) and J(PH)≈7 cps; CH$_2$)[f].
M(PPh$_2$CH$_3$)(CH$_3$)$_2$	red	65	126–128	67.82 (67.80)	6.82 (6.83)	2.7 (br. s, C$_6$H$_5$); 5.57 (s, C$_5$H$_5$); 8.45 (d, J(PH)=9 cps; P-CH$_3$); 10.0 (d, J(PH)=6 cps; Co-CH$_3$)[f].
M(PPh$_2$CH$_3$)(CH$_3$)I	brown	37	95–96	48.67 (48.95)	4.65 (4.54)	
M(AsPh$_3$)(CH$_3$)$_2$	red	28	96–98	65.33 (65.23)	5.65 (5.69)	

[a] M = π-C$_5$H$_5$Co. [b] Measured in nitrogen filled capillary tube. All compounds melt with decomposition. [c] Tetramethylsilane as internal standard. s: singlet. d: doublet. t: triplet. br.: broad. [e] 60 Mcps; CDCl$_3$ as solvent. [f] 100 Mcps; C$_6$D$_6$ as solvent.

RESULTS AND DISCUSSION

Alkylcobalt complexes

The reaction of triphenylphosphine-π-cyclopentadienylcobalt diiodide (I)[6,7] with methylmagnesium iodide in ether at the temperature of melting ice afforded red crystalline triphenylphosphine-π-cyclopentadienyldimethylcobalt (II)* and brown microcrystalline triphenylphosphine-π-cyclopentadienylmethylcobalt iodide (III) (eqn. (1)). A mixed dialkylcobalt complex, triphenylphosphine-π-cyclopentadienyl-methylbenzylcobalt (IV), was prepared from the reaction of (III) with benzyl Grignard

$$\pi\text{-}C_5H_5Co(PPh_3)I_2 + CH_3MgI \rightarrow$$
$$\text{(I)}$$

$$\pi\text{-}C_5H_5Co(PPh_3)(CH_3)_2 + \pi\text{-}C_5H_5Co(PPh_3)(CH_3)I \qquad (1)$$
$$\text{(II)} \hspace{5cm} \text{(III)}$$

$$\pi\text{-}C_5H_5Co(PPh_3)(CH_3)I + PhCH_2MgCl \rightarrow$$

$$\pi\text{-}C_5H_5Co(PPh_3)(CH_3)(CH_2Ph) \qquad (2)$$
$$\text{(IV)}$$

reagent (eqn. (2)). The reaction of (I) with benzyl Grignard reagent gave triphenylphosphine-π-cyclopentadienyldibenzylcobalt (V). Diphenylmethylphosphine and triphenylarsine analogues were also prepared by a similar procedure. The compounds thus prepared are summarized in Table 1.

The dimethylcobalt compounds are stable in air, especially in the solid state and even their benzene solutions can be handled in air for a fairly long time without any apparent decomposition. However, replacement of the methyl radical by the benzyl radical decreases their thermal stabilities and stabilities to air in the order, (II) > (IV) > (V). As with the nickel compounds[2], the arsine-substituted compound is less stable than the phosphine analogue.

In the proton NMR spectra of the benzyl derivatives, the resonance at τ 6.85 and 7.15 of (V) and τ 6.75 and 8.30 of (IV) may be assigned to the two protons of the methylene of the benzyl group. Different chemical shifts of the benzyl methylene protons may be derived from the hindered rotation of the benzyl group. There are three rotational isomers when we assume restricted rotation of the benzyl group. They are shown as projections to the plane perpendicular to the cobalt–methylene

(a)   (IV) R = CH₃   (b)   (V) R = PhCH₂   (c)
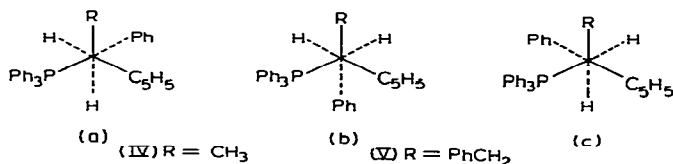
carbon axis. Even if the benzyl groups are rotating so rapidly that the three conformations are equally populated, the two methylene protons are not necessarily equal. However, the spectrum should result in an AB spectrum in that case. On the basis of the large chemical shift difference of the two methylene protons in these

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* The same compound was prepared independently by King[6].

compounds, we may assume only one conformation of the three isomers for (IV) and (V), probably (a) which is thought to be a sterically less hindered conformation. Each resonance of the methylene protons appeared as an approximate triplet because of the coupling with the geminal proton and ^{31}P nucleus (J(HH) and J(PH) $\approx$ 7 cps).

Attempts to prepare other alkyl compounds such as ethyl, propyl, and phenyl derivatives were unsuccessful probably for steric reasons and the inherent instability of their σ bond. We assumed the intermediate formation of an unstable cobalt complex with a vacant coordination position in these cases, and attempted to co-ordinate diphenylacetylene to the assumed coordinatively unsaturated cobalt atom.

Diphenylacetylenecobalt complexes

When equimolar amounts of (I) and tolane in tetrahydrofuran were treated dropwise with an ethereal solution of isopropylmagnesium bromide at $-15°$, black crystals were obtained as the main product. The reaction of the compound with iodine gave (I) and tolane in good yield. The elemental analysis and the relative intensities of the proton NMR spectrum showed the compound to be triphenylphos-phine-π-cyclopentadienyl-diphenylacetylenecobalt, π-C$_5$H$_5$Co(PPh$_3$)(PhC$\equiv$CPh) (VI). The green-colored solution of (VI) in organic solvents such as benzene is air sensitive but the compound can be readily handled in air in the solid state.

In the infrared spectrum of (VI), the carbon-to-carbon stretching frequency of the acetylenic linkage appeared at 1818 cm^{-1}, suggesting a decrease in bond order. Broadly speaking, there are two types of bonding of acetylene to a transition metal; one is a π-bonding using a single π-electron pair of a triple bond and the other two σ-bondings between them. The infrared stretching frequency of acetylenic linkage was conveniently used to define such bondings. For example, platinum and tungsten complexes such as (Ph$_3$P)$_2$Pt(PhC$\equiv$CPh)[8] and W(CO)(PhC$\equiv$CPh)$_3$[9] which show absorption near 1700 cm^{-1} were reported to be of the latter type, and a manganese complex such as π-C$_5$H$_5$Mn(CO)$_2$(CF$_3$C$\equiv$CCF$_3$)[10] which shows absorption at 1919 cm^{-1} was reported to be of the former type. The frequency of (VI) observed does not indicate one type in preference to the other. Thus, we can only suggest a structure such as (VIa) or (VIb), or probably an intermediate structure between them.

(VIa)   (VIb)
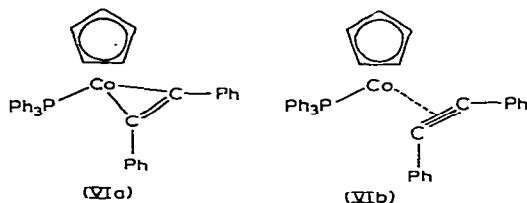
When excess of tolane over the amount of (I) was used in a similar procedure to that in the preparation of (VI), and the reaction was carried out at 0° or room temperature, very air-stable dark red-brown crystals were obtained. On the basis of the elemental analysis and the relative intensities of the proton NMR spectrum, the compound was formulated as π-C$_5$H$_5$Co(PPh$_3$)(PhC$\equiv$CPh)$_2$ (VII). This compound was obtained in a better yield by the reaction of (VI) with tolane and also by the re-action of (II) or (V) with tolane at elevated temperature. A five-membered ring structure containing cobalt was ascribed to (VII) in view of the chemical reactions such as the formation of π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt[11] in 60% yield

when (VII) was heated above its melting point and the formation of π-cyclopenta-dienyl-π-tetraphenylcyclopentadienonecobalt[12] in 77% yield when it was treated with carbon monoxide at 100° under pressure.

$$\text{(VII)} \qquad \text{(VIII)}$$
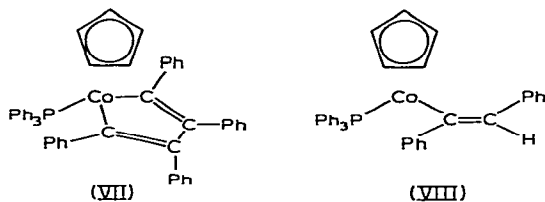
When equimolar amounts of (I) and tolane in tetrahydrofuran were treated with isopropylmagnesium bromide at $-30°$, dark brown crystals were obtained as the main product. This compound does not undergo the reaction with olefins having electron-withdrawing substituents to give olefin complexes but remains unchanged, although compound (VI) reacts easily as mentioned in a later section. π-$C_5H_5Co(CO)_2$ was detected when this compound was treated with carbon monoxide at 100° under pressure and trans-stilbene was isolated in good yield when it was treated with lithium aluminum hydride in tetrahydrofuran.

These observations and the elemental analysis, indicated that the compound was triphenylphosphine-π-cyclopentadienylstilbenylcobalt, π-$C_5H_5Co(PPh_3)$-$(CPh=CHPh)$ (VIII). The magnetic susceptibility measurement of (VIII) at room temperature showed the existence of one unpaired electron ($\mu=1.79$ B.M.) and supported a structure containing a divalent cobalt atom. It is known that metal hydrides can react with olefins and acetylenes to give alkylmetal and alkenylmetal complexes[13]. In our experiment, the formation of (VIII) suggested the transient existence of hydride species such as π-$C_5H_5Co(PPh_3)H$. The occurrence of the hydride proton should be due to the β-hydrogen of the σ-bonded isopropyl group which is probably formed at the initial stage of the reaction, because the use of phenyl Grignard reagent instead of the isopropyl reagent did not give (VIII) although compounds (VI) and (VII) were obtained.

Reactions of π-$C_5H_5Co(PPh_3)(PhC\equiv CPh)$

Chatt and co-workers prepared a series of complexes of types $Pt(PPh_3)_2$-$(RC\equiv CR)$[8] and $Pt(PPh_3)_2(RHC=CHR)$[14]. They observed that the acetylene complexes were more stable than the olefin complexes because olefin could be replaced by acetylene. In contrast to this, Baddley and Venanzi[15] found that tetracyanoethylene easily displaced phenylacetylene from $Pt(PPh_3)_2(PhC\equiv CH)$.

We have found that olefins substituted with electron-withdrawing groups displace diphenylacetylene from (VI). The reaction of (VI) with fumaronitrile proceeded readily at room temperature and gave air-stable red crystals. An elemental analysis of the crystals showed that diphenylacetylene in (VI) was replaced by fumaronitrile. The proton NMR spectrum of this complex was fully consistent with the formula, π-$C_5H_5Co(PPh_3)(NCCH=CHCN)$ (IX), on the basis of relative intensities. A sharp singlet at τ 5.34 in the spectrum may be assigned to the five equivalent π-cyclopentadienyl protons; a broad peak at $\tau \sim 2.4$ may be assigned to the aromatic protons of coordinated triphenylphosphine, and a triplet at τ 8.72 and a broad doublet at τ 7.10 may be assigned to the two olefinic protons of the fumaronitrile group. Non-

equivalence of the two olefin protons can be explained by coordination of fumaro-nitrile to cobalt. If we assume a three-membered ring structure for the complex for convenience, we can illustrate three stereoisomers, one of *trans* configuration (d) and two of *cis* configuration (e and f).
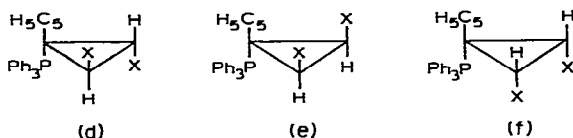

Compound (IX) in which the fumaronitrile group in the complex retains its original *trans* configuration may explain the multiplicities of the spectrum. Thus, the two protons of olefin are split ($J(HH) = 10$ cps) from each other and one of the two protons is split ($J(HP) = 10$ cps) by the ^{31}P nucleus. A broad doublet at τ 7.10 suggests a weak coupling of the other proton with the ^{31}P nucleus. On the other hand, if we postulate configuration (e) or (f) for this complex, the resonances of the two equivalent olefinic protons would appear as a doublet or a singlet depending on the coupling with the ^{31}P nucleus. We are unable to decide which proton couples more strongly with the ^{31}P nucleus. However, we assume that the proton in the *cis* position to the tri-phenylphosphine shows a triplet because it is known that $J_{cis} > J_{trans}$ in the usual cyclopropyl derivatives[16].

A similar procedure was used to prepare an analogous dimethyl fumarate complex, $\pi\text{-}C_5H_5Co(PPh_3)(trans\text{-}CH_3OOCCH{=}CHCOOCH_3)$ (X), and a dimethyl maleate complex, $\pi\text{-}C_5H_5Co(PPh_3)(cis\text{-}CH_3OOCCH{=}CHCOOCH_3)$ (XI). The original olefin geometry was retained in these complexes as shown by regeneration of the corresponding olefins from the ligand exchange reaction with fumaronitrile (confirmed by gas–liquid chromatography). The proton NMR spectra of (X) and (XI) were also consistent with the structure in which the original olefin geometry was retained. Corresponding to the different environment of the methyl ester groups in (X), methyl proton resonances appeared at τ 6.24 and 7.10 as a singlet, respectively. Resonance of one of the olefin protons appeared at τ 7.77 as a triplet ($J(HH)$ and $J(HP) \approx 10$ cps). Resonance of the other olefin proton was obviously included in a peak of methyl protons at τ 6.24 on the basis of relative intensities. A shoulder at τ 6.42 was assigned as a part of an expected doublet. On the other hand, methyl proton resonance in (XI) appeared at τ 6.28 as a singlet and olefin protons at τ 8.43 as a doublet ($J(HP) = 8$ cps). The appearance as a doublet of the olefin protons suggests the existence of only one isomer of two kinds of *cis* configuration. Because of the possibility of steric hindrance of the carbomethoxy group with a bulky triphenyl-phosphine ligand in the case of configuration (f), we suggest configuration (e) for (XI).

As we have already mentioned above, the reaction of (VI) with tolane gave (VII). Analogously, phenylacetylene and dimethyl acetylenedicarboxylate afforded $\pi\text{-}C_5H_5Co(PPh_3)(PhC{\equiv}CPh)(PhC{\equiv}CH)$ (XII) and $\pi\text{-}C_5H_5Co(PPh_3)(PhC{\equiv}CPh)$ $(CH_3OOCC{\equiv}CCOOCH_3)$ (XIII) based on elemental analyses. No replacement of diphenylacetylene was observed and thus we assumed both compounds also have a five-membered ring, "cobaltacyclopentadiene" structure, by analogy with (VI). In the proton NMR spectrum of (XII), no signal corresponding to an olefinic proton, which should be derived from the phenylacetylene moiety, was observed.

It has been reported that in a vinyl iron compound, $\pi\text{-}C_5H_5Fe(CO)_2$-$CH=CH_2$[17], the chemical shift of an olefinic proton attached to a carbon atom directly bonded to an iron atom appeared at τ 3.07 and those of *cis* and *trans* olefinic protons to an iron atom at τ 4.68 and 4.18. On the basis of this and the relative intensity ratio of the proton NMR spectrum of (XII), we may assume that the peak of the olefinic proton resonance was included in the broad peak of phenyl protons. Thus, we propose structure (XIIa) rather than (XIIb) for this compound. The exclusive formation of (XIIa) is probably due to steric considerations:

(XIIa)   (XIIb)   (XIII)
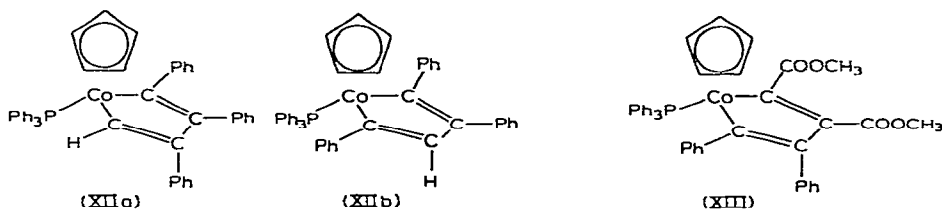
When compound (XII) was treated with carbon monoxide, air-stable dark red crystals were obtained. Elemental analysis of the crystals showed that triphenyl-phosphine had been replaced by carbon monoxide. Absence of a carbonyl group directly bonded to a metal was evident from the infrared spectrum. The absorption of the carbonyl group appeared at 1573 cm^{-1} (KBr disk) and suggested a similar structure to that known for π-cyclopentadienyl-π-tetraphenylcyclopentadienonecobalt which absorbed at 1573 cm^{-1} (KBr disk)*.

Proton NMR spectrum of this compound showed a singlet at τ 5.28 assigned to π-cyclopentadienyl protons, a singlet at τ 4.15 assigned to an olefinic proton, and broad peaks at $\tau \sim 2.5$ assigned to phenyl protons. Thus, it may be concluded that the compound is π-cyclopentadienyl-π-triphenylcyclopentadienonecobalt (XIV).

(XIV)   (XV)
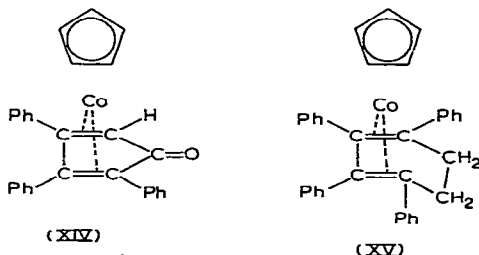
Reactions of π-$C_5H_5Co(PPh_3)(PhC\equiv CPh)_2$

Ferracyclopentadiene complex is known[18] to react with carbon monoxide to give a cyclopentadienone iron complex. The reaction of compounds (VII) and (XII) with carbon monoxide gave π-cyclopentadienyl-π-tetraphenylcyclopentadienone-cobalt and (XIV) as already described above. When tolane was used instead of carbon

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* Peaks at 1573, 1583, and 1603 cm^{-1} in the present compound and at 1573, 1592, and 1603 cm^{-1} in π-cyclopentadienyl-π-tetraphenylcyclopentadienonecobalt were observed in this region, in which the second peaks were the strongest. We tentatively assigned 1573 cm^{-1} as the carbonyl stretching frequencies because the latter compound and the tetramethyl-cyclopentadienone analogue were reported[12] to absorb at 1569 cm^{-1}.

monoxide, hexaphenylbenzene was a product. We attempted to insert ethylene into the σ-bonds of carbon–cobalt of (VII). When (VII) was heated at 150° in an autoclave with ethylene under pressure, very air-stable red crystals of π-cyclopentadienyl-π-1,2,3,4-tetraphenylcyclohexadienecobalt (XV) were obtained. The proton NMR spectrum of (XV) showed a broad peak of aromatic protons centered at τ 2.9, a sharp singlet peak of π-cyclopentadienyl protons at τ 5.30, and two unsymmetrical broad doublets ($J \approx 10$ cps) of *exo* and *endo* protons of methylene groups at τ 7.68 and 8.60.

The mass spectrum of (XV) showed a very weak parent ion peak at m/e 509, a strong ion peak at m/e 507 corresponding to the ion of π-cyclopentadienyl-1,2,3,4-tetraphenylbenzenecobalt, and a strong ion peak at m/e 384 corresponding to the ion of 1,2,3,4-tetraphenylcyclohexadiene.

An attempt to prepare compound (XV) by direct reaction of 1,2,3,4-tetraphenylcyclohexadiene with π-cyclopentadienyldicarbonylcobalt was unsuccessful, although the reaction had been successfully employed for the preparation of some diene complexes of π-cyclopentadienylcobalt by King et al.[19].

The reaction of (VII) with fumaronitrile did not give a similar product but gave (IX).

EXPERIMENTAL

All reactions were carried out in a nitrogen atmosphere. Melting points were determined on a Yanagimoto hot-stage apparatus unless otherwise stated. Proton NMR spectra were made on a Varian A-60, a Hitachi–Perkin Elmer R-20, or a Japan Electron Optics JNM 4H-100 spectrometer, with tetramethylsilane as an internal standard. Infrared spectra were obtained with a Jasco DS-402G spectrophotometer. The mass spectrum was obtained at 75 eV with a Niphondenshi JPS-1 mass spectrometer.

Preparation of π-$C_5H_5Co(L)I_2$, $L = PPh_3$, PPh_2CH_3, *and* $AsPh_3$

According to the literature[6,7], these compounds were prepared from π-$C_5H_5Co(CO)I_2$ and the corresponding phosphines or arsine in nearly quantitative yields. The color, melting points, analyses, and proton NMR spectra are as follows.

π-$C_5H_5Co(PPh_3)I_2$: Blue-black. 169–172° (dec.). PMR (in $CDCl_3$): 2.0~2.8 τ (C_6H_5); 4.94 τ (singlet, C_5H_5).

π-$C_5H_5Co(PPh_2CH_3)I_2$: Blue-black. 152° (dec. in nitrogen-filled capillary). (Found: C, 37.79; H, 3.31. Calcd.: C, 37.40; H, 3.14%.) PMR (in $CDCl_3$): 1.9~2.7 τ (C_6H_5); 4.95 τ (singlet, C_5H_5); 7.55 τ (doublet, $J(HP) = 11$ cps; CH_3).

π-$C_5H_5Co(AsPh_3)I_2$: Green-black. 199–200° (dec. in nitrogen-filled capillary). (Found: C, 40.59; H, 3.07. Calcd.: C, 40.38; H, 2.95%.) PMR (in $CDCl_3$): 2.2~2.8 τ (C_6H_5); 4.89 τ (singlet, C_5H_5).

Preparation of alkylcobalt complexes

A slurry of triphenylphosphine-π-cyclopentadienylcobalt diiodide (6.4 g) in benzene was treated dropwise with a Grignard reagent prepared from magnesium (1.5 g), methyl iodide (9 g), and ether (60 ml). A red-colored solution resulted. After stirring for 30 min, aqueous ammonium chloride was added at the temperature of melting ice and the organic layer was dried with sodium sulfate. After the solvent had

been removed under reduced pressure, the residue was redissolved in benzene and chromatographed on alumina. An orange-red zone and a brown zone were observed. The first red fraction eluted with benzene was collected and the solvent was evaporated under reduced pressure almost to dryness. After the addition of hexane (20 ml), the solution was kept in a refrigerator to give red crystals of π-C$_5$H$_5$Co(PPh$_3$)(CH$_3$)$_2$ (II) (2.23 g).

The second brown fraction eluted with benzene was collected. A similar procedure to that above gave a brown powder of π-C$_5$H$_5$Co(PPh$_3$)(CH$_3$)I (III) (0.07 g). For a better yield of (III), the following method was used. To an ice-cooled slurry of triphenylphosphine-π-cyclopentadienylcobalt diiodide (5.1 g) in benzene (150 ml) was added a Grignard reagent prepared from magnesium (0.25 g), methyl iodide (1.5 g), and ether (50 ml), dropwise for 2 h under vigorous stirring. A similar procedure to that above gave (II) in 8% yield (0.27 g) and (III) in 13% yield (0.56 g).

A mixed dialkylcobalt complex was prepared as follows. To an ice-cooled solution of (III) (0.56 g) in benzene (20 ml) was added a Grignard reagent prepared from magnesium (0.25 g), benzyl chloride (1.3 g) and ether (20 ml). A similar procedure to that above gave red crystals of π-C$_5$H$_5$Co(PPh$_3$)(CH$_3$)(CH$_2$Ph) (IV) (0.26 g).

All other alkylcobalt complexes were prepared by a similar procedure. Their melting points, yields, analyses, and proton NMR spectra are summarized in Table 1.

Reactions of π-C$_5$H$_5$Co(PPh$_3$)I$_2$ (I) with isopropylmagnesium bromide in the presence of tolane

(1) *Reaction in the presence of equimolar amounts of tolane at* $-15°$. To a mixture of (I) (6.4 g) and tolane (1.8 g) in tetrahydrofuran (40 ml) was added isopropyl-magnesium bromide (30 mmole) in ether (30 ml) dropwise at $-15°$. The resulting green-brown solution was kept stirring for 20 min and hydrolysed with aqueous ammonium chloride. The organic layer was separated and dried with sodium sulfate. After removal of the solvent under reduced pressure, the residue was dissolved in a small amount of benzene and chromatographed on alumina with benzene–hexane mixture (1/1) as the eluent. A dark-red colored eluate was obtained and the alumina column became green, from which a green eluate was obtained when benzene was used as eluent. The compound obtained from the dark red eluate will be described later because it was obtained in a better yield by a reaction at a lower temperature. The green fraction was concentrated and hexane was added to the residue. The solution was kept in a refrigerator overnight to give black crystals of π-C$_5$H$_5$Co(PPh$_3$) (PhC≡CPh) (VI) (1.0 g, 18%). These crystals were usually contaminated with red-brown crystals which were identified as (VII). For analytical purposes, the crystals were recrystallized from benzene–hexane, m.p. 140°. (Found: C, 78.59; H, 5.37; mol. wt., 530 (cryoscopic in benzene). C$_{37}$H$_{30}$PCo calcd.: C, 78.72; H, 5.36%; mol. wt., 565. PMR (in C$_6$D$_6$): ~3 τ (C$_6$H$_5$); 5.17 τ (C$_5$H$_5$)).

A solution of (VI) (0.31 g) in benzene–tetrahydrofuran (1/1, 10 ml) was treated dropwise with a solution of iodine (0.14 g) in tetrahydrofuran (5 ml) at room temperature. The resulting solution was evaporated to dryness under reduced pressure. The residue was crystallized from benzene to give black crystals (0.30 g, m.p. 169–172° (dec.)). The infrared spectrum of the crystals was identical with that of (I). The mother liquid was passed through a short alumina column and the solvent was evaporated to give pale yellow crystals (0.07 g). Sublimation of the crystals gave colorless crystals

(0.06 g, m.p. 59–60°). No depression of a mixed melting point with tolane was observed.

(2) *Reaction in the presence of excess tolane.* To an ice-cooled solution of (I) (1.3 g) and tolane (1.4 g) in tetrahydrofuran (10 ml) was added isopropylmagnesium bromide (5 mmole) in ether (5 ml), dropwise. The resulting red-brown solution was kept stirring for 1 h at room temperature and hydrolysed with aqueous ammonium chloride. The organic layer was dried with sodium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed on alumina with benzene as eluent. The orange-red eluate was collected and the solvent was evaporated almost to dryness. After addition of hexane, the solution was kept in a refrigerator overnight to give red-brown crystals of π-$C_5H_5Co(PPh_3)(PhC{\equiv}CPh)_2$ (VII) (0.3 g, 20%), m.p. 193–194° (dec.). (Found: C, 82.57; H, 5.57; mol. wt., 757 (vapor pressure osmometric in CH_2Cl_2). $C_{51}H_{40}PCo$ calcd.: C, 82.47; H, 5.43%; mol. wt., 743. PMR (in $CDCl_3$): 2.5~3.6 τ (C_6H_5); 5.18 τ (C_5H_5)).

(3) *Reaction in the presence of equimolar amounts of tolane at* $-30°$. To a mixture of (I) (7.0 g) and tolane (2.0 g) in tetrahydrofuran (50 ml) was added isopropylmagnesium bromide (30 mmole) in ether (30 ml) dropwise at $-30°$. The resulting brown-red solution was kept stirring for 1 h and hydrolysed with aqueous ammonium chloride. The organic layer was dried with sodium sulfate. After removal of the solvent under reduced pressure, the residue was dissolved in benzene and chromatographed on alumina with benzene–hexane mixture (1/1) as the eluent. The dark-red colored eluate was concentrated and hexane added to the residue. The solution was kept in a refrigerator overnight to give a dark brown solid (3.1 g). The infrared spectrum of the solid showed the presence of a small amount of (VI). For elimination of (VI), the solid was dissolved in benzene and dimethyl maleate (0.5 g) was added*. Chromatography of the resulting solution on alumina with benzene as eluent and concentration of the eluate followed by the addition of hexane gave dark brown crystals of π-$C_5H_5Co(PPh_3)(CPh{=}CHPh)$ (VIII) (1.35 g, 22%), m.p. 139° (in nitrogen-filled capillary). (Found: C, 78.71; H, 5.64. $C_{37}H_{31}PCo$ calcd.: C, 78.58; H, 5.53%.) These crystals were shown to be paramagnetic by Gouy balance measurements. χ_{md}^{cor}: 1366×10^{-6} cgsu (290°K; diamagnetic correction calculated from Pascal's constants: 339×10^{-6} cgsu).

To the solution of (VIII) (0.57 g) in tetrahydrofuran (20 ml) was added lithium aluminum hydride portion-wise under ice cooling. After stirring for 30 min, the resulting dark brown solution was hydrolysed with methanol–water mixture. Benzene (20 ml) was added and the organic layer was separated. After evaporation of the solvent, the residue was chromatographed on alumina with benzene as eluent. The eluate was concentrated to give white crystals (0.14 g) which were recrystallized from methanol to give white flakes (0.07 g, m.p. 124–125°). The infrared spectrum was identical with that of authentic *trans*-stilbene.

Reactions of triphenylphosphine-π-cyclopentadienyldialkylcobalt with tolane

The solution of (II) (0.42 g) and tolane (0.5 g) in benzene (15 ml) was heated at reflux temperature for 4 h. The resulting red-brown solution was chromatographed on alumina with benzene as eluent. The red-brown eluate was concentrated under

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* Only (VI) was allowed to react with dimethyl maleate to give (XI) which was readily separated by alumina chromatography.

reduced pressure, followed by the addition of hexane. The solution was kept in a refrigerator to give red-brown crystals (0.75 g, 49%, m.p. 192–194°). The infrared spectrum of the crystals was consistent with that of (VII). Further treatment of the mother liquid gave small amounts of π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt (0.06 g, 13%, m.p. 264°) which was identified by means of the infrared spectrum.

A similar procedure gave (VII) (0.31 g, 34%) from the reaction of (V) (0.70 g) with tolane (0.70 g).

Reactions of π-C₅H₅Co(PPh₃)(PhC≡CPh) (VI) with olefins having electron-withdrawing substituents

(1) *Reaction with fumaronitrile.* A mixture of (VI) (0.11 g) and fumaronitrile (0.08 g) in benzene (20 ml) was heated at 70°. The green color disappeared immediately and a red color appeared. After concentration, the solution was chromatographed on alumina to give a pale yellow zone followed by a red-brown zone. The yellow zone was eluted with benzene and the eluate was discarded. The red-brown zone was eluted with a mixture of benzene and ethyl acetate (2/1) to give a red solution. After evaporation of the solvent, the residue was crystallized with benzene–hexane to give air-stable dark red crystals of π-C₅H₅Co(PPh₃)(NCCH=CHCN) (IX) (0.04 g, 44%), m.p. 157° (dec.). (Found: C, 69.86; H, 4.93; N, 6.21. $C_{27}H_{22}N_2PCo$ calcd.: C, 69.83; H, 4.78; N, 6.03%. PMR (in CDCl₃): ∼2.4 τ (C₆H₅); 5.34 τ (singlet, C₅H₅); 7.10 τ (broad doublet, $J = 10$ cps; CH); 8.72 τ (triplet, $J = 10$ cps; CH).

This compound is soluble in chloroform and benzene, and sparingly soluble in ether, alcohol, acetone, hexane and carbon tetrachloride.

(2) *Reactions with dimethyl-fumarate and -maleate.* A similar procedure to that above gave dark-red crystals of π-C₅H₅Co(PPh₃)(trans-CH₃OOCCH=CHCOOCH₃) (X) and π-C₅H₅Co(PPh₃)(cis-CH₃OOCCH=CHCOOCH₃) (XI) in about 20% yield, from the reaction of (VI) with dimethyl-fumarate and -maleate.

(X) M.p. 202–203° (in nitrogen-filled capillary tube). (Found: C, 65.72; H, 5.54. $C_{29}H_{28}O_4PCo$ calcd.: C, 65.66; H, 5.54%. PMR (in CDCl₃): ∼2.5 τ (C₆H₅); 5.55 τ (singlet, C₅H₅); 6.24 τ (singlet, CH₃ and a part of CH); 6.42 τ (shoulder, a part of CH); 7.10 τ (singlet, CH₃); 7.77 τ (triplet, $J = 10$ cps)).

(XI) M.p. 150° (in nitrogen-filled capillary tube). (Found: C, 65.10; H, 5.29. $C_{29}H_{28}O_4PCo$ calcd.: C, 65.66; H, 5.54%. PMR (in CDCl₃): ∼2.5 τ (C₆H₅); 5.47 τ (singlet, C₅H₅); 6.28 τ (singlet, CH₃); 8.43 τ (doublet, $J = 8$ cps; CH).

Reactions of π-C₅H₅Co(PPh₃)(PhC≡CPh) (VI) with acetylenes

(1) *Reaction with tolane.* A mixture of (VI) (0.22 g) and tolane (0.20 g) in benzene (5 ml) was heated under reflux. The green color turned to a red-brown color in a few minutes. The solution was chromatographed on alumina with benzene as eluent. The red eluate was concentrated under reduced pressure, followed by the addition of hexane to give red-brown crystals (0.17 g, 59%, m.p. 189–191° (dec.)). The infrared spectrum of the crystals was consistent with that of (VII).

(2) *Reaction with phenylacetylene.* A mixture of (VI) (0.45 g) and phenylacetylene (0.30 g) in benzene (25 ml) was heated at 60° for 10 min. The resulting dark brown solution was concentrated and chromatographed on alumina. The column was eluted with a mixture of benzene and hexane (1/1) and the eluate was discarded.

Then, an orange-red fraction eluted by benzene was collected and concentrated. The addition of hexane to the residue gave dark brown crystals of $\pi\text{-}C_5H_5Co(PPh_3)$-$(PhC\equiv CPh)(PhC\equiv CH)$ (XII) (0.12 g, 22%), m.p. 180–182° (dec.). (Found: C, 81.14; H, 5.63. $C_{45}H_{36}PCo$ calcd.: C, 81.06; H, 5.44%. PMR (in $CDCl_3$): 2.5~3.6 τ (broad complex, C_6H_5 and Co–CH=); 5.18 (singlet, C_5H_5).)

(3) *Reaction with dimethyl acetylenedicarboxylate*. A mixture of (VI) (0.22 g) and dimethyl acetylenedicarboxylate (1.0 g) in benzene (10 ml) was heated at 60° for 10 min. The resulting brown-red solution was chromatographed on alumina. After the eluate by benzene was discarded, the orange-red band was eluted by benzene–ethyl acetate (3/1). Evaporation of the solvent and crystallization of the residue from benzene–hexane mixture gave orange-red crystals of $\pi\text{-}C_5H_5Co(PPh_3)(PhC\equiv CPh)$ $(CH_3OOCC\equiv CCOOCH_3)$ (XIII) (0.01 g, 6%), m.p.: 119–121° (dec.). (Found: C, 73.41; H, 5.27. $C_{43}H_{36}O_4PCo$ calcd.: C, 73.08; H, 5.14%. PMR (in $CDCl_3$): 2.5~3.3 τ (complex, C_6H_5); 5.05 τ (singlet, C_5H_5); 6.54 and 6.80 τ (singlet, CH_3).)

Reaction of $\pi\text{-}C_5H_5Co(PPh_3)(PhC\equiv CPh)(PhC\equiv CH)$ (XII) with carbon monoxide

In a stainless steel autoclave, (XII) (0.11 g) in benzene (10 ml) was treated with 100 atm. pressure of carbon monoxide at 80° for 5 h. The resulting solution was chromatographed on alumina and eluted by benzene–ethyl acetate (5/1). Concentration of the eluate and addition of hexane to the residue gave red crystals of π-cyclopentadienyl-π-triphenylcyclopentadienonecobalt (XIV) (0.02 g, 28%), m.p. 218–219°. (Found: C, 77.65; H, 5.00. $C_{28}H_{21}OCo$ calcd.: C, 77.78; H, 4.90%. PMR (in $CDCl_3$): ~2.6 τ (C_6H_5); 4.15 τ (singlet, =CH–); 5.28 τ (singlet, C_5H_5).)

Reactions of $\pi\text{-}C_5H_5Co(PPh_3)(PhC\equiv CPh)_2$ (VII)

(1) *Thermal reaction*. In an evacuated sealed tube, (VII) (0.10 g) was heated at 200° in an oil bath for 30 min. The resulting solid was washed out with benzene and chromatographed on alumina with benzene as eluent to give an orange solution. After evaporation of the solvent almost to dryness, hexane was added to the residue. The solution was kept in a refrigerator to give orange crystals (0.04 g, 60%, m.p. 264–268°). The infrared spectrum of the crystals was identical with that of authentic π-cyclopentadienyl-π-tetraphenylcyclobutadienecobalt.

(2) *Reaction with carbon monoxide*. In a stainless steel autoclave, (VII) (0.22 g) in benzene (30 ml) was treated with 90 atm. pressure of carbon monoxide at 100° for 4 h. Evaporation of the solvent and crystallization of the residue from benzene–hexane gave red crystals (0.12 g, 77%, m.p. 330°). The infrared spectrum of the crystals was consistent with that of authentic π-cyclopentadienyl-π-tetraphenylcyclopenta-dienonecobalt. (Found: C, 79.88; H, 4.98. $C_{34}H_{25}OCo$ calcd.: C, 80.31; H, 4.96%. PMR (in $CDCl_3$): 2.2~2.9 τ (complex multiplet, C_6H_5); 5.10 τ (singlet, C_5H_5).)

(3) *Reaction with ethylene*. In a stainless steel autoclave, (VII) (0.50 g) in benzene (10 ml) was heated at 150° for 3 h with 45 atm. pressure of ethylene. The resulting red solution was concentrated, followed by the addition of hexane to give air-stable red crystals (0.25 g). They were recrystallized from benzene–hexane for analytical use, m.p. 206–208°. (Found: C, 82.43; H, 5.81; mol. wt., 494 (cryoscopic in benzene). $C_{35}H_{29}Co$ calcd.: C, 82.66; H, 5.75%; mol. wt., 509. PMR (in $CDCl_3$): 2.9 τ (broad singlet, C_6H_5); 5.30 τ (singlet, C_5H_5); 7.68 and 8.60 τ (unsymmetrical broad doublet, J = 10 cps; CH_2–CH_2).)

(4) *Reaction with fumaronitrile.* In a sealed tube, (VII) (0.50 g) and fumaronitrile (0.20 g) in benzene (20 ml) were heated at 140° for 4 h. The resulting brown-red solution was chromatographed on alumina to give yellow, and red-brown bands. Elution of the yellow band with benzene and evaporation of the solvent gave a yellow solid (0.03 g). The infrared spectrum of the solid was identical with that of π-cyclopenta-dienyl-π-tetraphenylcyclobutadienecobalt. Elution of the red-brown band with benzene–ethyl acetate (2/1) and evaporation of the solvent gave dark red crystals (0.11 g, m.p. 156–157° (dec.)). The infrared spectrum of the crystals was identical with that of (IX) prepared from (VI) and fumaronitrile.

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