

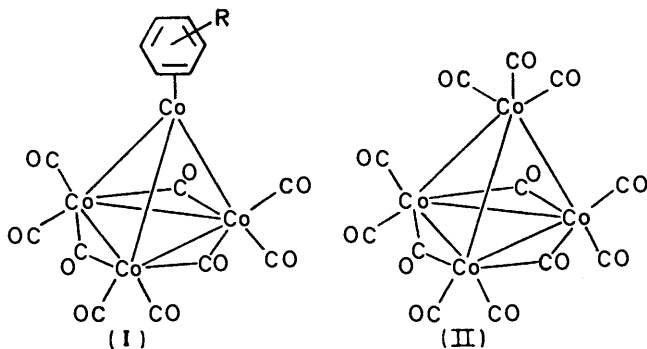
Organocobalt Complexes. Part I. Arene Complexes derived from Dodecacarbonyltetracobalt

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A series of tetranuclear arenecobalt carbonyls, $\text{ArHCo}_4(\text{CO})_9$, are formed by treating hexacarbonylacetylenedicobalt complexes, $(\text{R}^1\text{C}_2\text{R}^2)\text{Co}_2(\text{CO})_6$, with arenes in the presence of norbornene derivatives, or from the cobalt carbonyls $\text{Co}_4(\text{CO})_{12}$ and $\text{Co}_2(\text{CO})_8$ by direct reaction with arenes. Stable complexes are obtained from alkyl- and alkoxybenzenes, but not from halogeno- or acyl derivatives. The spectroscopic properties of the new complexes are reported.

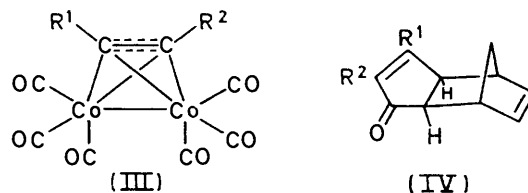
ARENE complexes of many transition metals have been studied during the last fifteen years and the interaction of the Group VI metal hexacarbonyls with arenes to give the corresponding arene tricarbonyl complexes was one of the earliest methods of preparation.¹ Only one other example of the direct displacement of three carbonyl groups by arenes has recently been described,² that of the trinuclear cobalt complexes $\text{RCCo}_3(\text{CO})_9$ ($\text{R} = \text{Me}$, Ph , or F) at 130° to give several complexes of the type $\text{RCCo}_3(\text{CO})_8(\text{ArH})$. The reactive hexacarbonyl of vanadium reacts³ with arenes under mild conditions, but with valence disproportionation to give ionic complexes $[(\text{ArH})\text{V}(\text{CO})_4][\text{V}(\text{CO})_6]$ and dodecacarbonyltriruthenium reacts with refluxing alkylbenzenes in complex fashion to give the hexaruthenium carbide clusters,⁴ $(\text{ArH})\text{Ru}_6\text{C}(\text{CO})_{14}$.

To these examples we now add the ready reaction of the carbonyls of cobalt to yield a new series of complexes of the constitution $(\text{ArH})\text{Co}_4(\text{CO})_9$. This composition, and the presence of characteristic bridging as well as terminal carbonyl stretching frequencies in the i.r., suggested the formulation (I) derived by simple replacement of the apical carbonyl groups from the structure⁵



of dodecacarbonyltetracobalt (II). Indeed the complexes can be formed easily from the latter compound at

temperatures in the range $50\text{--}100^\circ$. The well-known decomposition of octacarbonyldicobalt to the tetranuclear carbonyl (II) in arenes or other solvents at such temperatures⁶ means that the simpler carbonyl, $\text{Co}_2(\text{CO})_8$, can serve as starting material almost equally well. However, as reported in our preliminary communication,⁷ we first encountered the new complexes (I) during our study of the reaction of acetylenehexacarbonyldicobalt complexes (III) with norbornadiene in arene solvents. The majority of the arene complexes now reported have been made by this route; while requiring one additional step, the mildness of the conditions available and the ease of isolation of the products make it as convenient as the more direct method. The major organic products of these reactions are the ketones (IV) which form the subject of the following paper.



The arene complexes (I) are greenish-black crystalline solids whose structure has been confirmed by an X-ray study of the *p*-xylene complex.⁸ Their preparations and n.m.r. spectra are summarised in the Tables. In their n.m.r. spectra, the aromatic protons are shifted to higher fields by *ca.* 1.2 p.p.m. as compared with the parent arenes in CDCl_3 solution, and suffer a further shift of *ca.* 0.65 p.p.m. in C_6D_6 due to the shielding effect of the solvent. The latter effect is equally marked in methyl and methoxy-substituents. The resonance positions of the ring protons are at lower field than those in other arene-metal complexes, *e.g.* tricarbonyl(*m*-xylene)-chromium:⁹ τ (CDCl_3) 4.59, 5.03, and 5.05, carbidotetradecacarbonyltoluenehexaruthenium:⁴ τ (CDCl_3) 4.51, hexacarbonylethylidyne-silylenetricobalt:² τ 4.54.

¹ H. Zeiss, P. J. Wheatley, and H. J. S. Winkler, 'Benzenoid-Metal Complexes', Ronald Press, New York, 1966.

² B. H. Robinson, J. Spencer, and R. Hodges, *Chem. Comm.*, 1968, 1480; B. H. Robinson and J. L. Spencer, *J. Chem. Soc. (A)*, 1971, 2045; *cf.* M. D. Brice, R. J. Dellaca, B. R. Penfold, and J. L. Spencer, *Chem. Comm.*, 1971, 72.

³ F. Calderazzo, *Inorg. Chem.*, 1964, **3**, 1207; 1965, **4**, 223.

⁴ B. F. G. Johnson, R. D. Johnston, and J. Lewis, *Chem. Comm.*, 1967, 1057; *J. Chem. Soc. (A)*, 1968, 2865; *cf.* R. Mason and W. R. Robinson, *Chem. Comm.*, 1968, 468.

⁵ C. H. Wei, *Inorg. Chem.*, 1969, **8**, 2384.

⁶ See *e.g.* L. Ungvary and L. Marko, *Inorg. Chim. Acta*, 1970, **4**, 324.

⁷ I. U. Khand, G. R. Knox, P. L. Pauson, and W. E. Watts, *Chem. Comm.*, 1971, 36.

⁸ D. W. Hudson and O. S. Mills, personal communication.

⁹ W. R. Jackson, W. B. Jennings, S. C. Rennison, and R. Spratt, *J. Chem. Soc. (B)*, 1969, 1214.

The most characteristic features of the i.r. spectra are the bridging carbonyl bands, which occur in the range 1810—1825 cm^{-1} ; cf. 1859 cm^{-1} for octacarbonyldicobalt and 1865 cm^{-1} for the tetranuclear carbonyl (II). Only the benzene complex has yielded a satisfactory mass spectrum, which shows the parent ion, progressive loss of the nine CO groups to $(\text{C}_6\text{H}_6)\text{Co}_4$ (the base peak), and then cleavage of the arene to leave Co_4 .

As seen from Table 1, complexes are readily formed

The preparation of the last compound has been improved.

We have been unable to isolate analogous arene-rhodium complexes from the thermal reaction of $\text{Rh}_4(\text{CO})_{12}$ with alkylbenzenes.

EXPERIMENTAL

All reactions were carried out under nitrogen. Detailed descriptions are given only for the general methods.

TABLE 1

Arene	Yield (%) *	Complexes $(\text{ArH})\text{Co}_4(\text{CO})_9$				Found (%)		Required (%)	
		τ (ring protons)		τ (Me)		C	H	C	H
		CS_2	C_6D_6	CS_2	C_6D_6				
C_6H_6	36	3.83	4.75			31.9	1.2	31.8	1.1
PhMe	28	3.95		7.48		32.9	1.3	33.1	1.4
<i>o</i> - $\text{Me}_2\text{C}_6\text{H}_4$	36	4.05		7.60		34.6	1.7	34.4	1.7
<i>m</i> - $\text{Me}_2\text{C}_6\text{H}_4$	37	4.08 (m)	4.70, 4.78	7.53	8.02	34.6	1.7	34.4	1.7
<i>p</i> - $\text{Me}_2\text{C}_6\text{H}_4$	39	4.07		7.46		34.4	1.8	34.4	1.7
1,3,5- $\text{Me}_3\text{C}_6\text{H}_3$	49	4.10	4.71	7.52	7.95	35.45	2.0	35.5	2.0
1,2,4,5- $\text{Me}_4\text{C}_6\text{H}_2$	35		4.70		7.98	36.7	2.25	36.6	2.25
C_6HMe_5	22		4.62		7.90, 7.99,	37.5	2.3	37.7	2.5
					8.00 [1 : 2 : 1]				
C_6Me_6	21				7.87	38.7	2.8	38.75	2.8
PhEt	19	4.00		8.86 (t)		34.7	1.6	34.4	1.7
				$[\text{CH}_2, 7.10$ (q)]					
PhOMe	15	3.93, 4.27 [2 : 3]		6.05		32.4	1.35	32.5	1.3
<i>o</i> - $\text{MeC}_6\text{H}_4\cdot\text{OMe}$	18		4.68, 5.07		6.74, 7.91	33.2	1.7	33.4	1.6
<i>p</i> - $\text{MeC}_6\text{H}_4\cdot\text{OMe}$	20		4.77 [ABq]		6.73, 8.03	33.4	1.5	33.4	1.6
3,5- $\text{Me}_2\text{C}_6\text{H}_3\cdot\text{OMe}$	23		4.59 [2H], 4.98		6.59, 7.86	34.9	1.95	34.6	1.9

* Method 1 with $(\text{PhC}_2\text{H})\text{Co}_2(\text{CO})_6$ + norbornadiene.

TABLE 2

Method	Diene	$\text{R}^1\text{C}_2\text{R}^2$ in (III)	Yields of $(\text{ArH})\text{Co}_4(\text{CO})_9$			
			$\text{ArH} = \text{C}_6\text{H}_6$	PhMe	<i>p</i> - $\text{Me}_2\text{C}_6\text{H}_4$	1,3,5- $\text{Me}_3\text{C}_6\text{H}_3$
1	Norbornadiene	PhC_2H	36	28	39	49
		C_2H_2	31	22	31	35
		MeC_2H		25		
		Ph_2C_2	7			
	Norbornene	PhC_2H		31	33	43
		C_2H_2			23	29
		MeC_2H		29		
		Ph_2C_2		8		
2(a)	2,3-Bismethoxycarbonylnorbornadiene	PhC_2H	19		26	
		C_2H_2		17		
		MeC_2H		21		
		Ph_2C_2		8		
2(b)			25		37	40
					21	26

from benzene and its alkyl derivatives. Methoxybenzenes give less stable complexes. Chlorobenzene formed a relatively unstable analogue in only trace amounts, and naphthalene, ethyl benzoate, and benzylidyne trifluoride probably gave similar complexes, but these proved too unstable to be isolated. No indication of complex formation could be found in reaction with cycloheptatriene, the only non-aromatic triene examined. In such cases, notably with chlorobenzene, the known¹⁰ carbonylcobalt complexes of norbornadiene were found as products. That these are not normally intermediates in the reaction was shown by the small amounts of product resulting when an arene and phenylacetylene were warmed with hexacarbonylnorbornadienedicobalt.

Method 1.—The products are described in Table 1. Acetylenehexacarbonyldicobalt (III; $\text{R}^1 = \text{R}^2 = \text{H}$) (2 g, 6.4 mmol) and norbornadiene (0.6 g, 6.5 mmol) in toluene (150 ml) were stirred at 60—70° for 4 h. The green solution was then evaporated *in vacuo*; the residue was redissolved in benzene–light petroleum and chromatographed on neutral alumina. Benzene first eluted a violet viscous oil (12 mg) showing only terminal metal-carbonyl stretching vibrations in the i.r. This was followed by *nonacarbonyltoluene-tetracobalt* (I; $\text{R} = \text{Me}$) (0.45 g, 22%) forming deep violet crystals (green solutions), decomp. above 160° without melting sharply. Further elution with chloroform gave the ketone (IV; $\text{R}^1 = \text{H}$, $\text{R}^2 = \text{Me}$) (0.41 g, 43%), described more fully in the following paper.

¹⁰ G. Winkhaus and G. Wilkinson, *J. Chem. Soc.*, 1961, 602.

Variations of this procedure involved the use of alternative cobalt complexes: (a) the phenylacetylene complex (III; $R^1 = H$, $R^2 = Ph$) (2.0 g, 5.15 mmol or 2.3 g, 5.93 mmol); (b) the methylacetylene complex (III; $R^1 = H$, $R^2 = Me$) (2.0 g, 6.1 mmol); or (c) the diphenylacetylene complex (III; $R^1 = R^2 = Ph$) (2.0 g, 4.3 mmol) and the replacement of norbornadiene by norbornene (0.6 g, 6.5 mmol) or 2,3-bismethoxycarbonylbicyclo[2.2.1]heptadiene (0.6 g, 2.9 mmol). Yields obtained by the different procedures, collected in Table 2, are based on the cobalt complex (III). For anisole and its *o*- and *p*-methyl derivatives only 100 ml was used and for solid arenes 2–3 g was used with iso-octane (100 ml) as solvent. The methoxy-substituted complexes (I) were prepared at 50–60° (3 h) and had lower decomposition temperatures (*ca.* 120°). The yields of these relatively unstable products are improved by carrying out the reactions at 40° for 6–8 h. The less stable arene complexes are always accompanied by dodecacarbonyltetracobalt (II) and sometimes by bis(dicarbonylnorbornadienecobalt).¹⁰ Thus the latter (mixed with a little hexacarbonylnorbornadienedicobalt)¹⁰ was the major cobalt-containing product (150 mg) recovered from an attempt to prepare a chlorobenzene complex by this method [using $PhC_2HCo_2(CO)_6$ and norbornadiene]; it was preceded on the chromatogram by unchanged phenylacetylene complex (III; $R^1 = H$, $R^2 = Ph$) (35 mg) and followed by $Co_4(CO)_{12}$ (50 mg). The norbornadiene complex (75 mg) was also isolated when the diphenylacetylene complex (III; $R^1 = R^2 = Ph$) served as starting material in the preparation of the toluene complex (I; $R = Me$) and the reaction was conducted at 100°; the latter product preceded the norbornadiene complex on the column. Only insignificant amounts of arene complex were formed when the foregoing bicycloheptene derivatives were omitted or replaced by the unreactive 2,3-bismethoxycarbonylbicyclo[2.2.1]hept-2-ene.

Method 2.—(a) *Using* $Co_4(CO)_{12}$. Dodecacarbonyltetracobalt (2 g, 3.5 mmol) and mesitylene (150 ml) were stirred at 60–70° for 6 h. Excess of mesitylene was removed under vacuum and the residue worked up as in Method 1. On chromatography an unidentified reddish-brown oil (15 mg) was followed by a green band yielding the complex (I; $R = 1,3,5-Me_3$) (0.83 g, 40%).

(b) *Using* $Co_2(CO)_8$. Octacarbonyldicobalt (2 g, 6 mmol) and mesitylene (100 ml) were stirred at 60–70° for 8 h. Work-up as before yielded the reddish-brown oil (25 mg) and the complex (I; $R = 1,3,5-Me_3$) (0.46 g, 26%). The longer reaction time required and lower yields obtained by this method are consistent with initial conversion of the binuclear into the tetranuclear carbonyl. Evolution of CO was noted during both these reactions.

I.r. Spectra.—All the complexes (I) have similar i.r. spectra in the carbonyl region with maxima (in CS_2) at 2065s, 2020vs, 2003s, and 1990m in the terminal and 1820 cm^{-1} (all $\pm 5 cm^{-1}$) in the bridging carbonyl region. The 1990 cm^{-1} peak was missing or barely discernible as a shoulder on the 2000 cm^{-1} peak in the cases of the benzene and toluene complexes.

*Hexacarbonylnorbornadienedicobalt.*¹⁰—Norbornadiene (1 g) and octacarbonyldicobalt (4 g) were stirred in light petroleum (b.p. 40–60°; 50 ml) at 40° until the bridging carbonyl frequency of the starting material (1860 cm^{-1}) had disappeared (2.5 h). At this point no peaks due to the bisnorbornadiene complex were discernible. Removal of the solvent *in vacuo*, extraction with ether, and evaporation of the filtered solution gave hexacarbonylnorbornadienedicobalt (1.7 g) as an orange solid, whose physical properties agreed with those reported.¹⁰

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