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Synthesis of Dicarbonyl(η^4-tricarbonylcobaltacyclopentadiene)cobalt Complexes from $Co_2(CO)_8$. A General Route to Intermediates in Cobalt Carbonyl Mediated Alkyne Trimerization

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We have shown that cobaltacyclopentadiene complexes, derived from cobalt carbonyl and two alkyne molecules and long believed to be intermediates in cyclotrimerization as well as in the formation of the (three-alkyne-derived) “flyover” complexes, can be isolated in selected cases if the mono(alkyne)−$Co_2(CO)_6$ complexes are treated at room temperature with just 1 equiv of alkyne in the presence of trimethylamine *N*-oxide. The complex (PhC=CHCMe=CMe)$Co_2(CO)_5$ has been characterized by X-ray crystallography.

Introduction

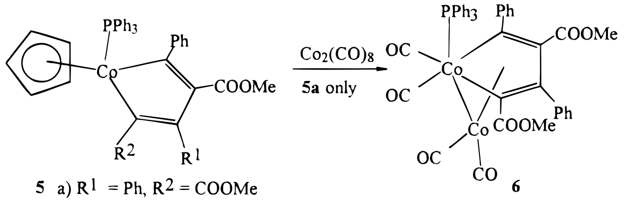
The reaction of octacarbonyldicobalt with almost any alkyne ($R^1C_2R^2$) yields 1:1 complexes, the well-known dicobaltatetrahedranes **1** (see Scheme 1). They are now widely used in a variety of ways as reagents in organic synthesis and have also long been recognized as intermediates in and catalysts for alkyne cyclotrimerization (although some reactions of complexes **1** with additional alkyne are limited by steric and possibly electronic effects).

The most thorough and comprehensive study of these compounds and their reactions appeared in an early paper (1961) by Krüerke and Hübel.[1] Inter alia they described the isolation of the complexes $Co_2(CO)_4$-($C_6R^1R^2R^3{}_2R^4{}_2$) from reaction of the mono(alkyne) compounds **1** with two further molecules of an alkyne ($R^3C_2R^4$), later shown[2] to have the “flyover” structure **3** (see following paper). They provided evidence however, that these were stable end products of a competing path, not intermediates in the cyclotrimerizations to arenes [**4a** and/or (rarely) **4b**]. Rejecting the unlikely possibility of simultaneous incorporation of two alkynes into complex **1**, Krüerke and Hübel searched for intermediates containing two alkyne units but had to report that “All attempts, starting from these complexes [$Co_2(CO)_6$-(RC_2R') and $Co_4(CO)_{10}(RC_2R')$], to isolate intermediate compounds with a system [derived] from two reactive alkyne ligands were without success.” It seemed most likely, therefore, that whatever 1:2 complexes might be involved were too short-lived for ready detection or isolation.

When, some 17 years later,[3] the highly strained cyclooctyne was shown to give a 1:2 complex as the major (66%) and stable product [together with **1**; R^1, R^2 = $(CH_2)_6$] and shown by X-ray crystallography to have the structure **2a**, reminiscent of a class of alkyne-derived ferracyclopentadienes, it was not so much viewed as filling a gap but rather as a very special case.

Two more recent examples, the bicyclic complex **2b**, obtained from a substituted *N*,*N*-dipropargylmethylamine,[4] and the bis(pentafluorothio) derivative **2c** from HC_2SF_5,[5] albeit alkynes of very different reactivity compared to cyclooctyne, could not escape being labeled special cases.

Three further complexes of a similar type have been reported, but all result from other reaction paths: Yamazaki and co-workers[6] obtained the triphenylphosphine-substituted analogue **6** as a product of the reaction of octacarbonyldicobalt with the mononuclear cobaltacyclopentadiene **5a**, a process which must involve complex ligand transfers and which did not occur with analogues including the symmetrical isomer **5b**. Moldes and co-workers[7] have obtained the simple diphenyl-substituted complex **2d** (10% yield) from a mixture of ethynylbenzene, $Fe_2(CO)_9$, $[Co(CO)_4]^-$, and trifluoroace-



5 a) R^1 = Ph, R^2 = COOMe
b) R^1 = COOMe, R^2 = Ph

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(1) Krüerke, U.; Hübel, W. *Chem. Ber.* **1961**, *94*, 2829.

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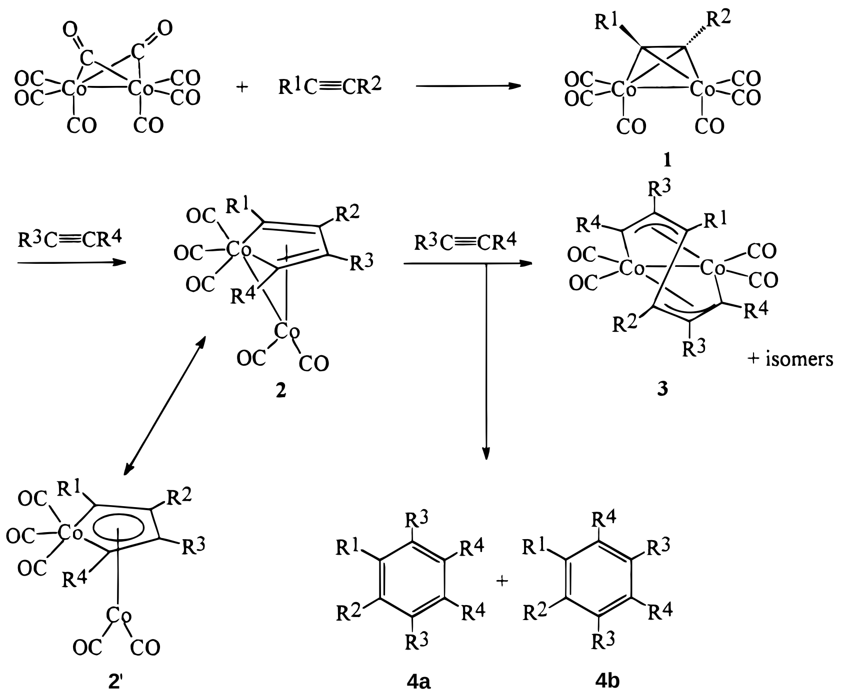
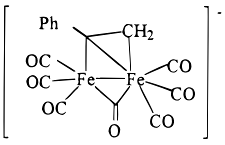
10.1021/om980544y CCC: $18.00

Scheme 1



	R^1	R^2	R^3	R^4		R^1	R^2	R^3	R^4
2a	$(CH_2)_6$		$(CH_2)_6$		**2i**	n-C_5H_{11}	H	H	n-C_5H_{11}
2b	H	$CMe_2N(Me)CMe_2$		H	**2j**	CH_2OMe	H	H	CH_2OMe
2c	SF_5	H	H	SF_5	**2k**	CH_2OMe	H	CH_2OMe	H
2d	Ph	H	H	Ph	**2l**	Ph	H	COOMe	COOMe
2e	COOMe	COOMe	COOMe	COOMe	**2m**	COOMe	H	COOMe	COOMe
2f	COOMe	H	H	COOMe	**2n**	Ph	H	Me	Me
2g	COOMe	Me	COOMe	Me	**2o**	COOMe	Ph	COOMe	Ph
2h	COOEt	Me	COOEt	Me	**2p**	H	H	H	H

tic acid, apparently by a process involving the anionic iron complex **7** as a source of at least one of the “alkyne” units and hence a metal exchange. These authors conclude “This shows that the formation of [**2**] is possible only in unusual circumstances (reaction conditions or particular alkynes).” Very recently[8] Giordano et al. reported a cobaltacyclopentadiene complex of this type, derived from two molecules of HC_2CMe_2OH, as having been formed from the corresponding flyover by a novel decomposition, apparently promoted by the silica of a TLC plate. This interesting result requires confirmation.



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We now describe a more directed and more widely applicable, though still limited, route to such complexes.

Results and Discussion

The failure, in most cases, to detect an intermediate (e.g., **2**), derived from two alkynes, when the mono(alkyne) complexes, **1**, react further with the same or different alkynes to give flyover complexes, **3**, or arenes, **4**, could be expected if the third alkyne molecule reacts much faster than the second under the chosen reaction conditions. The isolation of complexes **2** in the unusual cases mentioned in the Introduction led us to assume that similar structures are probably involved as transient intermediates in the above reactions. Hence, addition of the second alkyne would be accompanied by loss of just one molecule of carbon monoxide. Control of such a process would be aided by making available no more than 1 mole of alkyne/mol of complex and by using the lowest possible reaction temperature in order to slow the next step. Moreover, removal of one CO ligand by means other than alkyne displacement might well assist the first step. Our experience, particularly with a wide range of reactions of the type discovered by Khand et al.,[9] shows that amine *N*-oxides are not only well suited to this purpose but vary substantially in reactivity so that the reaction temperature and rate can be adjusted by a suitable choice of these oxidants.

We have therefore treated a variety of (alkyne)hexacarbonyldicobalt complexes with either the same

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[8] Giordano, R.; Sappa, E.; Predieri, G. *Inorg. Chim. Acta* **1995**, *228*, 139. These authors give the formula and analysis as $Co_2C_{15}H_{10}O_7$.

[9] Khand, I. U.; Knox, G. R.; Pauson, P. L.; Watts, W. E. *Chem. Commun.* **1971**, 36. This reaction is widely referred to as the Pauson–Khand reaction. For reviews see: (a) Schore, N. E. *Org. React.* **1991**, *40*, 1. (b) Schore, N. E. In *Comprehensive Organometallic Chemistry*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: London, 1995; Vol. 12, p 703.

Table 1. Reactions of $(R^1C_2R^2)Co_2(CO)_6$, 1, with Alkynes $R^3C_2R^4$

starting materials								products						
complex **1**				alkyne $R^3C_2R^4$				complex **1**		complex **2**			complex **3**[a]	
R^1	R^2	mg	mmol	R^3	R^4	mg	mmol	mg[b]	%	no.	mg	%[c]	mg	%
Ph	H	818	2.11	H	Ph	215	2.11	458	56	**2d**	302	31 (70)[d]		
Ph	H	9550	24.6	H	Ph	2570	24.6	5350	56	**2d**	3520	31 (70)		
COOMe	COOMe	593	1.38	COOMe	COOMe	197	1.38	373	63[e]	**2e**	373	24[e] (65)	117	
COOMe	H	839	2.27	H	COOMe	190	2.27	377	45	**2f**	164	17 (31)	31[f]	
COOMe	Me	1920	5.0	COOMe	Me	490	5.0	1350	70	**2g**	70	3 (10)	62 + 14[g]	
COOEt	Me	1290	3.25	COOEt	Me	364	3.25	983	76	**2h**	125	8 (33)	55 + 18	3 + 1[h]
n-C_5H_{11}	H	1780	4.67	H	n-C_5H_{11}	440	4.67	1370	77	**2i**	357	17 (74)		
CH_2OMe	H	621	1.68	H	CH_2OMe	120	1.68	478	77	**2j**	53	8 (35)		
										+**2k**	13	2 (8)		
COOMe	Ph	1560	3.49	COOMe	Ph	560	3.49	1150	74	**2o**	44	2 (8)	223	9[i]
COOMe	COOMe	721	1.68	H	Ph	172	1.68	122 (33)	17 (5)	**2d**	23	3		
										+**2l**	345	41 (49)		
COOMe	COOMe	1220	2.84	H	COOMe	240	2.84	756 (42)	62 (4)	**2m**	181	14 (37)		
Ph	H	2180	5.62	Me	Me	300	5.62	1680 (76)	54 (4)	**2n**	390	18 (40)		
Ph	H	1670	4.32	COOMe	COOMe	610	4.32	1020 (111)	61 (6)	**2l**	43	2 (5)	160	6
COOMe	COOMe	1890	4.42	Me	Me	240	4.42	1260 (30)	67 (2)	**2e**	72	3 (9)		
Me	Me	2120	6.20	H	Ph	640	6.20	1610 (120)	76 (5)	**2n**	373	12 (50)		

[a] For details see the following paper.[19] [b] Yield recovered and yield (in parentheses) from alkyne exchange. [c] Yield based on unrecovered complex **1** in parentheses. [d] Arene also isolated (978 mg, 13%).[a] [e] Use of NMO gives **1** (74%) + **2b** (19%). [f] Impure; contains arene. [g] Two isomers + arene (4 mg).[a] [h] Two isomers. [i] +arenes (167 mg, 10%).[a]

or a different alkyne together with an N-oxide. By this approach, we have indeed obtained all the cobaltacyclopentadienes, **2**, listed in Table 1. Of these, complex **2d** has previously been reported.[7] The yields, which we have not attempted to optimize, are low to modest, and in many cases (listed in the Experimental Section) the expected cobaltacyclopentadienes were detected either in only trace amounts or not at all. Our concern, however, in the present study was to show that the straightforward route does yield such complexes in "nonexceptional" cases and that they do react further to yield flyover complexes (**3**) and behave as catalysts of alkyne cyclotrimerization to arenes. The latter aspects are discussed in the following paper.[19]

Our initial study was devoted to the case of hexacarbonyl(dimethyl acetylenedicarboxylate)dicobalt reacting with the same alkyne to yield complex **2e**. This mixture failed to react at room temperature when trimethylamine N-oxide was added as its dihydrate, in contrast to the successful use of the much more active anhydrous form. Table 1 also shows that the latter could be replaced by anhydrous N-methylmorpholine N-oxide, ("NMO"), but with a slight lowering of yield. Use of tetrahydrofuran as sole solvent, in place of a 1:1 mixture with dichloromethane, gave a more complex mixture of products, while, in the synthesis of complex **2d**, use of acetone as solvent lowered the yield to 17%. The use of $Me_3NO/THF/CH_2Cl_2$ was therefore adopted for all other examples studied. As shown in Table 1, the long-known[10] alkyne exchange reaction plays a significant but never a dominant part. In some cases, recovery of the alkyne-exchanged hexacarbonyldicobalt complex is observed, while, in two cases, these react further to yield cobaltacyclopentadienes in which the initially coordinated alkyne is not present. Nevertheless, the fact that it occurs at all under the mild conditions used may suggest that it too is promoted by the removal of a CO ligand.

No simple pattern of behavior emerges from comparison of the successful and unsuccessful reactions. Although a majority of the former involve alkynes with ester and/or phenyl groups, they also include, e.g., 1-heptyne and if the 77% recovery of starting complex is considered, the 17% conversion becomes a 74% yield based on complex actually consumed. Moreover, among internal alkynes, whereas the diester complex and that of methyl 2-butynoate each reacted with the corresponding alkyne (giving **2e** and **2g**, respectively), methyl phenylpropiolate gave low yields and both diphenylethyne (tolan) and 2-butyne, long known to give stable mononuclear cyclopentadienylcobaltacyclopentadienes,[11] reacted with their hexacarbonyldicobalt complexes giving the corresponding arenes, without allowing detection of intermediates under our conditions. An attempt to make the di-*tert*-butyl-substituted complex (**2**; $R^1 = R^4 = Bu^t$; $R^2 = R^3 = H$) gave 2,5-di-*tert*-butylcyclopentadienone, a product previously obtained[1] from mercury–cobalt carbonyl with 3,3-dimethyl-1-butyne to yield "$Co_2Hg(CO)_6(Me_3CC_2H)_4$", followed by pyrolysis or bromine oxidation, and probably formed in the present work by degradation of the expected compound of type **2**. Despite the modest yield, this route to 2,5-di-*tert*-butylcyclopentadienone is more convenient than the known alternatives.[1,12]

Two of the "mixed" complexes included in Table 1 have been approached by treating the hexacarbonyldicobalt complex of one alkyne (i) with free alkyne (ii) and vice versa. Whereas, in the formation of the cobaltacyclopentadiene **2n**, the formation from (i) = PhC_2H and (ii) = C_2Me_2 compares reasonably with its alternative formation from (i) = C_2Me_2 and (ii) = PhC_2H (18% or 40% based on unrecovered starting complex vs 12% or 50% based on unreacted starting complex), the formation of complex **2l** from (i) = $C_2(COOMe)_2$ and (ii) = PhC_2H in 41% yield [with only 17% recovery of (i)] is in rather sharp contrast to its formation in only 2% yield

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(10) (a) Cetini, G.; Gambino, R.; Rossetti, R.; Sappa, E. *J. Organomet. Chem.* **1967**, *8*, 149. (b) Cetini, G.; Gambino, R.; Stanghellini, P. L.; Rossetti, R. *Rend.—Accad. Naz. 40 [Quaranta]* **1968**, [4] *18/19*, 45; *Chem. Abstr.* **1968**, *72*, 71104.

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

Molecule 1			
Bond Lengths			
Co(1)−Co(2)	2.498(1)	C(1)−O(1)	1.12(1)
Co(1)−C(1)	1.813(9)	C(2)−O(2)	1.14(1)
Co(1)−C(2)	1.785(9)	C(3)−O(3)	1.12(1)
Co(1)−C(3)	1.825(9)	C(4)−O(4)	1.14(1)
Co(2)−C(4)	1.741(9)	C(5)−O(5)	1.14(1)
Co(2)−C(5)	1.747(9)	C(6)−C(7)	1.51(1)
Co(1)−C(7)	1.992(7)	C(7)−C(8)	1.40(1)
Co(1)−C(11)	1.962(6)	C(8)−C(9)	1.52(1)
Co(2)−C(7)	2.011(7)	C(8)−C(10)	1.39(1)
Co(2)−C(8)	2.120(7)	C(10)−C(11)	1.43(1)
Co(2)−C(10)	2.108(7)	C(11)−C(12)	1.47(1)
Co(2)−C(11)	2.018(7)		
Bond Angles			
Co(2)−Co(1)−C(1)	132.1(3)	C(7)−Co(1)−C(11)	80.4(3)
Co(2)−Co(1)−C(2)	109.0(3)	Co(1)−Co(2)−C(4)	114.4(3)
Co(2)−Co(1)−C(3)	108.8(3)	Co(1)−Co(2)−C(5)	128.9(3)
Co(2)−Co(1)−C(7)	51.7(2)	C(4)−Co(2)−C(5)	92.9(4)
Co(2)−Co(1)−C(11)	52.1(2)	Co(1)−C(7)−C(6)	123.8(5)
C(1)−Co(1)−C(2)	104.6(4)	Co(1)−C(7)−C(8)	114.0(5)
C(1)−Co(1)−C(3)	104.9(4)	Co(1)−C(11)−C(12)	124.8(5)
C(1)−Co(1)−C(7)	95.2(3)	Co(1)−C(11)−C(10)	112.9(5)
C(1)−Co(1)−C(11)	93.9(3)	C(7)−C(8)−C(9)	124.4(6)
C(2)−Co(1)−C(3)	88.8(4)	C(7)−C(8)−C(10)	113.6(6)
C(2)−Co(1)−C(7)	91.4(3)	C(8)−C(10)−C(11)	115.1(6)
C(2)−Co(1)−C(11)	160.3(4)	C(10)−C(11)−C(12)	119.0(6)
C(3)−Co(1)−C(11)	92.7(3)		
Molecule 2			
Bond Lengths			
Co(3)−Co(4)	2.503(1)	C(18)−O(6)	1.13(1)
Co(3)−C(18)	1.794(8)	C(19)−O(7)	1.13(1)
Co(3)−C(19)	1.808(9)	C(20)−O(8)	1.13(1)
Co(3)−C(20)	1.802(8)	C(21)−O(9)	1.15(1)
Co(4)−C(21)	1.728(9)	C(22)−O(10)	1.14(1)
Co(4)−C(22)	1.738(9)	C(23)−C(24)	1.53(1)
Co(3)−C(24)	1.967(7)	C(24)−C(25)	1.41(1)
Co(3)−C(28)	1.965(7)	C(25)−C(26)	1.52(1)
Co(4)−C(24)	2.010(7)	C(25)−C(27)	1.41(1)
Co(4)−C(25)	2.116(8)	C(27)−C(28)	1.42(1)
Co(4)−C(27)	2.106(7)	C(28)−C(29)	1.49(1)
Co(4)−C(28)	2.011(7)		
Bond Angles			
Co(4)−Co(3)−C(18)	130.7(2)	C(24)−Co(3)−C(28)	80.2(3)
Co(4)−Co(3)−C(19)	103.3(3)	Co(3)−Co(4)−C(21)	120.1(3)
Co(4)−Co(3)−C(20)	114.1(2)	Co(3)−Co(4)−C(22)	127.1(3)
Co(4)−Co(3)−C(24)	51.8(2)	C(21)−Co(4)−C(22)	92.4(4)
Co(4)−Co(3)−C(28)	51.8(2)	Co(3)−C(24)−C(23)	123.0(5)
C(18)−Co(3)−C(19)	108.2(4)	Co(3)−C(24)−C(25)	119.7(6)
C(18)−Co(3)−C(20)	102.8(4)	Co(3)−C(28)−C(29)	125.4(5)
C(18)−Co(3)−C(24)	90.5(3)	Co(3)−C(28)−C(27)	114.1(5)
C(18)−Co(3)−C(28)	96.8(3)	C(24)−C(25)−C(26)	125.1(7)
C(19)−Co(3)−C(20)	90.4(4)	C(24)−C(25)−C(27)	112.5(7)
C(19)−Co(3)−C(24)	90.8(3)	C(25)−C(27)−C(28)	114.2(6)
C(19)−Co(3)−C(28)	153.5(3)	C(27)−C(28)−C(29)	117.8(6)
C(20)−Co(3)−C(28)	92.5(3)		

from (i) = PhC_2H and (ii) = $C_2(COOMe)_2$ [with 61% recovery of (i)]. More facile exchange of alkyne in the latter case partly accounts for the difference, but variation of the mono(alkyne) complexes in reactivity toward addition must also be important, as shown by the different extents of their recovery. Products of ligand exchange, including **2e** (3% yield), were the only results from the two approaches involving C_2Me_2 and $C_2(COOMe)_2$, but **2m** was isolated from (i) = $C_2(COOMe)_2$ and (ii) = HC_2COOMe. Similarly, cobaltacyclopentadienes were formed in the reaction of (i) = PhC_2H and (ii) = HC_2COOMe, but extensive ligand exchange and instability precluded satisfactory separation. The differing rates at which the cobaltacyclopentadienes react further to give flyovers and arenes are undoubtedly a major factor, and fast reactions must account both for low yields and for those cases where we failed to isolate such complexes although most of the mono(alkyne) complex had reacted.

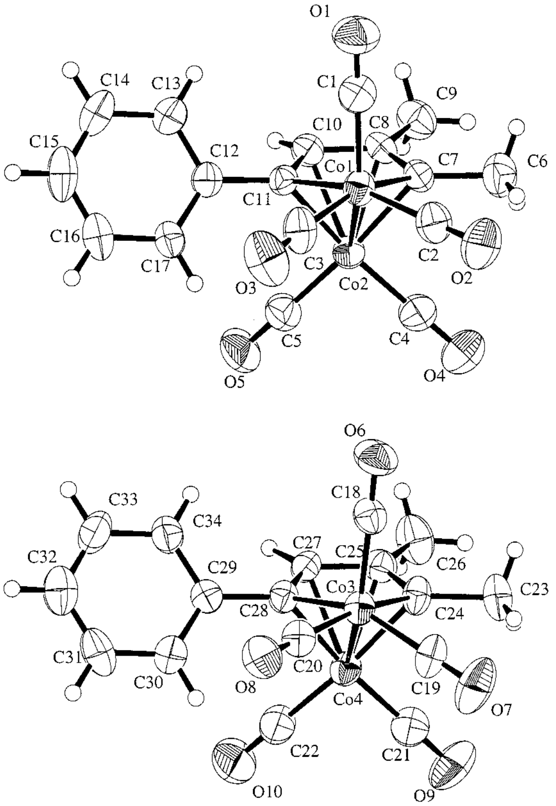

Figure 1. ORTEP plot of the two crystallographically unique molecules of **2n**. Thermal ellipsoids are drawn at the 40% level, and the atom numbering schemes are shown.

In the metal−carbonyl stretching region of the infrared spectra, the cobaltacyclopentadienes show a rather characteristic pattern of three bands: a very strong one at 2022−2067 cm^{-1} flanked by strong bands of approximately equal intensity at 2074−2101 and at 1968−1999 cm^{-1}. All the complexes **2** are orange or brown solids, of which **2d** and **2n** crystallized most readily. They were isolated after chromatography on silica, except for **2j**, **2k**, and **2n**, which required the use of neutral alumina or silica pretreated with triethylamine. For each series of derivatives the order of elution was **1**, **2**, **3**, then **4**.

X-ray Crystal Structure of 2n. As the known structures relate to symmetrical compounds,[3−7] we selected the unsymmetrical complex **2n** for X-ray crystallographic study. Selected bond lengths and angles are shown in Table 2, and the structure of **2n** is shown in Figure 1. The complex crystallizes with two unique molecules in the asymmetric unit, and since the complex is chiral (vide infra) and the space group is centric, both enantiomers coexist in the crystal. In addition to the known direct analogues (**2a**,[3] **2b**,[4] **2c**,[5] **2d**[7]) a range of related metallacyclopentadienes (**5a**, **5b**, **8a**,[13] **8b**,[14] **9**,[15]

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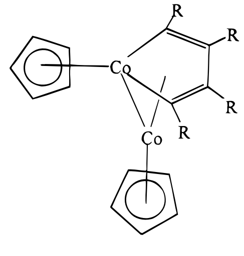
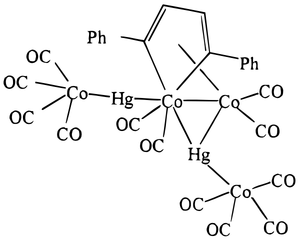


8 a) R = H
b) R = Me

$\mathbf{10}^{16}$) have also been structurally characterized. The key



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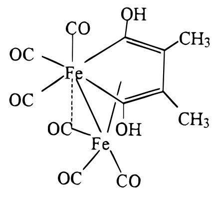

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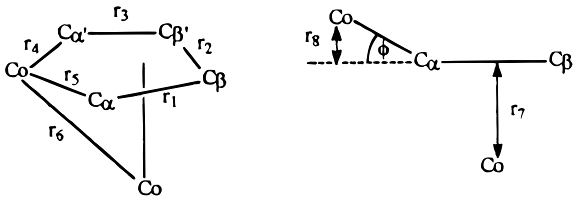
feature of the structure is the central η^5-cobaltacyclopentadiene unit and its relationship to the second cobalt atom (see Chart 1). Interestingly, this grouping is remarkably invariant between the structures, apparently not being influenced to any significant degree by a range of different substituents either on the ring or on the cobalt atoms. This is illustrated in Table 3, where the key parameters for **2a**−**d** and **2n** are compared. In **2n**, the C_4 unit of the cobaltacyclopentadiene group is planar with a maximum deviation from the least-squares plane of 0.001(8) Å, while the C−C bond lengths are approximately equal (for molecule 1, 1.397(9), 1.389(9), and 1.428(9) Å; for molecule 2, 1.412(9), 1.412(9), and 1.415(9) Å), indicative of a delocalized system rather than a discrete diene structure. This is in keeping with the first structurally characterized complex of this type,[16] the $[HFe_2(CO)_8]^-$/2-butyne derived complex (**10**) which, with C−C bond distances of 1.423, 1.430, and 1.424 Å, also showed no bond alternation. It is inviting to formulate these complexes as **2′**, i.e. as analogues of $CpCo(CO)_2$, with the Cp ligand replaced by an aromatic Co-containing heterocyclopentadienyl ligand. It is not clear whether this is genuinely the case. For instance, the Co(1)−C(7), Co(1)−C(11), Co(3)−C(24), and Co(3)−C(28) bond lengths at an average of 1.972(11) Å are perhaps slightly shorter than typical Co−C σ-bonds (e.g., 1.998 and 1.996 Å in $[(\eta^5\text{-}1,2,3\text{-}C_5Me_3H_2)CoMe_2(PMe_3)]$[17a] and 2.016 Å in $[(\eta^4\text{-di-}(p\text{-tolylfulvalene})CoMe(PMe_3)_2]$[17b]) but are not strongly suggestive of the multiple-bond character which might be expected for an “aromatic” structure. In addition, the Co atoms in the heterocyclopentadienyl rings are disposed some 0.45 Å above the C_4 plane, resulting in an “envelope” conformation. The dihedral angles between the C_4 planes described by C(7), C(8), C(10), C(11) and by C(24), C(25), C(27), C(28) and the CoC_2 planes described by Co(1), C(7), C(11) and by Co(3), C(24), C(28) are 17.6 and 17.1° respectively. This parallels closely other observed structures. This degree of distortion may be expected to weaken any π-overlap with metal-based orbitals.

Chart 1



By analogy with the long-known $Fe_2(CO)_6$ analogue[18] and the predominant formation of 1,2,4-triphenylbenzene in most cyclotrimerization reactions of ethynylbenzene, complex **2d** was expected to have its phenyl substituents in the 2- and 5-positions of the cobaltacyclopentadiene ring. This was confirmed when the report of its independent synthesis and crystal structure analysis[7] became available. It is also consistent with the position of the phenyl group in complex **2n** (see above).

NMR Spectra and Regiochemistry of Cobaltacyclopentadienes 2. In principle, an unsymmetrical alkyne, XC_2Y, could yield three isomeric cobaltacyclopentadienes, **2**, the symmetrical complexes **A** and **B** (Chart 2) and the unsymmetrical isomer **C**. No simple pattern of regiochemistry emerges from the present work, and examples of **A** (Y = H), **C**, and possibly **B** (Y = H) have been found. There is compelling evidence from flyover formation[19] that methyl 2-butynoate yields at least one transient symmetrical cobaltacycle (**A** or **B**) as well as **C**; only one alkyne yielded two isolable isomers, **A** and **C**. The reasons for such diverse behavior are not obvious.

The substitution patterns for all the complexes **2**, except **2f** and **2j**, can be assigned with confidence by comparison of ^1H and ^{13}C NMR spectra (Tables 4 and 5) with those of the crystallographically characterized materials **2a**, **2b**, **2d**, and **2n**.[20] The results parallel assignments reported[21] for related iron complexes, e.g. **10**. The unsymmetrical 2,4-disubstituted structures (Chart 2; **C**), **2g**, **2h**, **2k**, and **2o**, are easily recognized because the ^1H NMR spectra exhibit two different signals for each substituent, X or Y, while the symmetrical complexes (Chart 2; **A**, **B**) exhibit a single signal for each substituent. Thus the product from 1-heptyne, **2i**, is assigned a structure (**A**, Y = H) analogous to **2d** on the basis of the similarity of the chemical shifts of the β-protons. This parameter is also used to assign structures **2l** and **2m** by comparison with **2n**. In these cases, the chemical shift of the β-proton falls in the range δ 6.0−6.3. Methyl propargyl ether is the only alkyne we have found to give both a symmetrical (**2j**, major product) and an unsymmetrical cobaltacyclopentadiene, **2k**. In the latter case, the α-H

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[16] Hock, A. A.; Mills, O. S. *Acta Crystallogr.* **1961**, *14*, 139.

[17] (a) Wakatsuki, Y.; Yamazaki, H. *J. Chem. Soc. Jpn.* **1985**, 586. (b) Klein, H.-F.; Auer, E.; Jung, T.; Rohr, C. *Organometallics* **1995**, *14*, 2725.

[18] (a) Hübel, W.; Braye, E. H. *J. Inorg. Nucl. Chem.* **1959**, *10*, 250. (b) Aime, S.; Milone, L.; Sappa, E. *J. Chem. Soc., Dalton Trans.* **1976**, 838. (c) Todd, L. J.; Hickey, J. P.; Wilkinson, J. R.; Huffman, J. C.; Folting, K. *J. Organomet. Chem.* **1976**, *112*, 167.

[19] Baxter, R. J.; Knox, G. R.; Moir, J. H.; Pauson, P. L.; Spicer, M. D. *Organometallics* **1999**, *18*, 206.

[20] Structure **2c** has also been confirmed by X-ray analysis,[5] but ^1H and ^{19}F NMR spectra each show *two* groups of signals suggesting the possible presence of an additional isomer.

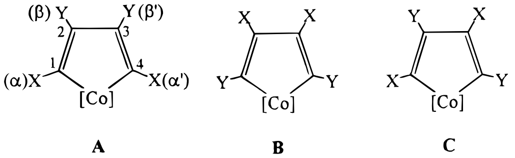
[21] Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; p 214.

Table 3. Comparison of the Structural Data for Cobaltacyclopentadiene Complexes[a]

complex	r_1, Å	r_2, Å	r_3, Å	r_4, r_5, Å	r_6, Å	r_7, Å	ϕ, deg	r_8, Å
2n, molecule 1	1.397(9)	1.389(9)	1.428(9)	1.992(7), 1.962(6)	2.498(1)	1.5577	17.6	0.4553
2n, molecule 2	1.412(9)	1.412(9)	1.415(9)	1.967(7), 1.965(7)	2.503(1)	1.5609	17.1	0.4423
2a	1.422(3)	1.428(3)	1.419(3)	1.973(2), 1.968(2)	2.4738(7)	1.5659(3)	14.2	0.3722(3)
2b	1.403(7)	1.402(7)	1.400(8)	1.971(6), 1.968(5)	2.474(1)	1.552(1)	17.7	0.457(1)
2c	1.41(2)	1.45(2)	1.39(2)	1.98(1), 1.97(1)	2.476(3)	1.551	15.8	0.420
2d	1.417(4)	1.399(5)	1.414(5)	1.982(3), 1.972(3)	2.503(1)	1.562	16.6	0.431

[a] Chart 1.

Chart 2

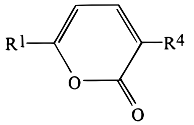


signal appears at δ 6.30 and the β-H at δ 7.03.[22] The chemical shift of the ring protons (δ 6.43) for the symmetrical isomer, **2j**, falls between the previously cited values for α-H and β-H, so that ^{1}H NMR alone does not permit an unambiguous decision in favor of orientation **A** or **B** (Chart 2; Y = H). A similar situation obtains for the symmetrical cobaltacyclopentadiene **2f** from methyl propiolate, which exhibits a ^{1}H NMR signal at δ 6.69. Strongly electron-attracting and deshielding groups, in, e.g., **2c** or **2m**, appear to exert little influence on $\delta(\beta\text{-H})$, and these protons in **2f** might be expected also to resonate in the range δ 6.0−6.3. The ^{1}H NMR chemical shifts of substituents other than hydrogen exhibit the expected trends. α-Methyl groups (δ 2.15) are slightly more shielded than β-methyl groups (δ 2.44), and there are small but significant differences between α- and β-methoxycarbonyl groups. However, these do not assist in assignment of **2f** or **2j** and the orientations have been deduced from ^{13}C NMR data.

^{13}C NMR data for the complexes **2** are more consistent and reinforce the ^{1}H-based structure assignments. The values for the ring carbons (Table 5) are found to fall into two quite distinct groups: All the α-carbons (i.e., those adjacent to Co) give signals in the range δ 138−176.5, whereas the β-carbon signals fall in the narrower range δ 103−122.[23] ^{13}C NMR signals of methyl substituents fall in regions characteristic of α (δ 29.4−30.7) and β (δ 16.7−17.45). The values for ester carbonyls also fall into two regions, α (δ 174−175) and β (δ 167). Collectively, the ^{13}C NMR data for the complexes **2** from methyl propiolate and from methyl propargyl ether are in favor of structures **2f** and **2j**, respectively. It was not possible to obtain suitable crystals for X-ray analysis, so the apparent ambiguity of ^{1}H assignments for these complexes remains unresolved.

Those complexes that have unsymmetrical cobaltacyclopentadiene groups are chiral, a fact which we have verified for complex **2l** by examining its ^{1}H NMR spectrum in the presence of (−)-Pr(hfc)$_3$. This caused an upfield shift of the whole spectrum and clear splitting of the signals due to the ring hydrogen and the methyl group of β-COOMe but not of the ester group closer to the cobalt atom. We surmise that coordination occurs between Pr^{3+} and the former group, whereas the α-COOMe group may be too hindered.

Reactions of Cobaltacyclopentadienes. The reactions of cobaltacyclopentadienes with alkynes, which lead to arenes and flyover complexes, are dealt with in the following paper.[19] From some of them, but also from other reactions, we obtained evidence that the formation of cobaltacyclopentadienes is reversible. One example is provided by the reactions of methyl propiolate, which, surprisingly, had not been among the many alkynes investigated by Hübel et al.[1,24] The preparation of cobaltacyclopentadiene **2f** (vide supra) yields an unusually complex mixture of byproducts, including a 1,3,5-trisubstituted flyover complex, *only* the symmetrical (1,3,5-) trimethyl benzenetricarboxylate, and pyrone **11f**.



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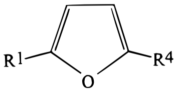

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However, complex **2f** reacts thermally[25] with a further molecule of methyl propiolate to give a 99% yield of a mixture of trimethyl benzene-1,2,4- and -1,3,5-tricarboxylates in a ratio similar to that of the Co$_2$(CO)$_8$-catalyzed thermal trimerization. But neither the 1,3,5 substituted flyover complex nor the arene can arise via a symmetrical structure, but only via the unsymmetrical 2,4-disubstituted cobaltacyclopentadiene (**2**, $R^1 = R^3 =$ COOMe, $R^2 = R^4 =$ H), which was not detected. We conclude that this last complex reacts too rapidly with free alkyne to accumulate but must be formed reversibly from complex **2f** via fission to free alkyne and a mono(alkyne) complex, thus establishing the equilibrium shown in Scheme 2.

More direct evidence for such cleavage of the cobaltacyclopentadienes comes from degradative reactions of the 2,5-diphenyl-1-cobaltacyclopentadiene **2d**. When this complex is heated alone [in hexane or in acetonitrile/toluene (1:1)] or heated with sulfur (in benzene) or with carbon monoxide, it gives 1,2,4-triphenylbenzene as the principal product, in the last case in as high as 83% yield. The rapid room-temperature oxidation of this complex, **2d**, with ceric ammonium nitrate also gives the same arene as the main product, accompanied by 2,5-diphenylfuran, **12d**, and 3,6-diphenyl-2*H*-pyran-2-one, **11d**. Oxidation with trimethylamine *N*-oxide (6

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[22] The ^{1}H NMR spectrum of **2k** is unusual and suggests a mixture of conformers or rotamers. The single α- and β-protons each appear as pairs of singlets which are *not* cross-ring coupled. Each MeO group is a singlet, but the corresponding (diastereotopic) CH$_2$O groups appear as temperature-dependent AB multiplets with the less shielded β-CH$_2$ more strongly influenced than the α-CH$_2$: β-CH$_2$, $\Delta\delta(\text{AB}) = 0.09$ ppm at 313 K, $\Delta\delta(\text{AB}) = 0.17$ ppm at 233 K; α-CH$_2$, $\Delta\delta(\text{AB}) = 0.07$ ppm at 313 K, $\Delta\delta(\text{AB}) = 0.11$ ppm at 233 K.

[23] The β-carbon of **2a** is reported[3] to give a signal at δ 138; for **2b**, the corresponding value is δ 140.[4]

[24] Hübel, W.; Hoogzand, C. *Chem. Ber.* **1960**, *93*, 103.

[25] A room-temperature reaction of **2f**, methyl propiolate, and *N*-oxide gives <5% yield of the isomeric arenes.

Table 4. ^{1}H NMR Data for Complexes 2 (CDCl$_3$; δ)

complex	R^1	R^2	R^3	R^4
2d	7.72−7.36 (m, 5H)	6.01 (s, 1H)		
2e	3.81 (s, 3H)	3.85 (s, 3H)		
2f	3.83 (s, 3H)	6.69 (s, 1H)		
2g	2.15 (s, 3H)	3.90 (s, 3H)	2.44 (s, 3H)	3.81 (s, 3H)
2h	2.16 (s, 3H), 4.25−4.39 (m, 2H)	1.34 (t, 3H, $J = 7.1$ Hz)	2.45 (s, 3H)	1.29 (t, 3H, $J = 7.1$ Hz) 4.25−4.39
2i	0.91 (t, 3H, $J = 7.0$ Hz), 1.36 (m, 4H), 1.63 (m, 2H), 2.51 (t, 1H, $J = 2.8$ Hz), 2.89 (t, 1H, $J = 2.8$ Hz)		6.11 (s, 1H)	
2j	3.45 (s, 3H), 4.30 (s, 2H)	6.43 (s, 1H)		
2k[a]	6.303, 6.313 (1H)	3.965 (dd2H), 3.057 (s3H)	7.026, 7.039 (1H)	3.66 (dd, 2H), 3.03 (s, 3H)
2l	7.22−7.41 (m, 5H)	6.23 (s, 1H)	3.86 (s, 3H)	3.84 (s, 3H)
2m	3.850 (s, 3H)	6.23 (s, 1H)	3.856 (s, 3H)	3.845 (s, 3H)
2n	7.28−7.39 (m, 5H)	6.29 (s, 1H)	2.45 (s, 3H)	2.17 (s, 3H)
2o	3.27 (s, 3H)	7.28−7.46 (m, 5H)	3.57 (s, 3H)	7.28−7.46 (m, 5H)
2p	3.50 (s, 1H)	3.75 (s, 1H)		

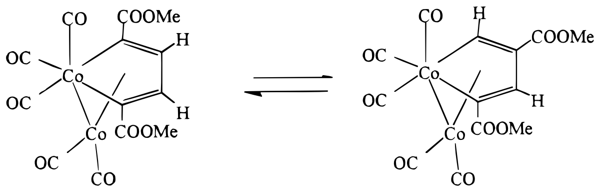
[a] See text; toluene-d_8.

Table 5. ^{13}C NMR Data for Complexes 2 (CDCl$_3$, δ)[a]

complex	C^1(α)	C^2(β)	C^3(β')	C^4(α′)	other[a]
2d	148.62	114.66	114.66	148.62	128.06, 128.35, 129.05, 138.83
2e	138.77	103.64	103.64	138.77	R^1, 53.52, 174.43; R^2, 53.21, 167.43
2f	139.26	116.75	116.75	139.26	53.11, 173.53
2g	135.57	117.52	114.20	166.33	R^1, 53.03, 174.23; R^2, 17.41; R^3, 52.57, 167.24; R^4, 30.65
2h	138.12	119.17	114.41	165.91	R^1, 14.39, 62.33, 173.75; R^2, 17.36; R^3, 14.27, 61.86, 167.49; R^4, 30.62
2i	168.85	117.22	117.22	168.85	14.19, 22.68, 31.80, 33.73, 47.25
2j	176.47	114.22	114.22	176.47	58.79, 80.91
2k	168.86	122.02	114.45	174.53	R^2, 58.88, 72.25; R^4, 59.05, 80.09
2l	148.81	114.61	109.88	139.77	R^1, 128.05, 128.46, 128.72, 134.11; R^3, 52.99, 164.02; R^4, 52.99, 173.79
2m	140.17	117.53	109.91	140.09	R^1, 53.51, 173.58; R^3, 53.22, 167.84; R^4, 53.54, 175.98
2n	150.2	114.44	121.07	165.25	R^1, 127.76, 128.14, 129.73, 132.12; R^3, 16.73; R^4, 29.43
2o	139.46	122.11	102.12	147.48	R^1, 52.38, 173.15; R^2, R^4, 127.25, 127.83, 127.98, 128.70, 129.07, 133.49, 133.91; R^3, 52.34, 165.77

[a] For numbering of the ring carbon atoms and substituents see Scheme 1 and Chart 2. [b] All complexes exhibited Co−*C*O signals in the region δ 198−205.

Scheme 2



equiv, THF, 30 min in air) yields a complex mixture of at least 10 metal-free organic compounds. This mixture was analyzed by a combination of column and thin-layer chromatography and LC-MS. Apart from the aforementioned compounds, products with stoichiometries (PhC$_2$H)$_3$CO, (PhC$_2$H)$_4$, (PhC$_2$H)$_4$CO, and (PhC$_2$H)$_4$(CO)$_2$ were detected, but not isolated pure. Since no free phenylethyne is initially available, the formation of triphenylbenzene is only possible if the organic portion of the complex undergoes fission to give back free alkyne and/or its cobalt complex under remarkably mild conditions. Further reactions involving such cleavage are included in the following paper.[19]

Experimental Section

General Remarks. All reactions were carried out under a dry nitrogen atmosphere, and solvents were purified and dried under nitrogen before use. Anhydrous trimethylamine *N*-oxide was obtained by recrystallization from hot DMF.[26] Co$_2$(CO)$_8$ was obtained from Strem Chemicals and used as purchased. Chromatography was carried out using either silica gel (230−400 mesh) or ungraded alumina, neutralized under ethyl acetate, washed with ethanol and water, and oven-dried. Melting points were obtained in open capillaries and are uncorrected. ^{1}H NMR and ^{13}C NMR spectra were recorded at frequencies of 400.134 and 100.614 MHz, respectively, both being referenced to an internal solvent standard.

Reactions of Alkynes with (Alkyne)hexacarbonyldicobalt Complexes (2). General Procedure. Equimolar amounts (as specified in Table 1) of alkyne complex **2** and anhydrous trimethylamine *N*-oxide in tetrahydrofuran/dichloromethane (20 mL each on a 3 mmol or smaller scale, increased in proportion for larger scale reactions) were stirred at room temperature for 45−90 min, experience (following reactions by TLC) having shown that this time led generally to the best yields of cobaltacyclopentadienes. Variations from this procedure are noted below for individual products. All were isolated by column chromatography. Known products (including starting complexes and flyover complexes (**3**) described in the following paper[19]) were identified by comparison of IR and/or ^{1}H NMR spectra with those of authentic samples. Quantities of materials are given in Table 1, and ^{1}H and ^{13}C NMR data for the cobaltacyclopentadienes are listed in Tables 4 and 5.

Typical Procedure. Formation of Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,2,3,4-tetrakis(methoxycarbonyl)-1,3-butadiene-1,4-diyl]dicobalt (2e). Under nitrogen, hexacarbonyl(dimethyl acetylenedicarboxylate)dicobalt (593 mg, 1.38 mmol) was dissolved in a mixture of tetrahydrofuran (20 mL) and dichloromethane (20 mL). Dimethyl acetylenedicarboxylate (197 mg, 1.38 mmol) was added to the stirred solution, followed by solid trimethylamine *N*-oxide (81 mg, 1.38 mmol). After being stirred at room temperature for 90 min, the solution was filtered through Kieselguhr; the filtrate was

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

evaporated on a rotary evaporator, and the solid was chromatographed on a silica gel column. Complex **2e** was eluted using ether/petroleum ether (4:1) and obtained as a brown solid. IR (hexane, cm^{-1}): ν_{CO} 2096, 2045, 1989; $\nu_{C=O}$ 1724. Anal. Calcd for $C_{17}H_{12}Co_2O_{13}$ (M_r = 541.8940): C, 37.6; H, 2.2. Found: C, 37.7; H, 2.2. MS (m/z): 542.9079 ($M^+ + 1$). It was followed by the flyover complex (**3**, $R^1 = R^2 = R^3 = R^4$ = COOMe) (117 mg) whose characterization is included in the following paper.[19]

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,4-diphenyl-1,3-butadiene-1,4-diyl]dicobalt (2d).[7] This compound formed orange crystals. IR (hexane, cm^{-1}): ν_{CO} 2081, 2056, 2032, 1977. Anal. Calcd for $C_{21}H_{12}Co_2O_5$: C, 54.6; H, 2.6. Found: C, 54.6; H, 2.7.

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,4-bis(methoxycarbonyl)-1,3-butadiene-1,4-diyl]dicobalt (2f). This compound, eluted from silica by petroleum ether/ether (2:1), was obtained as a brown solid. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2101, 2067, 2040; $\nu_{C=O}$ 1707. Anal. Calcd for $C_{13}H_8Co_2O_9$ (M_r = 425.8832): C, 37.6; H, 2.2. Found: C, 38.4; H, 2.7. MS (m/z): 425.8924 (M^+).

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,3-bis(methoxycarbonyl)-2,4-dimethyl-1,3-butadiene-1,4-diyl]dicobalt (2g). This compound was obtained as a brown solid, eluted by hexane/ether. IR (hexane, cm^{-1}): ν_{CO} 2088, 2038, 1992; $\nu_{C=O}$ 1727. Anal. Calcd for $C_{15}H_{12}Co_2O_9$ (M_r = 454.1213): C, 39.7; H, 2.7. Found: C, 39.8; H, 2.7. LRMS (m/z): 426 ($M^+ - CO$).

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,3-bis(ethoxycarbonyl)-2,4-dimethyl-1,3-butadiene-1,4-diyl]dicobalt (2h). This compound was eluted from silica by petroleum ether/ether (1:1) and obtained as a brown solid. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2086, 2033, 1982; $\nu_{C=O}$ 1712. Anal. Calcd for $C_{17}H_{16}Co_2O_9$ (M_r = 481.9458). MS (m/z): 454.9729 ($M^+ + H - CO$; calcd 454.9587).

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,4-di-*n*-pentyl-1,3-butadiene-1,4-diyl]dicobalt (2i). This compound was eluted from silica by hexane and obtained as an orange solid. IR (hexane, cm^{-1}): ν_{CO} 2074, 2022, 2012, 1972. Anal. Calcd for $C_{19}H_{24}Co_2O_5$ (M_r = 450.2629). LRMS (m/z): 421 ($M^+ - H - CO$).

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,4-bis(methoxymethyl)-1,3-butadiene-1,4-diyl]dicobalt (2j). This compound was eluted with petroleum ether/ether (1:1) and obtained as an orange solid. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2092, 2023, 1968. Anal. Calcd for $C_{13}H_{12}Co_2O_7$ (M_r = 398.1005). LRMS (m/z): 397 ($M^+ - H$). It was followed by **pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,3-bis(methoxymethyl)-1,3-butadiene-1,4-diyl]dicobalt (2k).** IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2085, 2026, 1968. Anal. Calcd for $C_{13}H_{12}Co_2O_7$ (M_r = 398.1005). LRMS (m/z): 371 ($M^+ + H - CO$).

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,2-bis(methoxycarbonyl)-4-phenyl-1,3-butadiene-1,4-diyl]dicobalt (2l). This compound was eluted from silica by petroleum ether/ether (1:1) and obtained as brown crystals. IR (hexane, cm^{-1}): ν_{CO} 2095, 2047, 1997; $\nu_{C=O}$ 1737, 1724. Anal. Calcd for $C_{19}H_{12}Co_2O_9$ (M_r = 502.1653): C, 45.45; H, 2.4. Found: C, 45.8; H, 2.6. LRMS (m/z): 502 (M^+).

This complex was prepared in two ways (see Table 1). When obtained from ethynylbenzene and the cobalt complex of dimethyl acetylenedicarboxylate, the products, in order of elution, were (i) hexacarbonyl(ethynylbenzene)dicobalt (5%), (ii) complex **2d** (3%), (iii) unstable complex **3** ($R^1 = R^4$ = Ph; $R^2 = R^3$ = H) (trace), (iv) unreacted starting complex (17%), and (v) complex **2l**. When dimethyl acetylenedicarboxylate and the complex of ethynylbenzene were the precursors, (i), (iv), and (v) were followed by **3** (R^1 = Ph; R^2 = H; $R^3 = R^4$ = COOMe).

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,2,4-tris(carbomethoxy)-1,3-butadiene-1,4-diyl]dicobalt (2m). This compound was eluted using ether/petroleum ether (1:1) (following the propiolate and dicarboxylate hexacarbonyldicobalt complexes) and obtained as a brown solid. IR (CH_2Cl_2, cm^{-1}): ν_{CO} 2104, 2053, 1999; $\nu_{C=O}$ 1723. Anal. Calcd for $C_{15}H_{10}Co_2O_{11}$ (M_r = 484.1042): C, 37.2; H, 2.1. Found: C, 37.2; H, 2.0. LRMS (m/z): 456 (M^+-CO).

Pentacarbonyl[μ-(1,2,3,4-η-1,4-η)-1,2-dimethyl-4-phenyl-1,3-butadiene-1,4-diyl]dicobalt (2n). This compound was eluted using hexane [following $(Me_2C_2)Co_2(CO)_6$ and $(PhC_2H)Co_2(CO)_6$] and obtained as an orange-brown solid. IR (hexane, cm^{-1}): ν_{CO} 2077, 2056, 2025, 1972, 1940. Anal. Calcd for $C_{17}H_{12}Co_2O_5$ (M_r = 414.1457): C, 49.3; H, 2.9. Found: C, 49.35; H, 2.4. MS (m/z): 386.1421 ($M^+ - CO$).

Pentacarbonyl[μ-(1,2,3,4-η:1,4-η)-1,3-bis(methoxycarbonyl)-2,4-diphenyl-1,3-butadiene-1,4-diyl]dicobalt (2o). This compound was obtained as a brown solid, eluted by hexane/ether. IR (hexane, cm^{-1}): ν_{CO} 2091, 2043, 2033, 1966; $\nu_{C=O}$ 1737, 1716. Anal. Calcd for $C_{25}H_{16}Co_2O_9$ (M_r = 578.2631): C, 51.9; H, 2.8. Found: C, 52.0; H, 2.8. LRMS (m/z): 578 (M^+).

Negative Results. Failure to observe more than trace quantities of cobaltacyclopentadienes was recorded in the following cases. The percentage of unreacted starting complex, **1**, is given in brackets with the percentage of alkyne-exchange product, **1**, from “mixed” systems in parentheses: PhC_2H with the complexes of FcC_2H [77] or HC_2COOMe; Ph_2C_2 with the complexes of Ph_2C_2 [98], $C_2(COOMe)_2$ [76], or PhC_2H [87 (8)]; $C_2(COOMe)_2$ with the complexes of C_2Me_2 [56] or $C_2(SiMe_3)_2$ [86]; C_2Me_2 with the complexes of C_2Me_2 [94], C_2H_2 [67 (16)], Bu^tC_2H [86 (5)], or HC_2CH_2OMe [77 (5)]; $HC_2C_5H_{11}$ with the complex of PhC_2H [93]; MeC_2SiMe_3 with the complexes of MeC_2SiMe_3 [97] or PhC_2H [81 (6)]; HC_2COOMe with the complex of PhC_2H [78 (9)]; $C_2(CH_2OH)_2$ with the complexes of $C_2(CH_2OH)_2$ [97], $C_2(COOMe)_2$ [83 (5)], or PhC_2H; $C_2(SiMe_3)_2$ with the complex of $C_2(COOMe)_2$ [92 (4)]; or any of the alkynes $C_2(CH_2Cl)_2$, HC_2CH_2Cl, HC_2CH_2OH [85], $HC_2CH(OH)C_6H_{11}$ [96], $HC_2CH_2NMe_2$ [71], $HC_2CH_2OSO_2Ph$, and $PhC_2P(O)(OEt)_2$[27] with their own complexes. C_2H_2 yielded a very unstable brown complex, possibly **2p**, showing ν_{CO} (CH_2Cl_2, cm^{-1}) 2088, 2031, 1969 and ^1H NMR ($CDCl_3$) δ 3.75 (s), 3.50 (s) (ratio 1:1).

Reaction of 3,3-Dimethyl-1-butyne with Its Hexacarbonyldicobalt Complex. Carried out as for the above preparations of complexes **2**, the reaction of the alkyne (0.23 g, 2.84 mmol) with the complex (1.05 g, 2.84 mmol) in dichloromethane (15 mL) and THF (15 mL) yielded unreacted $[(Bu^tC_2H)Co_2(CO)_6]$ (704 mg, 67%), eluted from silica by hexane and followed by 2,5-di-*tert*-butylcyclopenta-2,4-dienone [71 mg, 15.4% (46% based on unrecovered complex)]: orange crystals; IR ν_{CO} 1715 cm^{-1}; ^1H NMR δ ($CDCl_3$) 6.42 (s), 1.15 (s) (1:9) [lit.[12] ν_{CO} (CCl_4) 1710 cm^{-1}; δ (CCl_4) 6.33 (s), 1.13 (s) (1:9)]; ^{13}C NMR δ ($CDCl_3$) 202, 140.4, 135.9, 32.4, 29.9.

Reactions of the Diphenylcobaltacyclopentadiene Complex 2d. (a) Thermolysis under Carbon Monoxide. The complex (204 mg) in hexane (75 mL) was placed in a 200 mL steel autoclave under 110 atm of CO and heated to 80 °C for 24 h. After cooling, the filtered solution was evaporated, and the solid was chromatographed on silica. Hexane eluted 1,2,4-triphenylbenzene (101 mg, 75%), mp 119−120 °C, $C_{24}H_{18}$ (M_r = 306). LRMS (m/z): 306 (M^+), followed by a more polar fraction (43 mg) containing a mixture of 2,5-diphenylfuran, m/z 220 (M^+), and 3,6-diphenyl-2*H*-pyran-2-one, m/z 248 (M^+). IR: ν_{max} 1723, 1626, 1553, 1358 cm^{-1}. ^1H NMR, δ ($CDCl_3$): 7.91−7.71 (m, 4H), 7.59 (d, J = 7.2 Hz, 1H), 7.51−7.38 (m, 6H), 6.81 (d, J = 7.2 Hz, 1H).

(b) Thermolysis in Acetonitrile/Toluene. The complex (414 mg) was refluxed in acetonitrile/toluene (1:1, 30 mL) for 24 h and worked up as above to yield 1,2,4-triphenylbenzene (185 mg, 68%).

(c) Oxidation. The complex (261 mg, 0.56 mmol) was stirred in acetonitrile, and ceric ammonium nitrate (1.0 g, 1.8

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(27) Baxter, R. J.; Knox, G. R.; McLaughlin, M.; Pauson, P. L.; Spicer, M. D. *J. Organomet. Chem.*, in press.

Table 6. Crystal Data and Experimental Details of the Crystal Structure Determination for 2n

Crystal Data	
empirical formula	$C_{17}H_{12}Co_2O_6$
mol wt	414.15
cryst color	red
cryst size, mm	$0.45 \times 0.15 \times 0.05$
space group	$P\bar{1}$ (No. 2)
a, Å	7.146(2)
b, Å	14.663(3)
c, Å	16.502(5)
α, deg	87.71(2)
β, deg	85.05(3)
γ, deg	87.58(2)
V, Å^3	1720.0(9)
Z	4
ρ_{calcd}, g cm^{-3}	1.599
μ(Mo Kα), cm^{-1}	19.51
F(000)	832.00
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, deg	$0.94 + 0.35 \tan \theta$
θ range	2.5−24
index ranges	h, 0 to 8; k, −16 to 16; l, 18 to −18
Solution and Refinement	
no. of reflcns measd	5484
no. of unique reflcns	5369 ($R_{int} = 0.031$)
no. of obsd relections ($I > 1.00\sigma(I)$)	3200
no. of variables	434
GOF	1.25
R	0.062
R_w	0.044
residual electron density, e Å^{-3}	+0.57 to −0.47

mmol) was added, causing a rapid color change. The major product was again 1,2,4-triphenylbenzene.

(d) Reaction with Sulfur. The complex (231 mg) was heated in refluxing benzene (20 mL) for 12 h with a large excess of sulfur (1 g). The only isolable product was 1,2,4-triphenylbenzene.

Crystal Structure Determination of 2n. Red crystals of $C_{17}H_{12}Co_2O_5$ (**2n**) suitable for X-ray diffraction studies were obtained by slow evaporation of an *n*-hexane/benzene solution at 0 °C. A crystal having dimensions $0.45 \times 0.15 \times 0.05$ mm was mounted in a glass capillary. Data collection was performed at 22 °C. The complex crystallizes in the triclinic space group $P\bar{1}$, and accurate cell dimensions were obtained from 20 precisely centered reflections in the range $16.58 \leq 2\theta \leq 22.68°$. Data collection in the range $2.5 \leq \theta \leq 24°$ was performed using $\omega-2\theta$ scans on a Rigaku AFC7S diffractometer with graphite-monchromated Mo Kα radiation. A total of 5484 reflections were recorded, of which 5369 were unique ($R_{int} = 0.031$). An empirical absorption correction (ψ scans) was applied to the data, and they were also corrected for Lorentz and polarization effects. The structure was solved by direct methods (SIR92)[28] and expanded using Fourier techniques (DIRDIF92).[29] Full-matrix least-squares refinement based on 3200 observed reflections ($I > 1.00\sigma$(I)) with all non-H atoms anisotropic converged with $R = 0.062$, $R_w = 0.044$, and GOF = 1.25. A total of 434 parameters were refined, and the residual electron density was in the range +0.57 to −0.47 e Å^{-3}. H atoms were included in calculated positions. Experimental details are summarized in Table 6.

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Supporting Information Available: Text giving additional experimental details for the structure determination and tables of atomic coordinates, anisotropic displacement parameters, interatomic distances, bond angles, and least-squares planes (23 pages). Ordering information is given on any current masthead page.

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