Formation of Arenes and of Tetracarbonyl(hexatrienediyl)dicobalt ("Flyover") Complexes from Co$_2$(CO)$_8$[†]

R. John Baxter, Graham R. Knox,*,[‡] Jennifer H. Moir, Peter L. Pauson, and Mark D. Spicer*,[‡]

Department of Pure and Applied Chemistry, University of Strathclyde, 295 Cathedral Street, Glasgow G1 1XL, Scotland

Received June 29, 1998

The cobalt carbonyl mediated cyclotrimerization of alkynes to yield both arenes and "flyover" complexes (which contain a C$_6$Co$_2$ ring) has been reexamined with particular regard to the intermediacy of cobaltacyclopentadienes. Since the latter can now be obtained in controlled fashion from (alkyne)Co$_2$(CO)$_6$ and can react with a third alkyne under mild conditions by using trimethylamine-*N*-oxide as promoter, the incorporation of three different alkynes into both arenes and flyovers has become possible. Cobaltacyclopentadienes, like their precursors, catalyze alkyne cyclotrimerization, but flyovers do not do so under comparable conditions and hence are not on the main reaction path to arenes. In some circumstances cleavage of cobaltacyclopentadienes must occur to account for the observed arene products. Crystal structures of two flyover complexes are reported.

Introduction

Cyclotrimerization of alkynes has long been known to be catalyzed by a wide range of organo- (and other) transition metal compounds. Organocobalt compounds are among the more widely used and have contributed to our understanding of the reaction paths by permitting the isolation of some intermediates or potential intermediates. Probably best-known are the elegant and extensive studies by Vollhardt and co-workers (see, e.g. ref 1[1]) using dicarbonylcyclopentadienylcobalt as catalyst. The majority and much the most successful of their work, however, relates to the cocyclization of diynes with bis(trimethylsilyl)ethyne and the more general utility of their preferred catalyst is much less well documented.

On the basis of the isolation of the stable cyclopentadienylcobaltacyclopentadiene complexes **3a** from reactions of alkynes with complexes (η-C$_5$H$_5$)CoL$_2$, **1** (where L = CO, PR$_3$, or an alkene), it is widely accepted that these or similar species are intermediates in cyclotrimerization.[2,3] Bis(η^2-alkyne) complexes, **2**, are believed to be formed first; it is less clear whether these collapse spontaneously to 16-electron complexes **3** or whether an additional ligand (L' or R$_2$C$_2$) is required so that compounds **2** are converted directly to the 18-electron cobaltacyclopentadienes **3a** or **4**. If **3** has a discrete
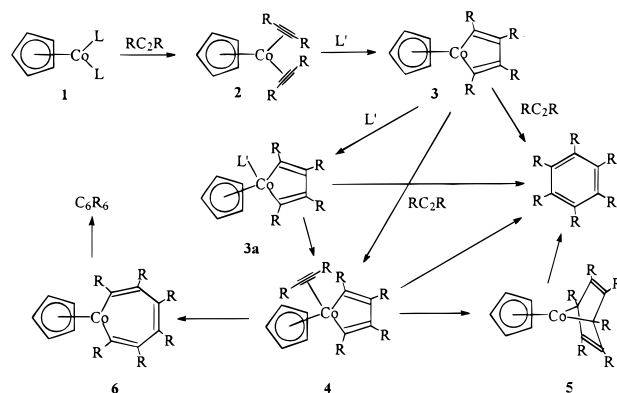
existence, its conversion to arene could occur in a single (Diels–Alder-like) step or via an adduct of type **4**. These and other variants of the possible transformations are collected in Scheme 1 and have been discussed in reviews, e.g., ref 4[4].

Although octacarbonyldicobalt, its mercury derivative Hg[Co(CO)$_4$]$_2$, Co$_4$(CO)$_{12}$, and the monoalkyne complexes (R^{1}C$_2$R^2)Co$_2$(CO)$_6$, **7**, and (R^{1}C$_2$R^2)Co$_4$(CO)$_{10}$ are also well-known to be good cyclotrimerization catalysts, surprisingly little has been added to our understanding of these systems since the pioneering studies of Walter Hübel and his group.[5] Even the effect on catalytic activity of replacing one or two carbonyl ligands in an

Scheme 1

---

* Corresponding Authors.
[†]We dedicate this paper to the late Owen S. Mills, whose determination of the first flyover structure[8] provided some of the early stimulus to our interest.
[‡] E-mail: g.r.knox@strath.ac.uk; m.d.spicer@strath.ac.uk.

(1) (a) Vollhardt, K. P. C. *Angew. Chem., Int. Ed. Engl.* **1984**, *23*, 539. (b) Vollhardt, K. P. C. *Pure Appl. Chem.* **1993**, *65*, 153.
(2) See e.g.: Yamazaki, H.; Yasufuku, K.; Wakatsuki, Y. *Organometallics* **1983**, *2*, 726, and earlier references cited therein. For a theoretical treatment see ref 3.
(3) Nomura, O.; Wakatsuki, Y.; Kitaura, K.; Yamazaki, H. *Sci. Pap. Inst. Phys. Chem. Res. (Jpn)* **1981**, *75*, 118 [*Chem. Abstr.* **1982**, *96*, 217992].

(4) Palyi, G.; Váradi, G.; Markó, L. In *Stereochemistry of Organometallic and Inorganic Compounds*; Bernal, I., Ed.; Elsevier: Amsterdam, 1986; Vol. 1, p 358 ff.
(5) (a) Hübel, W.; Hoogzand, C. *Chem. Ber.* **1960**, *93*, 103. (b) Krüerke, U.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2829. (c) Krüerke, U.; Hoogzand, C.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2917. (d) Hoogzand, C.; Hübel, W. *Tetrahedron Lett.* **1961**, 637. (e) Hoogzand, C.; Hübel, W. *Angew. Chem.* **1961**, *73*, 680. (f) Review: Hübel, W.; Hoogzand, C. In *Organic Synthesis* via *Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1968; p 273.
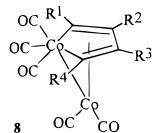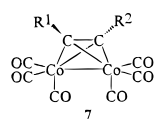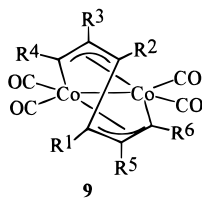
	R¹	R²
7a	COOMe	COOMe
7b	Me	Me
7c	Ph	COOMe
7d	Me	COOMe
7e	H	COOMe
7f	H	Ph

	R¹	R²	R³	R⁴
8a	COOMe	COOMe	COOMe	COOMe
8b	COOMe	Ph	COOMe	Ph
8c	COOMe	Me	COOMe	Me
8d	COOMe	H	H	COOMe
8e	COOMe	H	COOMe	H
8f	Ph	H	H	Ph
8g	Ph	H	COOMe	COOMe
8h	Ph	H	Me	Me

(alkyne)Co₂(CO)₆ complex, **7**, by triphenylphosphine has only fairly recently been assessed.[6] That these complexes, **7**, represent the first step when Co₂(CO)₈ or Hg[Co(CO)₄]₂ are used as catalysts is not in doubt, but Krüerke and Hübel[5b] were unable to isolate or detect intermediates derived from two alkyne units. The reasons for their failure to do so were explored in our study (see ref 7[7]), and conditions were devised which allowed isolation of at least a number of the expected "bisacetylene" complexes. Their structures, **8**, were established by comparison with known complexes of this type and by one X-ray crystallographic structure determination (**8h**). Their availability allowed us to examine their place in the catalytic sequence and to reinvestigate the later steps; here we present the results.

Results and Discussion

From some alkyne cyclotrimerizations Krüerke and Hübel[5b] isolated only trace quantities of deep violet colored tetracarbonyl("triacetylene")dicobalt complexes for which the "flyover" structure **9** was subsequently established crystallographically[8] (for structures of **D**–**G**

	Isomer	R¹	R²	R³	R⁴	R⁵	R⁶
9a	-	COOMe	COOMe	COOMe	COOMe	COOMe	COOMe
9b	G	Ph	COOMe	Ph	COOMe	Ph	COOMe
9c	F	Ph	COOMe	Ph	COOMe	COOMe	Ph
9d	D	COOMe	Me	Me	COOMe	COOMe	Me
9e	G	COOMe	Me	COOMe	Me	COOMe	Me
9f	F	Me	COOMe	Me	COOMe	COOMe	Me
9g	E	COOMe	Me	Me	COOMe	Me	COOMe
9h	F	H	COOMe	H	COOMe	COOMe	H
9i	-	Ph	H	H	Ph	COOMe	COOMe
9j	-	Me	Me	H	Ph	COOMe	COOMe
9k	-	Ph	H	COOMe	COOMe	COOMe	COOMe
9l	-	H	H	H	tBu	H	tBu
9m	E	CF₃	H	H	CF₃	H	CF₃
9n	E	SF₅	H	H	SF₅	H	SF₅
9o	F	Ph	COMe	Ph	COMe	COMe	Ph

in the diagram, see Scheme 3). However, it was not possible to deduce why only certain alkynes yielded flyovers and most of these were incompletely character-

(6) Sun, S.; Meng, Q.; Zhu, H.; Chen, W.; You, X. *Cuihua Xuebao* **1989**, *10*, 98 [*Chem. Abstr.* **1989**, *111*, 153269].
(7) Baxter, R. J.; Knox, G. R.; Pauson, P. L.; Spicer, M. D. *Organometallics* **1999**, *18*, 197.
(8) Mills, O. S.; Robinson, G. *Proc. Chem. Soc.* **1964**, 187.

ized. Their experiments with cotrimerization of two different alkynes did not establish any predictable pattern of behavior, regardless of the stoichiometry of the reaction; moreover, ligand exchange was clearly a significant factor for both arene and flyover formation. Nevertheless, thermal or oxidative degradation (using bromine) did indicate different oligomerization sequences and could be used to convert these flyovers efficiently and usefully to arenes (including compounds with adjacent bulky groups[5c–e] which are difficult to obtain in other ways), but the conditions required were clearly harsher than those available during catalytic cyclotrimerization. The conclusion therefore was that flyovers arise, probably from the same intermediates, but by a competing reaction path. This had, however, not been widely accepted, and in a number of later publications (e.g., refs 4 and 9[9]) the flyovers are clearly regarded as the last intermediates in the catalytic route to arenes. Subsequently there have been no systematic studies of the factors which dictate flyover formation, the oligomerization sequence of unsymmetrical alkynes (i.e. *head* to *head, head* to *tail*, etc.), and hence the regiochemistry of the products, apart from work by Dickson *et al.*[10] which focused entirely on fluorine-substituted alkynes. We noted[7] that flyover formation often occurred during cobaltacyclopentadiene preparation and the availability of these complexes, **8**, provided an opportunity to study the incorporation of the third alkyne unit. The results of these studies (reported below), mostly using the same alkynes as employed by Krüerke and Hübel,[5b] add considerable weight to their conclusions.

The full sequence of possible steps for alkyne trimerization by octacarbonyldicobalt can be written as in Scheme 2 (cf. ref 4), which, apart from the involvement of two cobalt atoms, has much in common with Scheme 1. The conversion of the alkyne complexes **7** to cobaltacyclopentadienes **8** is believed[7] to occur by a dissociative process and hence via a transient coordinatively unsaturated species, probably **7′**, which rapidly adds alkyne. Step **8** to **9**, which also involves loss of CO and incorporation of a further alkyne unit, may occur similarly. As in the previous case, this postulate led us to the successful use of amine-*N*-oxides to promote the reaction at room temperature. The possible steps are more numerous than for **7** to **8** since the loss of CO from complexes **8** can occur from either one of two different cobalt atoms, a choice which possibly determines whether coordination of the alkyne is followed by insertion to give the flyover or reductive elimination of an arene. The latter might also arise by a direct Diels–Alder-like addition of alkyne to the cobaltacyclopentadiene ring.

Trimerization of Dimethyl Acetylenedicarboxylate. Complexes derived from dimethyl acetylenedicarboxylate (DMAD) were studied initially, since the cobaltacyclopentadiene **8a** was readily isolable and its trimerization was known[5b] to give the flyover **9a** as well as hexamethyl benzenehexacarboxylate, **11**. We began by showing that treatment of the DMAD complex **7a** with 2 equiv of both the free alkyne and of trimethyl-

(9) Giordani, R.; Sappa, E.; Predieri, G. *Inorg. Chim. Acta* **1995**, *228*, 139.
(10) Dickson, R. S.; Fraser, P. J. *Aust. J. Chem.* **1972**, *25*, 1179.

Scheme 2
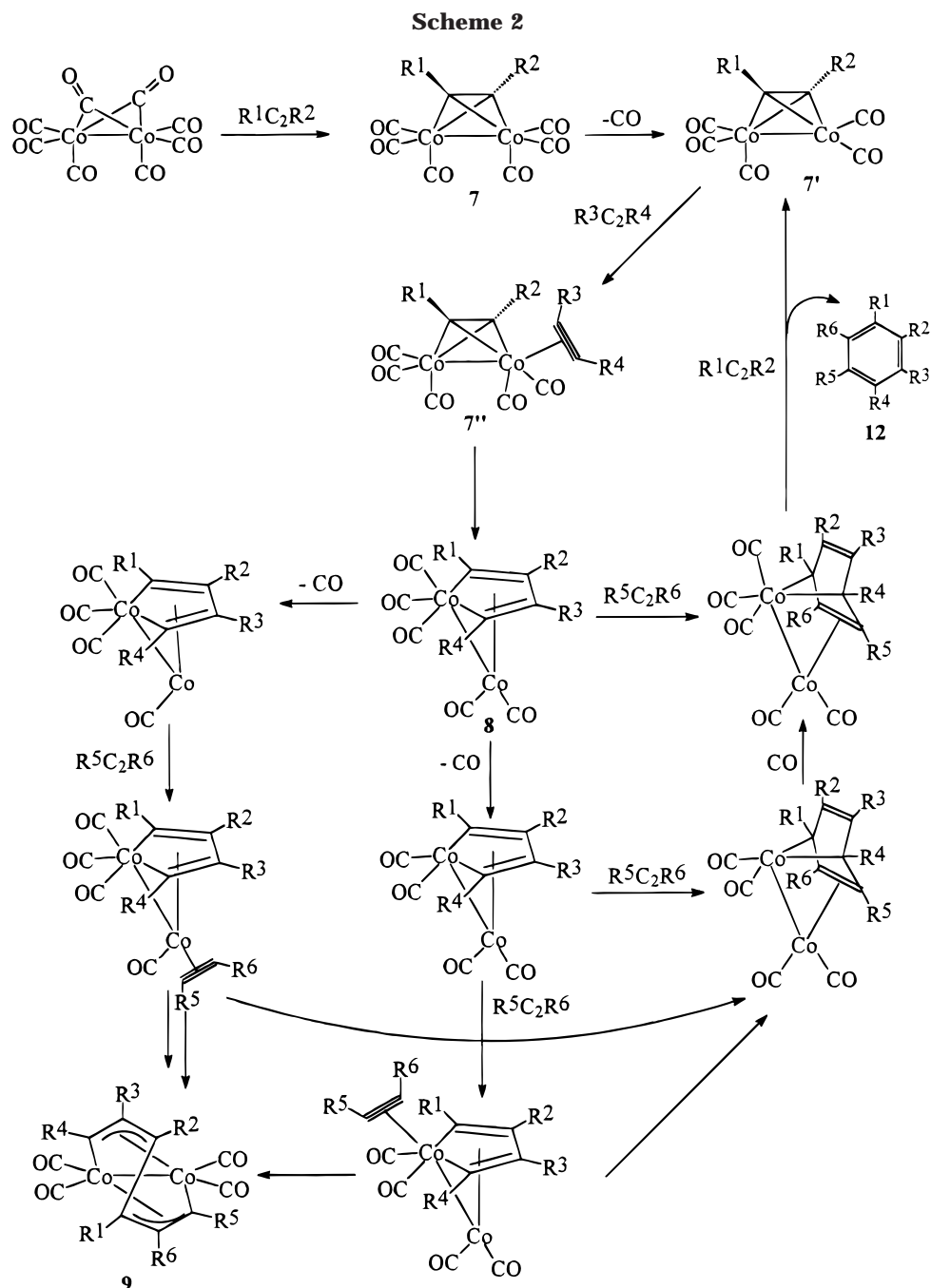
amine-*N*-oxide does indeed give both the flyover **9a** and hexamethyl benzenehexacarboxylate. For details see Table 1, which summarizes both reactions using Me₃NO at room temperature and reactions conducted without promoter in refluxing toluene (referred to below as "thermal reactions").

Experiment I is close to the optimum found for the reaction of the DMAD complex **7a** with free alkyne and Me₃NO, and the effect of minor variations in scale and conditions (not listed) served only to emphasize its reproducibility. Thus experiment II is essentially similar but indicates that there is a slow decrease of flyover and an increase of arene yield with time, due to the known thermal degradation of the former. Reaction in refluxing toluene also gave only slightly lower flyover yield together with significantly more arene (experiment III). In contrast to experiment I, use of the dihydrate of trimethylamine-*N*-oxide under the same conditions

yielded neither the flyover **9a** nor C₆(COOMe)₆ but only traces of unidentified organic products together with 75% of unreacted complex **7a**. However, in a much slower reaction between 2-butyne, its complex, **7b**, and the dihydrate (experiment IV), the complex was completely consumed, forming hexamethylbenzene (76%) as the only product; this complex did not yield either a cobaltacyclopentadiene, **8**, or a flyover complex, **9**.

When, in place of the monoalkyne complex, **7a**, the cobaltacyclopentadiene, **8a**, was treated with 1 equiv each of alkyne and *N*-oxide (experiment VII), the flyover was formed in 51% yield and accompanied by 6% of the arene, **11**. This and later examples show that, by reacting the intermediates **8**, when available, with alkynes at room temperature with trimethylamine-*N*-oxide as promoter, flyover complexes **9** become more readily available and can be made in more selective fashion.

Table 1. Formation of Products

expt no.	Precursor no.[b]	mg	mmol	Free Alkyne structure	mg (mL)	mmol	Me$_3$NO mg	mmol	method[a]	recovered precursor mg	%	product complex no.[b]	mg %	(%)[c]	arene no.[b]	mg (%)[c]
I	7a	621	1.45	C$_2$(COOMe)$_2$	410 (0.36)	2.90	90	1.45	II (3 h)	379	61	9a	256	27 (69)	11	49	12 (31)
II	7a	582	1.36	C$_2$(COOMe)$_2$	380 (0.33)	2.72	300	2.72	II (12 h)	358	58	9a	205	23 (55)	11	81	14 (33)
III	7a	880	2.06	C$_2$(COOMe)$_2$	600	4.12			I (15 min)	413	47	9a	284	21 (40)	11	298	34 (64)
IV	7b	207	0.61	C$_2$Me$_2$	70	1.23	160	1.44	II (room temp/ 3days)						12	75	76
V	7b	440	1.29	C$_2$Me$_2$	140	2.58			I (15 min)	198	45	10	88	12 (22)	12	73	35 (64)
VI	Co$_2$(CO)$_8$	680	2.0	C$_2$Me$_2$	430	8.0			I (2 h)			10	23	2[d]	12	289	67
VII	8a	2880	5.32	C$_2$(COOMe)$_2$	760 (0.65)	5.32	390	5.32	II (30 min)	317	11	9a	1770	51 (57)	11	90	6 (7)
VIII	Co$_2$(CO)$_8$	42	0.12	C$_2$(COOMe)$_2$	580 (0.50)	4.07			I (24 h)						11	153	26
IX	7a	26	0.06	C$_2$(COOMe)$_2$	580 (0.50)	4.07			I (24 h)						11	124	21
X	8a	53	0.10	C$_2$(COOMe)$_2$	1156 (1.0)	8.14			I (24 h)						11	48	4
XI	9a	67	0.10	C$_2$(COOMe)$_2$	1156 (1.0)	8.14			I (24 h)						11	48	4
XII	Co$_2$(CO)$_8$	230	0.67	MeC$_2$COOMe	480 (0.50)	5.0			I (24 h)			9d/9e +9f/9g	27 6	3 1	13	466	95[e1]
XIII	7d	260	0.67	MeC$_2$COOMe	420 (0.43)	4.33			I (24 h)			9d/9e +9f/9g	8 7	1 1	13	481	98[e2]
XIV	8c	300	0.66	MeC$_2$COOMe	360 (0.37)	3.68			I (24 h)						13	471	96[e3]
XV	Co$_2$(CO)$_8$	210	0.62	PhC$_2$COOMe	500	3.12			I (24 h)			9b/9c	286	39	14	304	61[e4]
XVI	8b	51	0.09	PhC$_2$COOMe	14	0.09	90	1.20	II (10 min)			9b/9c	5	12	14	1	3[e5]
XVII	8b	43	0.07	PhC$_2$COOMe	500	3.12			I (24 h)			9b/9c	54	100	14	396	76[e5]
XVIII	8d	112	0.26	HC$_2$COOMe	960	11.4			I (24 h)						15	989	99[e6]
XIX	Co$_2$(CO)$_8$	760	2.2	PhC$_2$H	2700	27			I (24 h)						16	2470	90
XX	8f	2250	4.87	PhC$_2$H	490 (0.52)	4.87	360	4.87	II (30 min)	520	23				16	850	57 (74)
XXI	7a	203	0.47	C$_2$Me$_2$	120	2.0			I (25 h)	12	4				17	47	40
XXII	8f	460	0.99	C$_2$(COOMe)$_2$	140 (0.12)	0.98	70	0.98	II (20 min)	230	50	9i	214	38 (76)	18	30	9 (18)
XXIII	8h	501	1.20	PhC$_2$COOMe	172 (0.15)	1.20	90	1.20	II (30 min)	45	9	9j	564	66 (72)[f]	19		22 (24)[f]
XXIV	8h	458	1.10	HC$_2$COOMe	93 (0.l)	1.10	83	1.10	II (45 min)						20	16	6
XXV[19]	8f	500	1.03	PhC$_2$H	500	5.0	380	5.0	II (24 h)						16	~200	~60
XXVI[19]	8f	105	0.23	C$_2$(COOMe)$_2$	154 (0.13)	1.08			I (48 h)						18	40	51
XXVII	8f	262	0.57	C$_2$(COOMe)$_2$	284 (0.25)	1.99	554	7.41	II (5 h)						18	g	18
XXVIII	8f	80	0.17	C$_2$(COOMe)$_2$	73 (0.077)	0.86									21	30	60
XXIX	8f	200	0.43	HC$_2$COOMe	80 (0.085)	0.95	170	2.27	II (24 h)						21	g	<10

[a] I = thermal reaction, reflux in toluene (time in parentheses); II = Me$_3$NO promoted reaction in THF/CH$_2$Cl$_2$ (1:1) at room temperature (unless otherwise specified; (time in parentheses); IIa = Me$_3$NO·2H$_2$O. [b] 10 = (Me$_2$C$_2$)Co$_4$(CO)$_{10}$; 11 = C$_6$(COOMe)$_6$; 12 = C$_6$Me$_6$; 13 = C$_6$Me$_3$(COOMe)$_3$ isomers; 14 = C$_6$Ph$_3$(COOMe)$_3$ isomers; 15 = C$_6$H$_3$(COOMe)$_3$ isomers; 16 = 1,2,4-C$_6$H$_3$Ph$_3$; 17 = 1,2-C$_6$Me$_4$(COOMe)$_2$; 18 = 1,2-(COOMe)$_2$-3,6-Ph$_2$-C$_6$H$_2$; 19 = 1,2-(COOMe)$_2$-3,4-Me$_2$-6-PhC$_6$H; 20 = 1-Ph-3,4-Me$_2$-5-(or 6-)(COOMe)C$_6$H$_2$; 21 = 1,4-Ph$_2$-2-(COOMe)C$_6$H$_3$. [c] Yield based on amount of precursor complex consumed (if different). [d] +C$_2$Me$_2$Co$_2$(CO)$_6$, 34 mg, 5%. [e] asymmetric (1,2,4-) to symmetric (1,3,5-) isomer ratios: (1) 81:19; (2) 77:23; (3) 75:25; (4) 87:13; (5) 90:10; (6) 71:29. [f] approximate yields (by NMR): these products failed to separate on silica. [g] Yield estimated by LC-MS.

Experiments VIII–X using the toluene reflux conditions and only catalytic amounts of Co$_2$(CO)$_8$ or complexes 7a or 8a all gave C$_6$(COOMe)$_6$ as the only significant product and in comparable amounts; the slightly better yield from Co$_2$(CO)$_8$ is attributable to the greater concentration of catalyst used. But the flyover 9a (experiment XI) yielded only the small quantity of the same arene expected from its own thermal decomposition, without incorporating any free alkyne as would be required if it were catalytically active under these conditions. Thus it must be bypassed in the cyclotrimerization using Co$_2$(CO)$_8$, or 7a, or 8a. There was also no insertion of a fourth alkyne to form a "tetraalkyne-bridged" complex of the type known in the cyclopentadienylmolybdenum series.[11]

Thus, the status of the flyover complexes of type 9 as the end products of an insertion sequence and not in the main path to arenes is confirmed. They are however, as Hübel's group had found, readily degraded to arenes, and we have used trimethylamine-*N*-oxide to effect the oxidative elimination/cyclization under very mild conditions and in excellent yield.

Trimerization of Unsymmetrical Alkynes. Having established that cobaltacyclopentadiene 8a could function as an intermediate in flyover formation, we turned our attention to the reactions of unsymmetrical alkynes. Scheme 3 demonstrates how an unsymmetrical alkyne, $R^1C_2R^2$, may yield three isomeric cobaltacyclopentadienes, A–C. Depending upon the orientation of the third molecule of inserting alkyne and the carbon–cobalt bond which is opened, these can lead to four isomeric flyovers, D–G. Furthermore, if one assumes that oxidative or thermal decomposition of the flyovers occurs without any C–C bond cleavage or rearrangement [this assumption has been verified for 9c–f and 9i], the derived arene would be formed (Scheme 4) by linking the carbons (*); i.e., the ordering of the backbone substituents on the flyover is retained in the derived asymmetric (1,2,4-) or symmetric (1,3,5- substituted) arene. For clarity, the usual "Z"-shaped backbone of the flyover is redrawn in Scheme 4 to show head-to-head, head-to-tail, etc., trimerization.

A simple example is provided by methyl phenylpropiolate (experiments XV–XVII; see "Note" in following square brackets), which reacted with its derived cobaltacyclopentadiene (C, 8b) and *N*-oxide to give a 90% yield of a mixture of two flyovers (G, 9b; F, 9c) in the ratio 9:1, contaminated by a trace of a third isomer, either D or E. [Note: Hübel et al.[5a] report that cyclotrimerization of methyl phenylpropiolate yields the 1,2,4-trisubstituted arene together with a flyover. A flyover complex was also obtained from the Co$_4$(CO)$_{10}$ complex of this alkyne, but the source of the flyover

(11) (a) Green, M.; Norman, N. C.; Orpen, A. G.; Schaverien, C. J. *J. Chem. Soc., Dalton Trans.* **1984**, 2455. (b) Green, M.; Jetha, N. K.; Mercer, R. J.; Norman, N. C.; Orpen, A. G. J. Chem. Soc., Dalton Trans. **1988**, 1843.

Scheme 3

Scheme 4
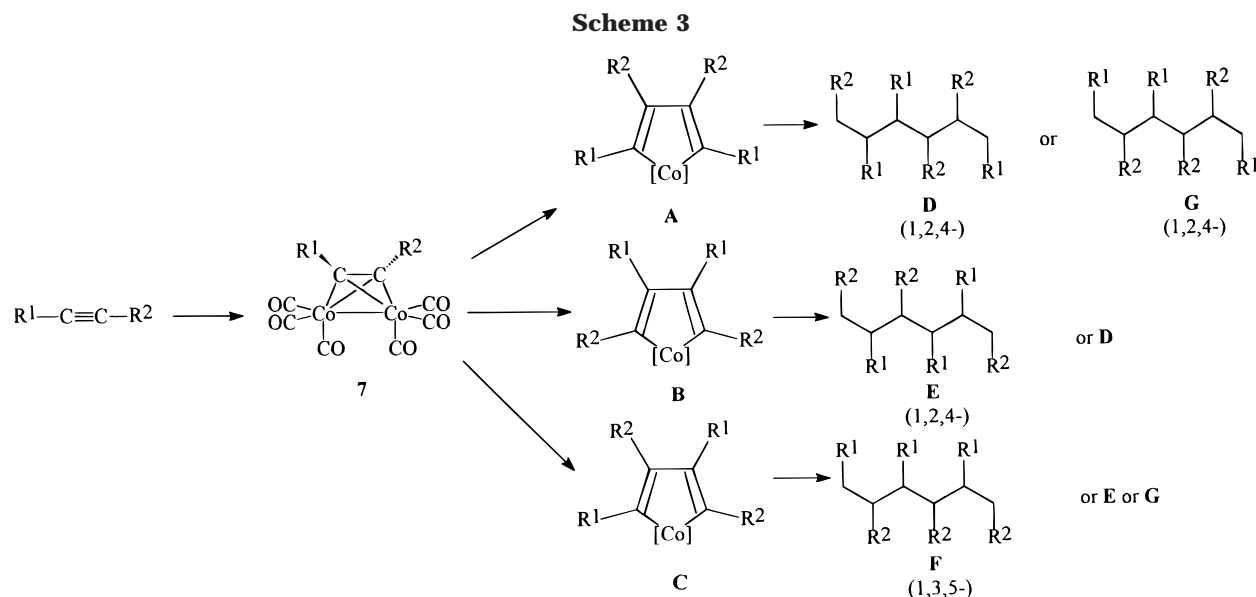
which was degraded by Br_2 to a 1,3,5-trisubstituted arene was not specified.[5b]] The structure of the isomer **9c** was confirmed by X-ray crystallography[12] and oxidative degradation to the 1,3,5-substituted arene. The structure of **9b** could be deduced by ^{1}H NMR spectroscopy (vide infra) and was confirmed by degradation of the mixture of flyovers to an arene mixture which was also analyzed by ^{1}H NMR using the distinctive chemical shifts of each ester $-OCH_3$ singlet. A similar 9:1 mixture of flyovers **9b,c** was produced as byproducts during the synthesis of **8b** from **7c**. They were also isolated (in 39% yield) from a thermal cyclotrimerization reaction of methyl phenylpropiolate using $Co_2(CO)_8$, but in this case the ratio (**G**, **9b**) to (**F**, **9c**) was about 3:1. In each of the above reactions a mixture of the respective trisubstituted arenes was also obtained, the ratio of 1,2,4- to 1,3,5- being approximately constant (9:1). Of importance is the observation that the same 9:1 ratio of arenes was obtained both from a thermal reaction between a catalytic amount of cobaltacyclopentadiene **8b** and methyl phenylpropiolate *and* the cyclotrimerization using $Co_2(CO)_8$, further implicating the intermediacy of **8b** in the latter process.

These results now permit a reinterpretation of other published work. The trimerization of 1-phenyl-1-butyn-3-one, PhC_2COMe, yielded the only previously characterized flyover complex with an alternating chain.[13] However, we believe that the authors of this work overlooked the difference between the arene, undoubtedly 1,3,5-triacetyl-2,4,6-triphenylbenzene, obtained from

this flyover and the arene obtained as the main cyclotrimerization product for which they obtained NMR data which clearly fit the unsymmetrical 1,2,4-isomer. Similarly an example from the work of Hübel et al.[5b] can now be rationalized. Cyclotrimerization of PhC_2Me gave a 90% yield of the 1,2,4-substituted arene together with a flyover which was degraded to the 1,3,5-substituted arene. Both of these examples reinforce the postulate[5f] that arenes and flyovers result from independent, competing pathways.

Complementary results were obtained from reactions of methyl 2-butynoate, but the flyovers derived from this alkyne were considerably less stable, so that comparative quantitative data are limited. The thermal cyclotrimerization with $Co_2(CO)_8$ (experiment XII) gave a mixture of the 1,2,4- and 1,3,5-arenes, **13**, in 95% yield. Two well-separated flyover fractions were also obtained by chromatography, but each was a mixture of two isomers. The first eluting, larger fraction contained (**D**, **9d**, 2.6%) and (**G**, **9e**, 0.4%), and the second fraction consisted almost entirely of the alternating chain isomer (**F**, **9f**, 0.98%) and a trace (0.02%) of a fourth isomer, believed to be (**E**, **9g**). The structures of these isomers were deduced by an internally consistent combination of ^{1}H NMR spectroscopy (vide infra) and *N*-oxide degradation to readily analyzed mixtures of the respective arenes. A similar thermal cyclotrimerization using **7d** as the catalyst (experiment XIII) gave similar results, viz., 98% conversion to an arene mixture and approximately 1% of each of the flyover mixtures. When **8c** was used as the catalyst (experiment XIV), only the arenes were isolated (96% conversion). However, the preparation of **8c** from **7c**[7] (10% yield) also gave flyovers **9d,e** (2.6%) and **9f,g** (0.6%) as byproducts, together with a trace (0.5%) of the arene mixture. The isolation of the major flyover (**D**, **9d**) is of particular interest, because, if it arises via a cobaltacyclopentadiene, only an unobserved and presumably unstable (α,α') isomer **A** or **B** could function as such an intermediate. Deliberate *N*-oxide promoted reaction of **8c** in the presence of alkyne, in contrast to the behavior of **8b**, did not yield any flyover but only the usual mixture of arenes, possibly because flyover degradation was more rapid

(12) Baxter, R. J.; Spicer M. D. *Acta Crystallogr. C.*, manuscript in preparation.
(13) Gervasio, G.; Sappa, E.; Markó, L. *J. Organomet. Chem.* **1993**, *444*, 203.
(14) Moldes, I.; Papworth, T.; Ros, J.; Alvarez-Larena, A.; Piniella, J. F. *J. Organomet. Chem.* **1995**, *489*, C65.

than formation under the reaction conditions. The composition of the arene mixtures appeared to be relatively invariant from each of the above five experiments; i.e., the isomer ratio (1,2,4-) to (1,3,5-) was 79: 21 ± 4%; similar turnover numbers (TON = 2.41 ± 0.04) for the cyclotrimerization catalysts $Co_2(CO)_8$, **7d**, and **8c** further support the intermediacy of **8c** in arene formation.

Anomalous behavior of the methyl propiolate derived cobaltacyclopentadiene **8d** obtained from **7e** has been mentioned in ref 7. Thermal cyclotrimerization reactions with either $Co_2(CO)_8$ or **8d** (experiment XVIII) gave 73: 27 ± 1% ratios of trimethyl 1,2,4- to 1,3,5-benzenetricarboxylates, **15**, and no flyover complexes. But the synthesis of (**8d**, **A**) had yielded an unstable flyover (**F**, **9h**), which degraded exclusively to the 1,3,5-trisubstituted arene, so that only an unsymmetrical cobaltacyclopentadiene (**8e**, **C**) could have been an intermediate. We conclude that this last complex reacts too fast with free alkyne to accumulate, whereas the symmetrical isomer **8d** reacts too slowly to give significant amounts of flyover under our standard conditions.

In contrast to the behavior of methyl propiolate, reactions of the terminal alkyne ethynylbenzene always yielded 1,2,4-triphenylbenzene to the exclusion of detectable amounts of the 1,3,5-isomer. Thus, thermal cyclotrimerization with $Co_2(CO)_8$ (experiment XIX),[5f] **7f**,[5f] and **8f**, the preparation of **8f** from **7f**, and the degradation of **8f** by *N*-oxide in the presence of ethynylbenzene (experiment XX) each yielded only the 1,2,4-arene; unisolable traces of a flyover were also observed.

Formation of Flyovers and Arenes from Two or Three Different Alkynes. Construction of mixed flyovers and/or arenes directly from the monoalkyne complexes (**7**) and a different alkyne succeeds well enough in some cases (e.g., arene **17**, experiment XXI) but is limited by the facile alkyne exchange processes to the use of the most stable of these complexes. The utilization of cobaltacyclopentadienes **8** offers the opportunity of better control; moreover, the isolation of the cobaltacyclopentadienes **8** derived from two different alkynes[7] makes possible the formation of both flyover complexes **9** and arenes derived from three different alkynes. In practice the suitability of specific examples is not easily predictable. Successful cases (see Table 1) include the reaction of complex **8f** derived from two molecules of ethynylbenzene, with DMAD to give flyover **9i** in 38% yield together with the corresponding arene, **18**, dimethyl 3,6-diphenylphthalate (9%; experiment XXII). An X-ray crystal structure determination[12] of **9i** showed that no cobaltacyclopentadiene rearrangement had occurred during flyover formation; oxidative degradation (with an excess of amine *N*-oxide) of this flyover, **9i**, to give the same arene, **18**, also demonstrated the absence of C–C bond cleavage.

Complex **8g** derived from one molecule of ethynylbenzene and one of DMAD failed to react with 2-butyne, but **8h** derived from ethynylbenzene and 2-butyne, although recovered unchanged (91%) from attempted reaction with 3,3-dimethyl-1-butyne, readily incorporated DMAD (experiment XXIII). The resulting flyover is degraded by trimethylamine-*N*-oxide oxidation to give the expected dimethyl 3,4-dimethyl-6-phenylphthalate,
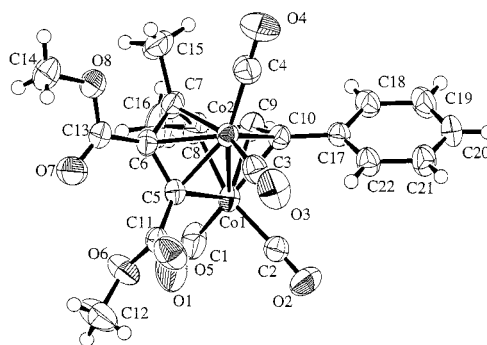
Figure 1. Ortep diagram of **9j** with thermal ellipsoids drawn at the 40% level and showing the atom numbering scheme.
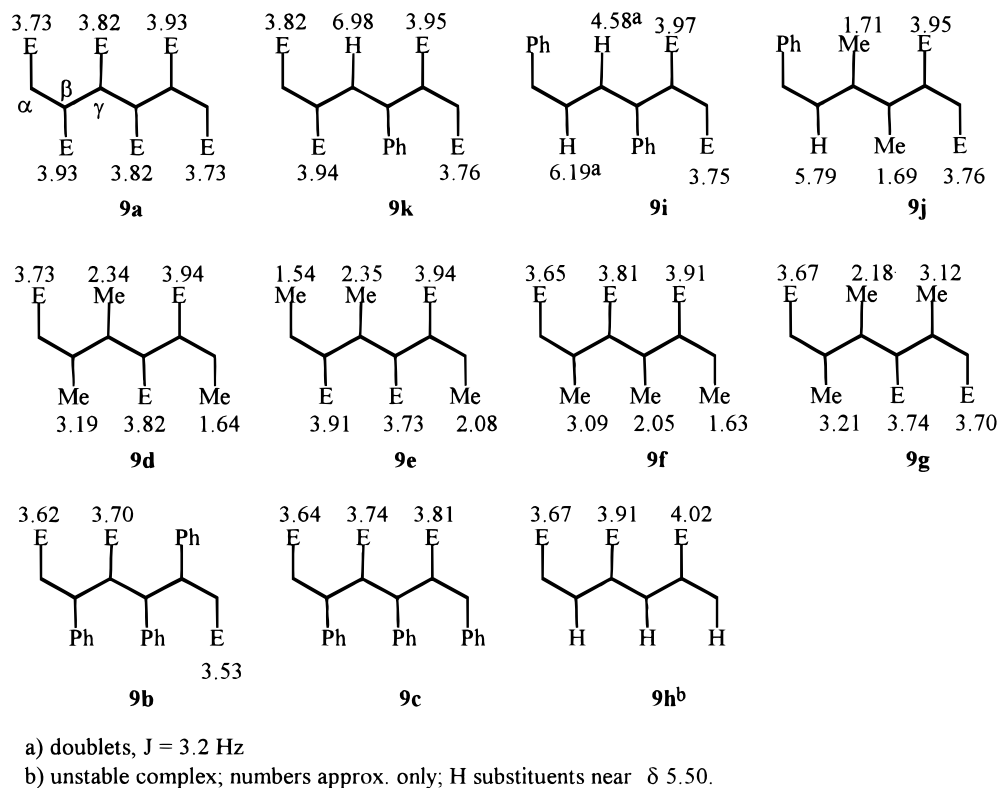
Scheme 5
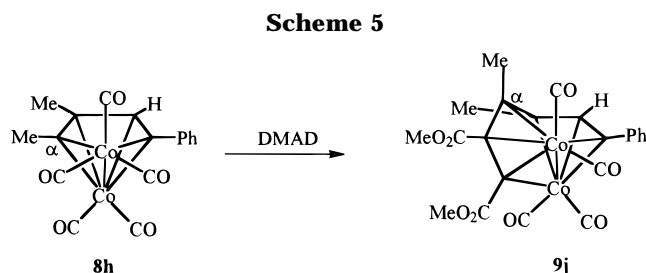
19, but this does not distinguish between two possible substitution patterns in the flyover. Its structure as **9j** was therefore established by X-ray crystallography and shows that insertion (of DMAD) had occurred, apparently exclusively, into the $Co-C_{Me}$ bond and not into the $Co-C_{Ph}$ bond (Figure 1). Scheme 5 shows that in relation to the cobaltacyclopentadiene precursor, **8h** (for structure see ref 7) this insertion has occurred with displacement of C_α and its appended methyl group from the original CoC_4 plane of **8h**. Flyover **9j** is the first known example constructed from three different alkynes, and its smooth degradation provides the first synthesis of a similarly derived arene. Insertion of methyl propiolate as the third alkyne into **8h** gave an arene believed to be methyl 2-phenyl-4,5-dimethylbenzoate, **20**,[15] rather than the isomer methyl 3-phenyl-5,6-dimethylbenzoate, but in this case no flyover was obtained (experiment XXIV).

Our next experiment investigated the possibility of achieving arene synthesis directly by *N*-oxide or thermal degradation of cobaltacyclopentadiene in the presence of *excess* alkyne, thus eliminating the flyover step. Although arenes were obtained, the results from *N*-oxide degradations were not encouraging: multicomponent mixtures, including products of alkyne exchange, caused separation difficulties and yields were usually low. Thus, by cobaltacyclopentadiene **8f**, reactions with excess ethynylbenzene, dimethyl acetylenedicarboxylate and methyl propiolate (experiments XXV, XXVII, and XXIX) gave **16**, **18**, and **21**, respectively. Thermal reactions leading to **18** and **21** (experiments XXVI and XXVIII) gave cleaner reactions and moderate yields (51 and 60%). In fact, triphenylbenzene, **16**, was produced in each of these reactions, providing further evidence

(15) ¹H NMR did not permit unambiguous identification of these isomers.
(16) Dickson, R. S.; Fraser, P. J.; Gatehouse, B. M. *J. Chem. Soc., Dalton Trans.* **1972**, 2278.
(17) Wessel, J.; Hartl, H.; Seppelt, K. *Chem. Ber.* **1986**, *119*, 453.

9a (E groups): 3.73, 3.82, 3.93 (top); α, β, γ; 3.93, 3.82, 3.73 (bottom)

9k E 3.82, H 6.98, E 3.95 (top); E 3.94, Ph, E 3.76 (bottom)

9i Ph, H 4.58[a], E 3.97 (top); H 6.19[a], Ph, E 3.75 (bottom)

9j Ph, Me 1.71, E 3.95 (top); H 5.79, Me 1.69, E 3.76 (bottom)

9d E 3.73, Me 2.34, E 3.94 (top); Me 3.19, E 3.82, Me 1.64 (bottom)

9e Me 1.54, Me 2.35, E 3.94 (top); E 3.91, E 3.73, Me 2.08 (bottom)

9f E 3.65, E 3.81, E 3.91 (top); Me 3.09, Me 2.05, Me 1.63 (bottom)

9g E 3.67, Me 2.18, Me 3.12 (top); Me 3.21, E 3.74, E 3.70 (bottom)

9b E 3.62, E 3.70, Ph (top); Ph, Ph, E (bottom); 3.53

9c E 3.64, E 3.74, E 3.81 (top); Ph, Ph, Ph (bottom)

9h[b] E 3.67, E 3.91, E 4.02 (top); H, H, H (bottom)

a) doublets, J = 3.2 Hz
b) unstable complex; numbers approx. only; H substituents near δ 5.50.

Figure 2. Most probable ^{1}H NMR assignments of substituents on the flyover chains (E = COOMe).

of facile C−C bond cleavage in **8f**. The reaction with methyl propiolate also gave a significant yield of trimethyl 1,2,4- and 1,3,5-benzenetricarboxylates, **15**, together with trace amounts of 2,5-bis(methoxycarbonyl)cyclopenta-2,4-dienone, 2,5-diphenylfuran, pyrones **22a** and **22b**,[18] and a compound [(HC$_2$COOMe)$_3$CO], possibly a tropone.
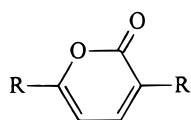
22 a) R = Ph
       b) R = COOMe

Attempts to induce reactions of the same flyover, **9a**, with another molecule of an alkyne (phenylethyne) or with carbon monoxide under pressure, were unsuccessful.

Structural Aspects. X-ray crystallography has played an important role in the characterization of these complexes. In addition to **9c**, **9i**, and **9j** (mentioned above), the crystal structure of **9a** has also been determined. Selected bond lengths and angles for **9j** are collected in Table 2, and the structure is depicted in Figure 1. The structures determined parallel closely the four previously reported flyover structures **9l**,[8] **9m**,[16] **9n**,[17] and **9o**[13] and thus will not be discussed in detail. However, it is noteworthy that the structural param-

(18) 2*H*-Pyran-2-ones have been observed previously as reaction products from alkynes and (C$_5$Me$_5$)Rh(CO)$_2$: Dickson, R. S.; Evans, G. S.; Fallon, G. D. *J. Organomet. Chem.* **1982**, *236*, C49.
(19) We thank Miss Laura Bauer for these experiments.
(20) Hocking, M. B.; van der Voort Maarschalk, F. W. *Can. J. Chem.* **1993**, *71*, 1873.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 9j

Co(1)−Co(2)	2.4584(7)	C(1)−Co(1)−C(2)	95.0(2)
Co(1)−C(1)	1.769(5)	C(3)−Co(2)−C(4)	95.5(2)
Co(1)−C(2)	1.790(4)	C(1)−Co(1)−Co(2)	148.8(1)
Co(2)−C(3)	1.805(4)	C(2)−Co(1)−Co(2)	104.4(1)
Co(2)−C(4)	1.771(4)	C(3)−Co(2)−Co(1)	107.1(1)
Co(1)−C(5)	1.962(3)	C(4)−Co(2)−Co(1)	144.1(1)
Co(1)−C(8)	2.036(8)	C(5)−Co(1)−C(10)	104.5(1)
Co(1)−C(9)	2.062(4)	C(5)−Co(2)−C(10)	102.6(1)
Co(1)−C(10)	1.995(3)	Co(1)−C(5)−Co(2)	77.0(1)
Co(2)−C(5)	1.986(3)	Co(1)−C(10)−C(2)	75.4(1)
Co(2)−C(6)	2.065(3)	C(5)−C(6)−C(7)	110.3(3)
Co(2)−C(7)	2.059(4)	C(6)−C(7)−C(8)	115.8(3)
Co(2)−C(10)	2.024(3)	C(7)−C(8)−C(9)	116.7(3)
C(5)−C(6)	1.406(5)	C(8)−C(9)−C(10)	113.4(3)
C(6)−C(7)	1.431(5)		
C(7)−C(8)	1.513(5)		
C(8)−C(9)	1.420(5)		
C(9)−C(10)	1.409(5)		

eters of the central Co$_2$(CO)$_4$C$_6$ cores of the flyover complexes remain remarkably constant from structure to structure given the diversity of functional groups appended to the C$_6$ chain.

Availability of this structural information has helped in establishing the correct assignment of NMR peaks. The ^{1}H NMR data for the flyovers prepared in this work (including reactions described in the preceding paper[7]) are shown in Figure 2. All our flyovers contain ester groups, and the accumulated data show that the chemical shift values of the COOCH_3 signals depend primarily on the positions (α, β, or γ) of these groups relative to the nearest cobalt atom, the groups in β-positions being least and those in the α-position most shielded (Figure 2).

Although the chirality of flyover complexes is evident from their structure and long recognized, we have succeeded in providing the first demonstration of this

Table 3. IR Spectra of Flyovers (cm^{-1} in Hexane)

no.	ν_{CO}	$\nu_{C=O}$
9a	2097, 2070, 2046	1742, 1720
9h	2080, 2049, 2029, 2021	1728
9k[a]	2084, 2057, 2031	1726
9d	2071, 2040, 2010	1722
9e	2068, 2035, 2019, 2002	1728
9i	2066, 2039, 2017, 2010	1740, 1712
9c	2070, 2045, 2024	1737
9j	2063, 2035, 2012, 2005, 1971	1748, 1730, 1713

[a] In dichloromethane.

property by examining the ^{1}H NMR spectrum of flyover **9a** with and without addition of the chiral shift reagent tris[(3-heptafluoropropyl)hydroxymethylene-(−)-camphorato]praseodymium(III). This causes upfield shifts and splitting of all three signals, with that of the γ-COOCH$_3$ (at δ 3.82) suffering the largest and that of the β-COOCH$_3$ (at δ 3.93) the least splitting, indicating that the praseodymium(III) coordinates most strongly to the central ester groups in the chain. Similar results were obtained with flyover **9c**.

Experimental Section

General remarks in the ref 7 apply, and methods are similar. Oligomerization reactions are summarized in Table 1, IR data for flyovers are in Table 3, and ^{1}H NMR data of flyover complexes are in Figure 2; for the numbering of arenes see footnotes of Table 1. Typical procedures follow.

Typical Procedures. Thermal Reactions. (a) Reaction III of Table 1. A mixture of DMAD (600 mg) and its complex, **7a**, (880 mg) in toluene (20 mL) was heated under reflux for 15 min. After cooling, the products were chromatographed on silica, eluting with light petroleum/ether (1:1). Unreacted complex **7a** (413 mg, 46%) was eluted first, followed by the known[5b] flyover complex **9a,** violet crystals from hexane (284 mg, 21%), and finally hexamethyl benzenehexacarboxylate (298 mg, 34%), colorless crystals from methanol, mp 72−73 °C, consistent with literature values.

(b) Reaction XXVI of Table 1. A mixture of DMAD (154 mg) and cobaltacyclopentadiene **8f** (105 mg) in hexane (20 mL) was stirred under nitrogen at room temperature for 24 h and then heated to reflux for 24 h. Chromatography (SiO$_2$; 3:1 petroleum ether/ether) separated **16** (10 mg, 22%) from unchanged DMAD followed by **18** (40 mg, 51%), white crystals (petroleum ether), mp 181 °C (lit.,[20] 192 °C), identified by MS, IR and NMR.

Trimethylamine-*N*-oxide Promoted Reaction. (a) Reaction VII of Table 1. To DMAD (760 mg) and the derived cobaltacyclopentadiene **8a**[7] (2.88 g) in tetrahydrofuran (THF) (15 mL) and dichloromethane (15 mL), anhydrous Me$_3$NO[21] (390 mg) was added and the mixture stirred for 30 min. Solvents and trimethylamine were removed on a rotary evaporator. The residue was chromatographed on silica, eluting with hexane plus slowly increasing proportions of ether. Unreacted complex **8a** (317 mg, 11%) was recovered first, followed by the flyover **9a** (1.77 g, 51%) and then **11**, C$_6$-(COOMe)$_6$ (90 mg, 6%).

(b) Reaction XXIX of Table 1. Cobaltacyclopentadiene **8f** (200 mg) and methyl propiolate (80 mg) were dissolved in dry THF (50 mL), anhydrous Me$_3$NO (170 mg) was added, and the mixture was stirred at ambient temperature for 24 h. After filtration through Kieselguhr, the solvent was removed and

(21) Soderquist, J. A.; Anderson, C. L. *Tetrahedron Lett.* **1986**, *27*, 3961.

(22) PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Smits, J. M. M.; Smykalla, C. DIRDIF Programme System; Technical report of the University of Nijmegen, The Netherlands, 1992.

Table 4. Experimental Details of the Crystal Structure Determination of 9j

Crystal Data	
mol formula	C$_{22}$H$_{18}$Co$_2$O$_8$
mol wt	528.25
cryst color	red-black prism
cryst size, mm	0.40 × 0.15 × 0.10
space group	$P\bar{1}$ (No. 2)
a, Å	10.782(1)
b, Å	11.675(1)
c, Å	8.877(1)
α, deg	97.09(1)
β, deg	94.78(1)
γ, deg	94.008(10)
V, Å^3	1101.4(3)
Z	2
ρ_{calcd}, g cm^{-3}	1.593
μ (Mo Kα), cm^{-1}	15.52
$F(000)$	536.00
Data Collection	
diffractometer	Rigaku AFC7S
radiation	Mo Kα
wavelength, Å	0.710 69
T, K	295
scan type	$\omega-2\theta$
scan rate, deg min^{-1}	16 (in ω)
scan width	0.73 + 0.35 tan θ
θ range, deg	2.5−27.5
index ranges	
h	0 to +12
k	−18 to +18
l	−12 to +10
Solution and Refinement	
reflcns measd	5311
unique reflcns	5042 (R_{int} = 0.028)
obsd reflcns	2974
no. of variables	290
$I >$	$2\sigma(I)$
GOF	1.27
R	0.033
R_w	0.036
residuals, e/Å^3	+0.28 to −0.27

the mixture was analyzed by HPLC, which showed the presence of at least 10 constituents. Column chromatography (SiO$_2$; petroleum ether/ether mixtures) allowed the separation of six fractions which were analyzed by combinations of ^{1}H NMR spectroscopy, HPLC, and LC-MS. The following compounds were identified:

Fraction 1: **16**, 1.5%. Fraction 2: 2,5-diphenylfuran, 1%. Fraction 3: arene **21**, <10%. Fraction 4: mixed isomers **15**. Fraction 5: lactones **22a** and **22b**. Fraction 6: contained a mixture of unidentified materials.

New Complexes. Flyover complexes **9h** and **9k** have only been obtained in very low yields during syntheses of cobaltacyclopentadienes (see Table 2 of ref 7); their spectra are included in Figure 2 and Table 3 alongside those of other flyovers described in the present (or both) papers. All are violet crystalline solids which elute from silica just ahead of, and in some cases are difficult to separate from, the derived arenes.

The following analytical data were obtained.

Compound **9a**: Anal. Calcd for C$_{22}$H$_{18}$Co$_2$O$_{16}$: C, 40.3; H, 2.8; M, 656. Found: C, 40.3; H, 2.8; M/r, 656.

Compound **9h**: Anal. Calcd for C$_{16}$H$_{12}$Co$_2$O$_{10}$: M, 482. Found: M/r, 482.

Compound **9k**: Anal. Calcd for C$_{24}$H$_{18}$Co$_2$O$_{12}$: C, 43.5; H, 3.1; M, 615.9462. Found: C, 43.5; H, 3.2; M/r, 615.9478.

Compound **9d**: Anal. Calcd for C$_{19}$H$_{18}$Co$_2$O$_{10}$: C, 43.5; H, 3.5; M, 524. Found: C,43.55; H, 3.5; M/r, 524.

Compound **9e**: Anal. Calcd for C$_{19}$H$_{18}$Co$_2$O$_{10}$: C, 43.5; H, 3.5; M, 524. Found: C, 43.7; H, 3.6; M/r, 524.

Compounds **9b/9c**: Anal. Calcd for C$_{34}$H$_{24}$Co$_2$O$_{10}$: C, 57.5; H, 3.4; M, 710. Found: C, 57.9; H, 3.55; M/r, 710.

^{13}C NMR (CDCl₃). Compound **9a**. δ 169.82, 168.56, 163.49, 126.92, 109.15, 107.33, 72.78, 53.46, 53.33.

Compound **9i**: δ 190.99, 173.14, 169.19. 164.50, 148.42, 140.55, 140.20, 138.97, 133.80, 133.53, 133.17, 128.92, 128.39, 128.06, 127.59, 127.33, 113.29, 108.925, 99.39, 92.30, 66.06, 52.73, 52.63, 52.30, 31.79, 22.86, 22.75, 22.08, 20.61, 16.55, 15.48, 14.32.

Oxidation of Flyovers. (a) Flyover **9a** (23 mg, 0.04 mmol) and Me₃NO·2H₂O (20 mg, 0.18 mmol) were combined in dichloromethane (25 mL). After being stirred for 5 min, the color of **9a** had disappeared. Evaporation and purification by chromatography on silica, eluting with ether/light petroleum, gave hexamethyl benzenehexacarboxylate (12 mg, 70%).

(b) Following the literature method,[5b] flyover **9c** (193 mg, 0.27 mmol) in carbon tetrachloride (10 mL) was cooled to 0 °C and a 10% solution of bromine in carbon tetrachloride was added dropwise until the violet color disappeared. Workup as in (a) yielded impure trimethyl 2,4,6-triphenylbenzene-1,3,5-tricarboxylate (92 mg, 71%), mp 193 °C (lit.,[5b] 215−219 °C), identified by ^{1}H NMR comparison.

X-ray Crystal Structure Determination of 9j. The crystal data and X-ray data collection and refinement details are summarized in Table 4. Crystals of **9j**, suitable for X-ray diffraction were obtained by slow evaporation of an *n*-hexane solution at 0 °C and were mounted (epoxy resin) on a glass fiber for data collection at 20 °C. The structure was solved by Patterson methods.[22] Structure expansion used Fourier techniques[23] and least-squares refinement with all non-H atoms anisotropic converged acceptably.[24]

Supporting Information Available: Text describing full experimental details for the crystal structure determinations of **9a** and **9j** and spectroscopic data for arenes and other metal free compounds and tables of atomic coordinates, anisotropic displacement parameters, bond lengths and angles, and least squares planes (29 pages). Ordering information is given on any current masthead page.

OM980545Q

(23) DIRDIF92: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Smits, J. M. M.; Smykalla, C. DIRDIF Programme System, Technical report of the University of Nijmegen, The Netherlands, 1992.
(24) *TeXsan*, Crystal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, 1992.