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π-CYCLOPENTADIENYL-LIKE DERIVATIVES OF COBALT: SYNTHESIS OF INDENYL- AND FLUORENYL-BIS(PHOSPHITE)-COBALT(I)

P. DIVERSI, A. GIUSTI, G. INGROSSO * and A. LUCHERINI

Istituto di Chimica Organica Industriale, Università di Pisa, Via Risorgimento 35, 56100 Pisa (Italy)

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Summary

The compounds $\{Co(C_9H_7)[P(OR)_3]_2\}$ (C_9H_7 = indenyl) and $\{Co(C_{13}H_9)[P(OR)_3]_2\}$ ($C_{13}H_9$ = fluorenyl) (R = C_2H_5, i-C_3H_7) have been prepared by treating $\{CoBr[P(OR)_3]_3\}$ with NaC_9H_7 and $NaC_{13}H_9$, respectively. The ^1H, ^{13}C NMR, IR, and mass spectra of the new compounds are discussed. The preparation of $\{Co(C_9H_7)(CO)[P(OR)_3]\}$ and $\{Co(C_{13}H_9)(CO)[P)OR)_3]\}$ is also reported.

Introduction

Numerous transition metal complexes containing indenyl ring systems have been prepared and a survey of their chemistry clearly shows that such compounds often exhibit higher reactivity, e.g. in ligand substitution reactions, than the corresponding isostructural cyclopentadienyl derivatives [1]. This difference has been explained on the basis of the postulated ability of the indenyl ligand, unlike the parent cyclopentadienyl ligand, to undergo facile bonding transformation from pentahapto to trihapto and vice-versa [1]. Indeed, indenyl group has been shown in some cases to be bonded to transition metals as a η^3 (π-allyl) ligand [2,3]. These peculiarities make indenyl derivatives of transition metals particularly attractive from a speculative point of view and also for their potential interest as homogeneous catalysts. In this connection the recent findings concerning some stoichiometric and catalytic reactions of bis(ethylene)(η^5-indenyl)rhodium(I) seem very promising [4].

The arguments which have been put forth for the description of the indenyl ligand in terms of "coordinative flexibility" can be extended, at least in principle, to the fluorenyl ligand, which can, indeed, be bonded to transition metals

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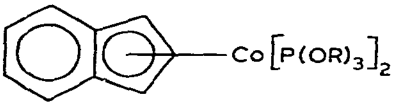
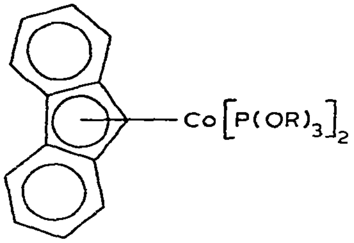
* To whom correspondence should be addressed.

in a π-arene (hexahapto) [5] or π-cyclopentadienyl (pentahapto) [4,6—9] or π-allyl (trihapto) [8] fashion.

On this basis we are studying the synthesis and the reactivity of Groups VIII indenyl- and fluorenyl-transition metal derivatives, and we describe below some cobalt(I) complexes of formula I and II which are the first indenyl and fluorenyl derivatives of cobalt(I). Compounds of this type are expected to exhibit interesting properties when compared with cyclopentadienyl- [10] and allyl-cobalt trialkylphosphite complexes [11].



(I)



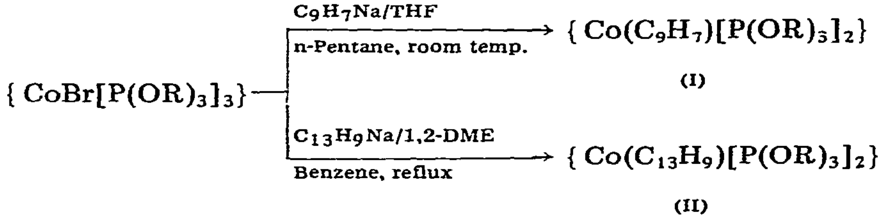
(II)

Results and discussion

At the beginning of this work we tried to prepare complexes of type I by treatment of di-η^5-indenylcobalt(II) with tertiary phosphites such as $P(OCH_3)_3$, $P(OC_2H_5)_3$, $P(O\text{-}i\text{-}C_3H_7)_3$, and $P(OC_6H_5)_3$, by analogy with the synthesis of the half-sandwich type compounds, $\{Co(C_5H_5)[P(OR)_3]_2\}$ [12]. Tetrahydrofuran or 1,3-dioxane were used as solvents and reactions were carried out at various temperatures. In all cases a reaction took place, but column chromatography of the reaction products revealed the presence of up to six unidentified compounds in addition to di-indenyl and unreacted diindenylcobalt(II).

Complexes I and II were more satisfactorily prepared by the reactions outlined in Scheme 1. The known [13] IIIa was prepared by a new, more convenient route (the yields are about three times higher than those reported) based upon the reduction of $CoBr_2$ with zinc in the presence of an excess of triethylphosphite. The violet highly air-sensitive IIIb was also prepared by this method in almost quantitative yields. The magnetic moment of this molecule is 3.06 BM, a value within the expected range for a high-spin d^8 complex [13].

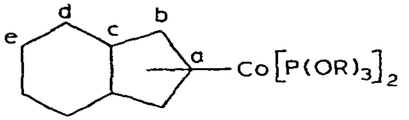
SCHEME 1



(a, R = C_2H_5; b, R - i-C_3H_7)

TABLE 1

^{1}H AND ^{13}C NMR DATA FOR COMPLEXES I [a]



Compound	H_a	H_b	H_d and H_e	R
Ia [b] (R = C_2H_5)	5.62m	4.50bs	6.85—7.23m	CH_2, 3.78m; CH_3, 1.13t[J(H—H)] 7 Hz
Ib [c] (R = i-C_3H_7)	5.72m	4.66m	6.7 —7.6m	CH, 4.66m; CH_3, 1.26bd[J(H—H)] 6 Hz

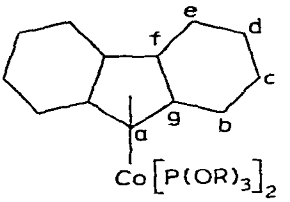
Compound	C_a	C_b	C_c	C_d or C_e	C_e or C_d	R
Ia [c] (R = C_2H_5)	86.2s	70.3s	104.9s	121.6s	121.7s	CH_2, 59.3d[J(C—P)] 13 Hz CH_3, 17.0d[J(C—P)] 3 Hz
Ib [c] (R = i-C_3H_7)	86.6s	69.1s	106.6s	121.7s	121.8s	CH, 67.5s CH_3, 25.1s

[a] δ values (ppm), TMS as internal standard; bd = broad doublet; bs = broad singlet; m = multiplet; s = singlet; t = triplet. [b] Measured in $(CD_3)_2CO$, at 37°C. [c] Measured in C_6D_6, at 37°C.

Some difficulties were encountered in the separation and purification of the indenyl derivatives, which are sticky liquids at room temperature. Accurate chromatographic separation on alumina was necessary, followed by extraction

TABLE 2

^{1}H AND ^{13}C NMR DATA FOR COMPLEXES II [a]



Compound	H_a	H_b, H_c, H_d, and H_e	R
IIa (R = C_2H_5)	3.43m	6.90—7.50m	CH_2, 3.96m; CH_3, 1.16t[J(H—H)] 6 Hz
IIb (R = i-C_3H_7)	3.60m	6.90—7.80m	CH, 4.46m; CH_3, 1.26d[J(H—H)] 6 Hz

Compound	C_a	C_b, C_c, C_d, and C_e	C_f	C_g	R
IIa (R = C_2H_5)	59.2d [J(C—P)] 5 Hz	121.6s; 121.8s; 123.9s; 122.2s	106.5s	94.6s	CH_2, 58.9d[J(C—P)] 8 Hz CH_3, 17.0d[J(C—P)] 3 Hz
IIb (R = i-C_3H_7)	55.6d [J(C—P)] 5 Hz	122.1s; 122.3s; 124.6s; 122.4s	108.0s	96.0s	CH, 67.7d[J(C—P)] 11Hz CH_3, 25.1d[J(C—P)] 5 Hz

[a] Measured in C_6D_6, at 37°C; δ values (ppm), TMS as internal standard; d = doublet, m = multiplet, s = singlet, t = triplet.

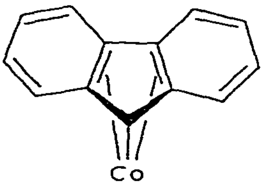
with water to remove the free phosphite. Both of the indenyl derivatives are deep-red, while the fluorenyl derivatives are red-brown deliquescent solids; all are diamagnetic and air-sensitive.

While Ia and Ib showed the expected mass-spectral features, IIa and IIb were too involatile for the mass spectra to be recorded.

Ia and Ib exhibit similar IR spectra, with bands indicative of coordinated indenyl groups [14]. Similarly, in the IR spectra of IIa and IIb there are a number of bands due to the fluorenyl ligand [14]. For all the complexes the bands due to phosphites occur at the expected frequencies.

The ^1H and ^{13}C NMR data (Tables 1 and 2) not only confirm the proposed formulation of I and II but also provide an insight into some structural details. The ^1H NMR spectra are consistent with the bonding formulation in which the indenyl and fluorenyl π-ligands are coordinated to the cobalt atom through their cyclopentadienyl-like moieties. Indeed, in all cases the general appearance of the spectra is in agreement with an approximate C_s symmetry type of the molecules, and the chemical shifts of the indenyl and fluorenyl protons are in agreement with the literature data [1,15]. For both the indenyl and fluorenyl complexes, the ^{13}C NMR spectra clearly confirm that the π-enyl ligands are anchored to the cobalt atom through the five-membered rings, as shown by the shift to high fields of the carbon atoms at the junction of fused five- and six-membered rings. In the case of the indenyl compounds Ia and Ib, the chemical shifts of these carbon atoms have values (δ 104.9 and 106.6 ppm, respectively) which are intermediate between the average values observed for the two basic bonding situations established for the π-indenyl ligand [2,3,16]: δ 87.0—98.3 ppm in the case of η^5-indenyl ligands characterized by a high π-electron delocalization, and δ 134.3 ppm in the case of a 1—3-η^3-indenyl group. In this connection, it is noteworthy that H_a in Ia and Ib, in contrast to data for most of the η^5-indenyl complexes previously reported, is shifted downfield with respect to H_b protons, so that a situation arises which is reminiscent of the classical pattern established for π-allylic systems.

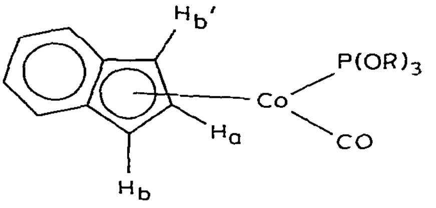
Interestingly, the H_a protons in IIa and IIb exhibit chemical shifts at substantially high fields in comparison with the figures such as δ 5.62, 4.83, 5.61, 5.23, 5.17 ppm measured for $[Mn(C_{13}H_9)(CO)_3]$ [6,7] $[Mn(C_{13}H_9)(CO)_2(PPh_3)]$ [6], $[Zr(CH_3)_2(C_{13}H_9)(C_{13}H_9)]$ [9], $[Rh(C_{13}H_9)(C_8H_{12})]$ [17], and $[Rh(C_{13}H_9)(C_8H_8)]$ [17]. This could be consistent with a situation in which some degree of π-electron localization arises, and therefore with a bonding model having some contribution from the localized form A. In favour of this



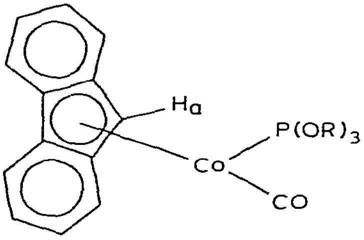
(A)

conclusion is the observation of a C_a—^{13}P coupling constant (5 Hz) (C_a's in the indenyl compounds Ia and Ib do not exhibit any observable C—^{31}P coupling constant). Finally, rather surprisingly, in the case of Ib no coupling with ^{31}P was observed for either type of carbon atom in the triisopropylphosphite groups.

Some reactions of complexes I and II were investigated with the aim of establishing whether they could undergo facile ligand-substitution reactions, thus testing the ability of these compounds to initiate an activation process under mild conditions. Complexes I and II were found to react with carbon monoxide at room temperature and at atmospheric pressure to give the monocarbonyl complexes IV and V.



(IVa, R = C_2H_5;
IVb, R = i-C_3H_7)



(Vb, R = i-C_3H_7)

Va (R = C_2H_5) was probably formed to a substantial extent in the reaction of IIa with CO as indicated by the presence of a strong band at 1940 cm^{-1} in the IR spectrum of the crude reaction mixture, but we could not obtain a sufficiently pure sample for further analyses.

The absorption of CO was rapid in all cases and amounted about 0.8 and 1 mol per mol of cobalt complex in the case of indenyl and fluorenyl complexes, respectively. Prolonged reaction times did not significantly change the outcome of reaction. The new compounds IV and V were characterized by ^1H NMR and IR spectroscopy (Table 3).

Of interest was the observation that the rate of CO absorption was higher in the case of fluorenyl compounds than that observed in the case of indenyl deriva-

TABLE 3

IR AND ^1H NMR DATA FOR COMPLEXES IV AND V

Compound	ν(CO) (cm^{-1})	^1H NMR (δ from TMS) [a]		
		Five-membered ring hydrogens	Six-membered ring hydrogens	R
IVa (R = C_2H_5)	1920 [b]	H_a, 5.60bs $H_{b,b'}$, 5.06bs	7.05—7.26m	CH_2, 3.73m CH_3, 1.20t[J(H—H)] 7 Hz
IVb (R = i-C_3H_7)	1920 [b]	H_a, 5.67bs $H_{b,b'}$, 5.01bs	7.00—7.28m	CH, 4.42m CH_3, 1.18d[J(H—H)] 7 Hz
Vb (R = i-C_3H_7)	1950 [c]	H_a, 3.53s	7.21—7.63m	CH, 4.80septet CH_3, 1.20d[J(H—H)] 6 Hz

[a] IVa and IVb in $(CD_3)_2CO$, Vb in C_6D_6; bs = broad singlet; d = doublet; m = multiplet; s = singlet; t = triplet. [b] Pure liquid. [c] Benzene solution.

tives. Even though we did not carry out any accurate kinetic study on the reaction this observation not only substantiates our predictions put forth in the introduction on the "coordinative flexibility" of the fluorenyl ligand, but also allows an interesting role to be foreseen for fluorenyl derivatives in organometallic chemistry and catalysis.

Experimental

All reactions involving organometallic compounds were carried out under dinitrogen using standard techniques for air-sensitive compounds. Diethyl ether and tetrahydrofuran were refluxed and distilled from sodium and then from lithium aluminium hydride. Unless otherwise noted other solvents were reagent grade, and were degassed under vacuum and dried over molecular sieves. The compounds C_9H_7Na [6], and $C_{13}H_9Na$ [14] were prepared as described in the references cited. Indene was purchased from Merck and was distilled before use. Triisopropylphosphite (Strem Chemicals), triethylphosphite (Fluka) and fluorene (Merck) were used without further purification. ^1H NMR spectra were obtained with a Varian T60 spectrometer, ^{13}C NMR spectra with a Varian XL 100 instrument and IR spectra with a 225 Perkin—Elmer instrument. Mass spectra were obtained with a Varian MAT Mod. CH7 spectrometer operating at 70 eV. Microanalyses were performed by the Laboratorio di Microanalisi of Istituto di Chimica Organica, Facoltà di Farmacia, Università di Pisa. Magnetic moments were measured by the Faraday method.

Preparation of tris(triisopropylphosphite)bromocobalt(I) (IIIb)

A mixture of $CoBr_2$ (0.02 mol), $P(O\text{-}i\text{-}C_3H_7)_3$ (0.12 mol), zinc dust (0.015 mol), and THF (180 ml) was stirred at room temperature for 24 h. The residual zinc was then filtered out and the resulting violet solution evaporated to dryness under high vacuum. The residue was extracted with pentane (30 ml) and the extracts concentrated to 20 ml. From this solution IIIb crystallized at room temperature as large deep-violet crystals (95% yield). (Found: C, 42.49; H, 8.24. $C_{27}H_{63}O_9BrP_3Co$ calcd.: C, 42.47; H, 8.31%). μ_{eff} 3.06 BM at 297 K.

Preparation of tris(triethylphosphite)bromocobalt(I) (IIIa)

A mixture of $CoBr_2$ (0.019 mol), $P(OC_2H_5)_3$ (0.073 mol), zinc dust (0.015 mol), and THF (180 ml) was stirred at room temperature for 24 h. The residual zinc was then filtered off and the resulting solution was evaporated to dryness under high vacuum. The solid residue was extracted with pentane (120 ml) and the extracts concentrated to 20 ml. From this solution IIIa crystallized at —30° C as brown crystals (30% yield). The compound was identical with a sample prepared as previously reported [13].

Preparation of bis(triethylphosphite)(η^5-indenyl)cobalt(I) (Ia)

A solution of IIIa (4.7 mmol) in pentane (80 ml) was treated with an equimolar amount of C_9H_7Na in THF to give a red-brown solution and a yellow solid. After stirring for 4 h at room temperature, the mixture was filtered and evaporated under vacuum. The resulting red oil was chromatographed on a 25 cm × 1 cm column of neutral alumina previously washed with benzene. Elution with benzene/pentane (1/2) gave an orange band which furnished an oil. This was dissolved in pentane, and the solution was extracted with degassed water, dried over Na_2SO_4, and evaporated to dryness to give Ia as a red oil (42% yield). (Found: C, 48.94; H, 7.30. Mol.wt. 506 (MS). $C_{21}H_{37}O_6P_2Co$ calcd.: C, 49.81; H, 7.36%. Mol.wt. 506.37). IR (net): 3050w, 2955s, 2900m, 2870m, 1480m, 1420m, 1365m, 1310m, 1260w, 1240w, 1155m, 1093m, 1030s, 925s, 745m cm^{-1}.

Preparation of bis(triisopropylphosphite)(η^5-indenyl)cobalt(I) (Ib)

A solution of IIIb (1.0 mmol) in pentane (60 ml) was treated with an equimolar amount of C_9H_7Na in THF at room temperature for 4 h. Work-up as above gave Ib as a red oil (37% yield). (Found: C, 59.90; H, 9.01. Mol.wt. 590 (MS). $C_{27}H_{49}O_6P_2Co$ calcd.: C, 59.99; H, 9.14%. Mol.wt. 590.53). IR (net): 3065w, 3025w, 2970s, 2920m, 2860w, 1455m, 1440m, 1370s, 1360m, 1315m, 1260m, 1240m, 1170m, 1135m, 1105m, 990s, 867m, 760m, 748m cm^{-1}.

Preparation of bis(triethylphosphite)(η^5-fluorenyl)cobalt(I) (IIa)

A solution of IIIa (2.0 mmol) in benzene (70 ml) was treated with equimolar amounts of $C_{13}H_9Na$ in 1,2-dimethoxyethane. The mixture was refluxed for 1 h, then stirred at room temperature for 3 h. After filtration and evaporation to dryness, a solid was obtained, this was extracted with pentane, and the pentane extracts were filtered then cooled to —30°C to give red-brown crystals of IIa (60% yield). (Found: C, 54.46; H, 7.00. $C_{25}H_{39}O_6P_2Co$ calcd.: C, 54.58; H, 7.08%). IR (net): 3060w, 3030w, 2970s, 2920m, 2890m, 1700w, 1600w, 1460m, 1430m, 1370m, 1240m, 1157m, 1092m, 1030s, 930s, 795m, 735s cm^{-1}.

Preparation of bis(triisopropylphosphite)(η^5-fluorenyl)cobalt(I) (IIb)

A solution of IIIb (1.9 mmol) in benzene (60 ml) was treated with an equimolar amount of $C_{13}H_9Na$ in 1,2-dimethoxyethane. The mixture was stirred at 80°C for 1 h then at room temperature for 3 h, and was then filtered. The filtrate was evaporated to dryness to give a brown solid. This was extracted with pentane and the combined extracts were cooled to —30°C to give brown crystals of IIb (33% yield). (Found: C, 58.09; H, 8.04. $C_{31}H_{51}O_6P_2Co$ calcd.: C, 58.21; H, 8.04%). IR (net): 3050w, 3020w, 2960m, 2920m, 2860m, 1705m, 1595m, 1450m, 1430m, 1365s, 1355s, 1250m, 1240s, 1170m, 1135m, 1100m, 995s, 812m, 735m cm^{-1}.

Preparation of (triethylphosphite)(carbonyl)(η^5-indenyl)cobalt(I) (IVa)

A solution of Ia (0.5 g) in benzene (25 ml) was kept for 2 h under CO (1 atm) at room temperature, then concentrated to 2 ml and chromatographated on a 20 cm × 1 cm column of alumina. Elution with benzene/pentane (1/10) gave an orange band, which gave IVa as a red oil (60% yield). (Found: C, 51.89; H, 5.98. $C_{16}H_{22}O_4PCo$ calcd.: C, 52.18; H, 6.02%). IR (net): 3040w, 2960s, 2910m, 2875m, 1920s, 1460w, 1415m, 1370m, 1310m, 1245w, 1155w, 1090m, 1020s, 930s, 805m, 747m cm^{-1}.

Preparation of (triisopropylphosphite)(carbonyl)(η^5-indenyl)cobalt(I) (IVb)

This preparation was carried out as described for IVa. Starting from Ib (0.6 g), IVb was obtained as a red oil (65% yield). (Found: C, 55.70; H, 6.90. $C_{19}H_{27}O_4PCo$ calcd.: C, 55.61; H, 6.87%). IR (net): 3070w, 3050w, 3040w, 2970s, 2925m, 2865w, 1920s, 1450m, 1435m, 1375m, 1310m, 1240m, 1220m, 1175m, 1100m, 998s, 950s, 875m, 765m cm^{-1}.

Preparation of (triisopropylphosphite)(carbonyl)(η^5-fluorenyl)cobalt(I) (Vb)

A solution of IIb (0.26 g) in benzene (15 ml) was kept under CO atmosphere (1 atm) for 30 min at room temperature. The mixture was evaporated to dryness under high vacuum. The red oily residue was dissolved in pentane (10 ml). From this solution red Vb crystallized at −30°C (60% yield). (Found: C, 59.87; H, 6.58. $C_{23}H_{30}O_4PCo$ calcd.: C, 60.00; H, 6.57%). IR (net): 3070w, 3050w, 3040w, 2970s, 2925m, 2865w, 1920s, 1450m, 1435m, 1375m, 1355m, 1310m, 1240m, 1220m, 1175m, 1100m, 998s, 950s, 875m, 765m cm^{-1}.

Acknowledgements

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