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Registry No. 1, 53859-89-5; 2, 89922-06-5; 3, 13211-09-1; 4, 89922-07-6; 5, 3510-99-4; 6a, 41686-58-2; 6b, 90024-40-1; CO, 630-08-0; $(CH_3CN)_2PdCl_2$, 14592-56-4; PPh_3, 603-35-0; LiCl, 7447-41-8; $ZnCl_2$, 7646-85-7; 3-chlorocyclohexene, 2441-97-6; allyltrimethyltin, 762-73-2; cyclohexene, 110-83-8; 7-methyl-1,6-octadien-4-one, 89922-08-7; allyl chloride, 107-05-1; 2,6-di-*tert*-butylpyridine, 585-48-8; 2,6-di-*tert*-butylphenol, 128-39-2; galvinoxyl, 2370-18-5; 1-chloro-3-methyl-2-butene, 503-60-6; 1-chloro-2-butene, 591-97-9; 3-chloro-1-butene, 563-52-0; 1-chloro-3,7-dimethyl-2,6-octadiene, 4490-10-2; methyl 4-chloro-2-butenoate, 15320-72-6; 4-bromo-2-butenonitrile, 42879-03-8; 3-chloro-5-carbomethoxycyclohexene, 89922-09-8; 3-chloro-2-methyl-1-propene, 563-47-3; prenyltrimethyltin, 17314-40-8; (2-methylallyl)tributyltin, 67883-62-9; 1,6-octadiene-4-one, 89922-10-1; 7,11-dimethyl-1,6,10-dodecatrien-4-one, 89922-11-2; methyl 5-oxo-2,7-octadienoate, 89922-12-3; 5-oxo-2,7-octadienonitrile, 89922-13-4; 3-(1-oxo-3-butenyl)-5-carbomethoxycyclohexene, 89922-14-5; 2,7-dimethyl-1,6-octadien-4-one, 89922-15-6; 2-methyl-1,6-heptadien-4-one, 89922-16-7; 7-methyl-2,5-octadien-4-one, 17208-21-8; 7,11-dimethyl-1,6,10-dodecatrien-5-one, 89922-17-8.

Correlations of Acetylenic and Carbonyl Stretching Frequencies in the (μ-Alkyne)hexacarbonyldicobalt Complexes. Evaluation of σ- and π-Bonding between Alkyne and Metal

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The $\nu(C{\equiv}C)$ stretching frequencies of a great variety of (μ-alkyne)hexacarbonyldicobalt complexes, (μ-$RC{\equiv}CR')Co_2(CO)_6$, have been determined unambigously and their variations on coordination related to the electronic nature of the substituents R and R′. Three linear relationships have been observed depending on the number of acceptor groups. Examination of the average carbonyl value of $\nu(C{\equiv}O)$ in these complexes also indicates the existence of the same classes, and, thus, these correlations combined with a stabilization on complexation are very useful to predict unknown frequencies. A combination of the changes $\Delta\nu(C{\equiv}C)$, which measure $\sigma + \pi$ transfers, and the changes $\Delta\nu(C{\equiv}O)$, which measure $\sigma - \pi$ transfers, allows separation of the σ- and π-components of the interaction between alkyne and metal.

Introduction

The molecular structures of numerous olefin and acetylene complexes have been investigated by X-ray techniques, however, a limited number of structural studies of (μ-acetylene)hexacarbonyldicobalt complexes are available.[1] The striking features to notice in these last examples are a cis bending of the alkyne substituents toward the configuration of the first excited state (with the Co—Co and C≡C bonds perpendicular to each other but not in the same plane) and a lengthening of the acetylenic triple bond with a concomitant drop in bond order. This lengthening is a direct consequence of synergic σ–π interactions and electron transfer.[2] More information on this point can be obtained by examining the frequencies and intensities of $\nu(C{\equiv}C)$ vibrations. Thus, an analysis of vibrational frequencies in the series of complexes $(RC{\equiv}CR')Co_2(CO)_6$ should provide considerable insight into the molecular structures and metal–ligand bonding.

Infrared spectroscopic studies of acetylene derivatives $(RC{\equiv}CR)Co_2(CO)_6$ have, to date, been limited largely to the $\nu(C{\equiv}O)$ region.[3-12] Only Dickson[13-17] and Iwashita[18-20] have examined $\nu(C{\equiv}C)$ vibrations in this type of complex. In particular, Iwashita has precisely determined the vibrational frequencies $\nu(C{\equiv}C)$ for the complexes $(RC{\equiv}CR)Co_2(CO)_6$ (R = R′ = H; R = H, R′ = D; R = R′ = D; R = H, R′ = CH_3; R = D, R′ = CH_3; R = R′ = CH_3).

In the present study a wide range of derivatives having substituents with electron-donating or-accepting properties have been analyzed in detail with the goal of correlating for the first time changes in $\nu(C{\equiv}C)$ and $\nu(C{\equiv}O)$ and using these changes as a probe of electronic structure. Thus, an evaluation of the effects of σ- and π-transfer between the alkyne and the cobalt atom has been carried out. Furthermore, correlations of the type described here have allowed an assignment of $\nu(C{\equiv}C)$ frequencies for

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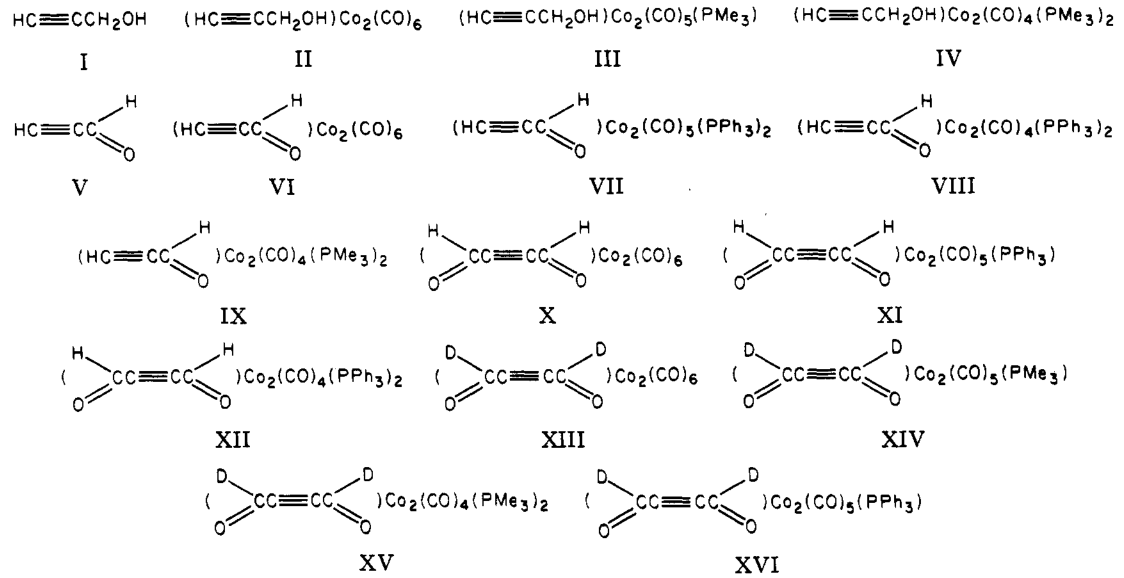
Chart I



certain unstable free acetylenes and for symmetrically substituted alkynes for which the $\nu(\mathrm{C{\equiv}C})$ stretching vibration is infrared inactive.

Results

In the initial search for some alkynes ($\mathrm{R = H, R' = CH_2OH; R = H, R' = CHO; R = R' = CHO}$) and their complexes, the IR spectra have been measured from 4000 to 200 cm^{-1} with the aim of determining with a fair degree of certainty the changes in vibrational frequencies on complexation, principally for $\nu(\mathrm{C{\equiv}C})$. The $\nu(\mathrm{C{\equiv}C})_c$ band of complexes, which might be expected to appear between 1300 and 1800 cm^{-1}, is difficult to detect on account of the presence of numerous other bands: $\nu(\mathrm{C{=}O})$, $\delta(\mathrm{C{-}H})$, and $\delta(\mathrm{O{-}H})$ in particular. To surmount this difficulty, specific derivatives of $\mathrm{(RC{\equiv}CR')Co_2(CO)_6}$ were synthesized and studied: mono- or disubstitution products with $\mathrm{PMe_3}$ or $\mathrm{PPh_3}$ and, importantly, deuterated alkyne compounds. The spectra of this large group of complexes (II → IV; VI → XVI, Chart I) have also allowed the unequivocal assignment of $\nu(\mathrm{C{\equiv}O})$, $\delta(\mathrm{Co{-}C{-}O})$, $\nu(\mathrm{Co{-}C_{CO}})$, and $\nu(\mathrm{Co{-}C_{ac}})$ frequencies. The data are listed in Table I.

Careful analysis of the spectroscopic data shown in Table I gave the following results.

$\nu(\mathrm{{\equiv}CH})$ Vibrations. These are detected without difficulty at $\simeq$3300 cm^{-1} in the free alkynes and at $\simeq$3100 cm^{-1} in their various complexes in agreement with the previous results of Iwashita[18-20] on the molecules $\mathrm{(RC{\equiv}CR')Co_2(CO)_6}$ ($\mathrm{R = R' = H; R = H, R' = D; R = H, R' = CH_3}$) and Kettle[12] from the Raman spectra of $\mathrm{(HC{\equiv}CH)Co_2(CO)_6}$. The drop in frequency on complexation is of order of 200 cm^{-1}.

$\nu(\mathrm{C{\equiv}O})$ Vibrations. These are situated, as expected, between 2120 and 1900 cm^{-1}.

$\nu(\mathrm{C{=}O})$, $\nu(\mathrm{C{\equiv}C})_c$, and $\delta(\mathrm{{-}CH})$ Vibrations. These are distributed among the bands at $\simeq$1660, $\simeq$1500, and $\simeq$1380 cm^{-1}, on which are superimposed bands at 1580 cm^{-1} due to $\mathrm{PPh_3}$ and 1480 cm^{-1} due to $\mathrm{PMe_3}$ and $\mathrm{PPh_3}$. In certain cases, most notably aldehydes, the bands at $\simeq$1660 cm^{-1} are due to $\nu(\mathrm{C{=}O})$ because they appear in the free alkynes and corresponding complexes with a variation in frequency on complexation by a value of $\leq$20 cm^{-1}.

The bands around 1580 cm^{-1} only appear in $\mathrm{PPh_3}$ complexes. Similar frequencies are found in other $\mathrm{PPh_3}$ derivatives, for example, $\mathrm{Ni(CO)_3(PPh_3)}$, $\mathrm{Mo(CO)_5(PPh_3)}$, ... they result from $\nu(\mathrm{C{=}C})$ of the aromatic rings. The bands at 1480 cm^{-1} only appear in $\mathrm{PMe_3}$ and $\mathrm{PPh_3}$ compounds. They are due to $\delta(\mathrm{C{-}H})$ of $\mathrm{PMe_3}$ or $\nu(\mathrm{C{=}C})$ of $\mathrm{PPh_3}$.

This leaves bands at $\simeq$1500 and 1380 cm^{-1} that can be attributed either to $\nu(\mathrm{C{\equiv}C})_c$ or $\delta(\mathrm{{-}CH})$. These assignments were distinguished by using deuterated complexes XIII–XVI that shifted the 1380 cm^{-1} band into the region of 1050 cm^{-1} ($\delta(\mathrm{C{-}H})/\delta(\mathrm{C{-}D})$ frequency ratio of 1.30, consistent with deuterium isotopic substitution).

Thus the $\nu(\mathrm{C{\equiv}C})_c$ vibrations in the complexes II–IV and VI–XvI have frequencies situated in the region of 1550–1490 cm^{-1}.

$\nu(\mathrm{C{-}C})$ Vibrations. For the pairs of compounds I/II and V/VI an increase in $\nu(\mathrm{C{-}C})$ frequency on complexation of approximately 60 cm^{-1} is observed: this result differs from that of Iwashita,[20] who found an increase of only 9 cm^{-1} from $\mathrm{HC{\equiv}CCH_3}$ to $\mathrm{(HC{\equiv}CCH_3)Co_2(CO)_6}$, but appoaches the change of 73 cm^{-1} noted for the couple $\mathrm{CH_3C{\equiv}CCH_3/(CH_3C{\equiv}CCH_3)Co_2(CO)_6}$.[20] In the other complexes X–XVI, $\nu(\mathrm{C{-}C})_{sym}$ is $\simeq$710 cm^{-1} and $\nu(\mathrm{C{-}C})_{asym}$ $\simeq$1118–1174 cm^{-1}, but the frequency shifts from the free alkynes are not known since these alkynes have not been isolated in the free state.

$\delta(\mathrm{Co{-}C{-}O})$ and $\nu(\mathrm{Co{-}C_{CO}})$ Vibrations. The first of these vibrations is attributed to bands situated between 570 and 510 cm^{-1} and the latter, to bands in the region of 510–420 cm^{-1}, as in the complexes $\mathrm{Co(CO)_4MX_3}$ ($\mathrm{MX_3 = SiCl_3, Si(OMe)_3, SiPh_3, SiEt_3, GeEt_3, SnEt_3, PbEt_3}$).[21] This assignment differs from the initial assignment of Iwashita[18] on $\mathrm{(HC{\equiv}CH)Co_2(CO)_6}$ but agrees with Kettle's studies[12] on several symmetrical complexes $\mathrm{(RC{\equiv}CR')Co_2(CO)_6}$ ($\mathrm{R = R' = H, CH_3, CF_3}$).

$\nu(\mathrm{Co{-}C_{ac}})$ Vibrations. The results obtained by Kettle,[12] from Raman studies of the complexes $\mathrm{(RC{\equiv}CR)Co_2(CO)_6}$ ($\mathrm{R = H, CH_3, CF_3}$), suggest that $\nu(\mathrm{Co{-}C_{ac}})_{sym}$ should appear as weak bands close to 400 cm^{-1} in the spectra of II–IV and VI–XVI rather than at $\simeq$600 cm^{-1} as indicated by Iwashita[18] for $\mathrm{(HC{\equiv}CH)Co_2(CO)_6}$. As will be evident later in this paper, the electronic distribution between an atom of cobalt and the alkyne moiety in $\mathrm{(RC{\equiv}CR')Co_2(CO)_6}$ closely resembles that between an olefin and iron in the tetracarbonyl olefin complexes $\mathrm{(olefin)Fe(CO)_4}$. Since the polarized Raman spectra of the latter show unambiguously[22] that an average ν(Fe—C-

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Table I. Principal IR Vibrations of HC_2CH_2OH (I), HC_2CHO (V), and the Complexes $(RC_2R')Co_2(CO)_{6-n}L_n$ (II–IV and VI–XVI)[a]

I	II	III	IV	V	VI	VII	VIII	IX	X	XI	XII	XIII	XIV	XV	XVI	assignmt
3306 vs	3098 m	3082 m		3275 s	3095 m			3068 w								$\nu(\equiv CH)$
	2096 s	2057 vs	2013 vs		2105 s	2072 vs	2026 vs	2023 vs	2112 s	2076 s	2033 s	2111 s	2077 s	2039 w	2079 s	$\nu(C\equiv O)$
	2057 vs	2002 vs	1967 sh		2065 vs	2025 vs	1979 vs	2018 vs	2081 vs	2025 vs	2001 s	2079 vs	2073 sh	1995 s	2025 vs	
	2030 vs	1987 s	1960 sh		2030 vs	2016 vs	1972 vs	1965 vs	2064 vs	2010 vs	1977 sh	2059 vs	2030 sh	1954 s	2009 vs	
	2026 vs	1946 s	1943 vs			2001 vs	1946 s	1957 vs	2055 vs	1984 vs	1969 s	2048 vs	2023 vs	1918 s	1983 vs	
	2007 sh		1939 vs			1978 s		1939 s	2036 vs		1955 s	2034 vs	2014 s			
			1928 sh								1939 sh		2005 s			
											1923 m		1998 s			
													1972 s			
				1671 s	1669 s	1652 s	1643 s	1628 s	1670 s	1665 sh	1654 s	1645 s	1660 s	1620 s	1650 s	$\nu(C=O)$
						1641 s			1661 s	1652 s	1617 sh	1630 sh	1647 s	1592 s	1633 s	
													1638 s			
2120 m	1535 m	1536 s	1529 m	2098 s	1498 s	1505 m	1493 m	1491 m	1542 s	1547 sh		1540 m	1554 m	1546 m	1547 sh	$\nu(C\equiv C)$
1450 m	1440 w	1451 m	1450 m	1383 m	1386 m	1361 w	1357 w		1371 m	1370 w	1382 vw	1050 m	1053 m	1060 w	1061 m	$\delta(-CH)$, $\delta(-CD)$
1409 s	1404 w				1363 m				1366 m	1360 w	1366 vw				1050 w	
									1118 s	1125 m	1130 w	1147 m	1141 m	1174 s	1149 m	$\nu(C-C)_{asym}$
905 s	972 s	980 sh		950 m	1001 m	1009 w		1010 w	717 s	705 m	707 m 701 m	713 m	712 w	715 m	707 m 704 m	$\nu(C-C)_{sym}$
	528 s	568 m	570 w		557 m	548 sh	558 m	567 m	550 sh	535 sh	540 sh	545 sh	562 w	580 m	555 sh	$\delta(Co-C-O)$
	517 vs	516 vs	538 m		520 s	532 sh	516 sh	540 sh	520 s	522 sh	524 sh	519 s	520 sh	540 m	532 sh	
					512 s	520 sh	510 s	530 s	505 s	510 s	517 s	508 s	509 s	524 s	522 sh	
						510 s									510 s	
	497 vs	498 vs	508 s		491 s	500 m		510 s	488 s	500 s	508 s	490 s	496 s	501 s	500 sh	$\nu(Co-C_{CO})$
	480 sh	438 m	499 s		445 m	470 w	490 m	500 sh	472 sh	460 sh	481 m	470 sh	464 m	467 m	470 sh	
	451 m	425 w	439 w			456 w	445 w	470 vw	443 m	430 m	461 w	440 m	435 m	431 w	446 m	
	427 w		423 w			444 w			423 w	420 w	445 w	426 w	425 sh		428 m	
						423 w					435 w				420 w	
	400 w		400 vw		378 w	352 vw	400 vw		391 w	400 w	406 w	388 w	390 w	395 w	399 w	$\nu(Co-C_{ac})_{sym}$

[a] Spectra were measured as KBr disks; except for I and II (solution in CS_2) and III, V, and VI as liquid films. The known vibrational frequencies of the ligands PMe_3 and PPh_3 are not reported.

Table II. IR Vibrations $\nu(\equiv CH)$, $\nu(C\equiv C)$, $\nu(C\equiv O)$, and $\nu(C=O)$ in Several Various Alkynes $RC\equiv CR'$ and Their Complexes $(RC\equiv CR')Co_2(CO)_6$

	A						B		C			D		E			F			
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20
R	H^e	H^e	H^d	H^e	H^d	H^c	Me^d	Ph^d	Me^e	Me^d	Et^d	H^e	H^e	$CH(OEt)_2$^{e}	Ph^e	$CH(OEt)_2$^{e}	CO_2Me^{d}	CHO^d	CHO^d	CF_3^{d}
R′	Ph	*n*-Bu	$C(CH_3)=CH_2$	*t*-Bu	CH_2OH	Me	Ph	Ph	*n*-Pr	Me	Et	CHO	CO_2Et	CN	CHO	CHO	CO_2Me	CHO	CN	CF_3
$\nu(\equiv CH)_a$[a]	3291	3310	3298	3307	3306	3305						3275	3265							
$\nu(\equiv CH)_c$[a]	3075	3100	3093	3090	3098	3100						3095	3085							
$\Delta\nu(\equiv CH)$	216	210	205	217	208	205						180	180							
$\nu(C\equiv C)_a$	2110	2119	2101	2104	2120	2142	2216	2221	2304	2312	2301	2098	2118	2220	2239	2248	2247	(2240)	(2252)	2305
$\nu(C\equiv C)_c$	1550	1548	1529	1521	1535	1550	1590	1590	1628	1629	1616	1498	1504	1565	1578	1580	1560	1542	1548	1594
$\Delta\nu(C\equiv C)$	560	571	572	583	585	592	626	631	676	683	685	600	614	655	661	668	687	(698)	(704)	711
$\nu(C\equiv O)$ A_1	2093	2092	2093	2091	2095	2093	2088	2087	2087	2088	2087	2105	2103	2109	2100	2104	2112	2112	2116	2123
B_1	2051	2047	2053	2047	2051	2053	2048	2046	2041	2044	2042	2065	2064	2073	2061	2065	2076	2081	2088	2091
A_1, B_2	2018	2013	2023	2014	2022	2025	2019	2013	2007	2017	2013	2030	2032	2043	2028	2034	2050	2059	2058	2055
$\nu(C\equiv O)_{av}$[b]	2054	2051	2056	2051	2056	2057	2052	2049	2045	2050	2047	2067	2066	2075	2063	2068	2079	2084	2087	2090
$\nu(C=O)_a$, $\nu(C=CH_2)_a$			1613									1671	1712		1659	1672	1726	1665		
$\nu(C=O)_c$, $\nu(C=CH_2)_c$			1614									1669	1707		1665	1669	1707	1659	1659	
$\Delta\nu(C=O)$, $\Delta\nu(C=CH_2)$			−1									2	5		−6	3	19	6		

[a] a = free alkyne; c = complexed alkyne. [b] av = average. [c] Data taken from ref 8 for $\nu(C\equiv O)$ and ref 20 for $\nu(C\equiv C)_c$. [d] KBr disk. [e] Liquid film.

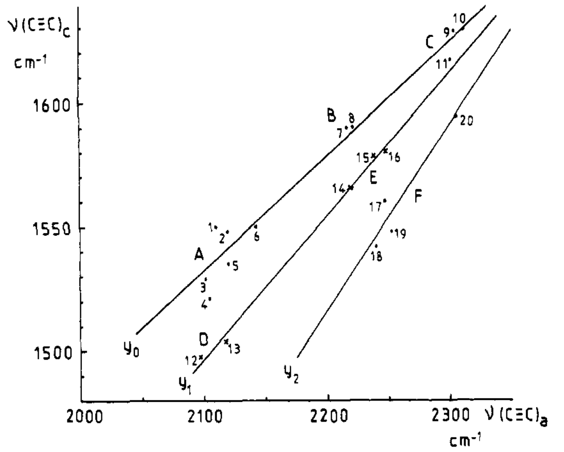

Figure 1. $\nu(C{\equiv}C)_c$ frequencies in the complexes as a function of $\nu(C{\equiv}C)_a$ frequencies of the corresponding free alkynes. Equations of the lines: $y_0 = 573.01 + 0.456\,67x$; $y_1 = 296.78 + 0.571\,373x$; $y_2 = -127.51 + 0.7468x$.

(olefin)) is 390 cm^{-1}, a similar frequency is expected for $\nu(Co{-}C_{ac})$ in the complexes $(RC{\equiv}CR')Co_2(CO)_6$.

Once the assignments have been established (vide supra) and with the availability of a great variety of alkynes and their complexes, the next step was to construct Table II, which contains unequivocal assignments for $\nu(C{\equiv}C)$. The range of $\nu(C{\equiv}C)_c$ frequencies is 1498–1629 cm^{-1}, and $\Delta\nu(C{\equiv}C)$, the change in frequency on coordination, varies from 560 to 711 cm^{-1} depending on the number and above all the electronic character of the substituents R and R′ on the acetylene.

The $\nu(C{\equiv}C)_a$ frequencies in the free monosubstituted alkynes (R = H) **1**–**6**, **12**, and **13** were detected unambiguously. For the remaining alkynes, the symmetric compounds **8**–**11**, **17**, and **20** have no IR-active $\nu(C{\equiv}C)$ bands and the dissymetric compounds exhibit generally two IR bands in the $\nu(C{\equiv}C)_a$ region, one of which is the first harmonic of the $\nu(C{-}C)$ vibration that occurs at 1100–1150 cm^{-1}.[24] In these cases we have taken the literature values for $\nu(C{\equiv}C)_a$: ref 23 for **8**, ref 23 and 24 for **9**, ref 24 for **9**–**11**, ref 25 for **14**, ref 26 for **17**, and ref 27 for **20**. The values shown in parentheses for **18** and **19** will be explained later.

Table II lists, in parallel data for $\nu(C{\equiv}C)_a$, $\nu(C{\equiv}C)_c$, and $\Delta\nu(C{\equiv}C)$ together with $\nu(C{\equiv}O)$ vibrational frequencies, the assignments that have been made in large part from the work of Bor.[3–9,11] In almost every case the $\nu(C{\equiv}O)$ spectra of liquids or solids exhibit three strong bands, the lowest of which is broad and contains the two components A_1 and B_2.

Discussion

When the values of $\nu(C{\equiv}C)_c$ of the coordinated acetylenes are plotted against the $\nu(C{\equiv}C)_a$ frequencies of the free ligands (Figure 1), quasi-linear relationships are evident for the compounds **1** → **11**, **12** → **16**, and **17** → **20**. The correlation coefficients obtained from best fits of the data for y_0, y_1, and y_2 are 0.983, 0.998, and 0.956, respectively.

A plot of $\Delta\nu(C{\equiv}C)$ vs. $\nu(C{\equiv}C)_a$ (Figure 2) shows obviously a closely similar grouping of compounds.

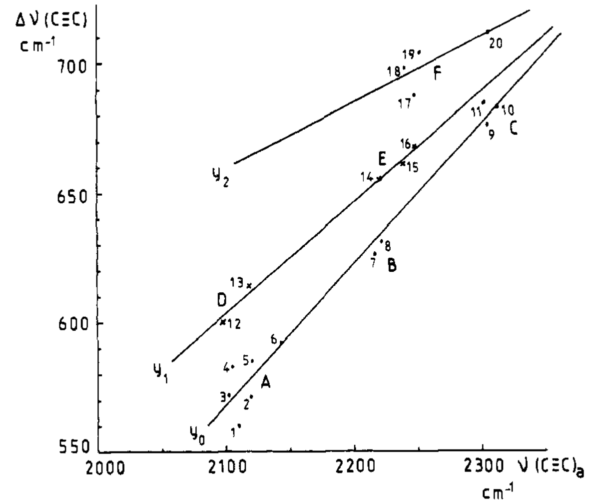

Figure 2. Changes in frequency, $\Delta\nu(C{\equiv}C)$, of alkynes on complexation as a function of $\nu(C{\equiv}C)_a$ frequencies of the corresponding free alkynes. Equations of the lines: $y_0 = -573.01 + 0.543\,33x$; $y_1 = -296.78 + 0.428\,627x$; $y_2 = 127.51 + 0.2532x$.

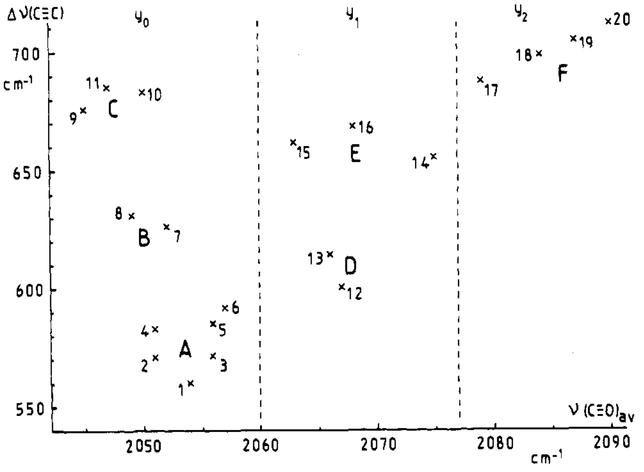

Figure 3. Changes in frequency, $\Delta\nu(C{\equiv}C)$, of alkynes on complexation as a function of the average carbonyl frequency $\nu(C{\equiv}O)_{av}$ in the complexes.

The straight line y_0 brings together those points that correspond to complexes having alkynes with electron donor or very poor acceptor substituents, and three zones are apparent: A for R = H and R′ = alkyl or phenyl (complexes **1**–**6**); B for R = alkyl or phenyl and R′ = phenyl (complexes **7** and **8**); C for R and R′ = alkyl (complexes **9**–**11**).

The function y_1 relates those complexes containing a single acceptor group in the α-position on the alkyne, and the points are grouped into two distinct zones: D for R = H and R′ = CHO or CO_2Et (complexes **12** and **13**); E for R = alkyl or phenyl and R′ = CHO or CN (complexes **14**–**16**).

Finally the line y_2 groups together the alkyne complexes possessing two acceptor groups, CHO, CN, CO_2Me, CF_3 (complexes **17**–**20**), and these points lie in the zone F.

The changes in $\Delta\nu(C{\equiv}C)$ as a function of the average carbonyl frequency $\nu(C{\equiv}O)_{av}$ for the complexes are shown in Figure 3. Not only are the same groups A, B, ..., and F found as previously (vide supra), but also the same zones y_0, y_1, and y_2. Thus the locations of the zones A–F are not fortuitous nor are the trends established by lines y_0, y_1, and y_2. The $\nu(C{\equiv}O)_{av}$ demarcation lines between y_0, y_1, and y_2 are 2060 and 2077 cm^{-1}.

The main feature derived from an examination of Figures 1 and 2 is that the higher the $\nu(C{\equiv}C)_a$ frequency, the

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greater the values of $\nu(\text{C}{\equiv}\text{C})_c$ and $\Delta\nu(\text{C}{\equiv}\text{C})$, whatever the nature of the groups R and R′ on the alkynes. We interpret this result as follows: the higher the $\nu(\text{C}{\equiv}\text{C})_a$ frequency, that is, the greater the population of free alkyne triple bond, the greater the σ donation from the alkyne to the $Co_2(CO)_6$ moiety *and/or* the π-back-donation from cobalt to alkyne because $\nu(\text{C}{\equiv}\text{C})_c$ is governed by the net $\sigma + \pi$ transfer.

Indeed, the generally accepted structure for metal–alkyne bonding involves σ-donation from the alkyne π-electron density to an empty metal p or d orbital and back-donation from a filled metal d (or dp hybrid) orbital to an alkyne π^*-orbital.[28] σ-donation reduces the π-electron density of the acetylenic triple bond and thus lowers the IR frequency. Back-donation into the π^*-level also weakens the triple bond. Thus, both σ- and π-coordination lower $\nu(\text{C}{\equiv}\text{C})$; their effect is additive ($\sigma + \pi$).

$\Delta\nu(\text{C}{\equiv}\text{C})$, which is a measure of $\sigma + \pi$ transfer, is only weakly perturbed by coupling of $\nu(\text{C}{\equiv}\text{C})$ to $\nu(\text{C—C})$. Moreover, it is well-known,[20] (this is confirmed by the magnitude of $\nu(\text{C}{\equiv}\text{C})_c$ (1560 ± 70 cm^{-1})) that the carbon–carbon bond in the complexes studied here is close to a double bond. So in electronic terms, $\Delta\nu(\text{C}{\equiv}\text{C})$, which is of the order of 650 cm^{-1}, is equivalent to a two-electron transfer.

Turning to the metal–CO interaction, the $\nu(\text{C}{\equiv}\text{O})$ frequency is a good indicator of the net charge on the metal. Previous work permits a quantitative estimate of this charge as a function of the decrease of $\nu(\text{C}{\equiv}\text{O})$: in the monoanion $Co(CO)_4^-$ the decrease is about 100 cm^{-1} with respect to $\nu(\text{C}{\equiv}\text{O})$ in the neutral compound $Co_2(CO)_8$.[29] A similar result is obtained when one or more carbonyl ligands are replaced by strong donor ligands.[30] It is thus possible to calculate the net charge transferred from the alkyne to the metal in the complexes $(\text{RC}{\equiv}\text{CR}')Co_2(CO)_6$. This quantity is given by the difference between σ-donation from and back-donation to the alkyne ($\sigma - \pi$).

$\Delta\nu(\text{C}{\equiv}\text{C})$ allows the calculation of $\sigma + \pi$, while $\Delta\nu(\text{C}{\equiv}\text{O})$ provides access to $\sigma - \pi$; therefore, the separate contributions σ and π can be easily deduced.

On this basis, $\Delta\nu(\text{C}{\equiv}\text{C})$ for the group of complexes A has an average value of 570 cm^{-1} (Figure 2 and Table II). Thus

$$\sigma + \pi = \frac{\Delta\nu(\text{C}{\equiv}\text{C})}{650} \times 2 \text{ electrons} = \frac{570}{650} \times 2 \text{ electrons} = 1.78 \text{ electrons}$$

$\nu(\text{C}{\equiv}\text{O})_{av}$ for complexes A is 2054 cm^{-1}, which implies a $\Delta\nu(\text{C}{\equiv}\text{O})$ of 14 cm^{-1}, as $\nu(\text{C}{\equiv}\text{O})_{av}$ for the three strong bands A_1, B_1, and A_1 (or B_2) of the carbonyl-bridged form of $Co_2(CO)_8$ in the solid state[7] is 2068 cm^{-1}. In accordance with the relationship given above, 100 cm^{-1} per electron, one calculates for complexes A (Figure 3 and Table II)

$$\sigma - \pi = \frac{\Delta\nu(\text{C}{\equiv}\text{O})}{100} = \frac{(2068 - \nu(\text{C}{\equiv}\text{O})_{av})}{100} = \frac{2068 - 2054}{100} = 0.14 \text{ electron}$$

The values for $\sigma + \pi = 1.78$ and $\sigma - \pi = 0.14$ imply $\sigma = 0.96$ and $\pi = 0.82$.

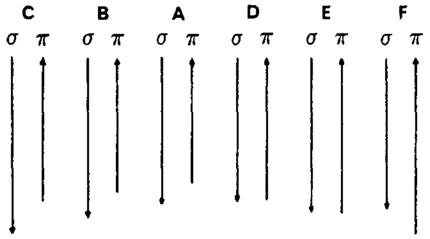

Figure 4. Relative σ and π parameters between alkyne and cobalt.

The above reasoning then provides all of the necessary elements to calculate separately the σ- and π-components of the interaction between the alkyne and the $Co_2(CO)_6$ moiety for the diverse series of complexes within the groups A–F.

	y_0						y_1				y_2
	C		B		A		D		E		F
σ(elect.)	1.15	↘	1.05	↘	0.96	~	0.94	↗	1.01	~	0.99
π(elect.)	0.94	↘	0.88	↘	0.82	↗	0.93	↗	1.02	↗	1.16

Although these values themselves provide only a rough estimate of the phenomenon, the relative ordering of the σ- and π-components is important. It can be seen that σ and π decrease from C to B to A and then increase again to F. Progressing through a given series, y_n (e.g., y_0, C → A), the greater the extent of σ-donation and π-back-donation, the greater is the electronic population of the triple bond. Moreover, comparison of the groups F, E, and B, which have more or less the same $\nu(\text{C}{\equiv}\text{C})_a$ (Figure 1), shows that the π-component decreases by the same amount (0.14 electron) from F to E and from E to B. Figure 4 illustrates clearly the various electron transfers: $\sigma > \pi$ for A, B, and C, then $\sigma \simeq \pi$ for D and E, and finally $\sigma < \pi$ for F.

All of these observations are in agreement with the fact that A, B, and C contain two electron-donating (or poorly attracting) groups, D and E contain one acceptor, and F contains two strong withdrawing substituents. When the R and R′ groups are electron donor, the acetylene π-electrons are more available for the donation of the π-electron density to a metal orbital of σ-symmetry. On the other hand, in the case of withdrawing substituents, electron density back-donation will flow easier from metal π-orbitals into a high antibonding π^*-orbital of the acetylene.

Before concluding, some justification of the values of $\nu(\text{C}{\equiv}\text{C})_a$ of the free alkynes corresponding to complexes **18** and **19** is necessary. These free ligand values could not be measured in the IR because of the symmetrical nature of the alkyne **18** or, alternatively, because the free ligand is too unstable (**19**). These frequencies were obtained by linear interpolation of $\Delta\nu(\text{C}{\equiv}\text{C})$ values for complexes **17** and **20** in parallel with the known values of $\nu(\text{C}{\equiv}\text{O})_{av}$ for the four complexes **17**–**20** (Figure 3). The extrapolated values should be accurate to ±5 cm^{-1}.

Conclusion

From the results of this study several important conclusions can be drawn.

1. The complexes $(\text{RC}{\equiv}\text{CR}'Co_2)(CO)_6$ are well suited for the examination and determination of changes in $\nu(\text{C}{\equiv}\text{C})_c$ as a function of the electronic character of the R and R′ groups on the alkyne. For these compounds $\nu(\text{C}{\equiv}\text{C})_c$ lies between 1490 and 1630 cm^{-1}; $\Delta\nu(\text{C}{\equiv}\text{C})$ varies in magnitude from 560 to 710 cm^{-1}.

2. By correlating changes in $\nu(\text{C}{\equiv}\text{C})$ and $\nu(\text{C}{\equiv}\text{O})$ frequencies, it is possible to evaluate the relative extent of σ- and π-bonding in these systems. Each of the two π-

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bonds of the alkyne releases approximately half of its population to form the σ-component (alkyne → metal), thus rendering *each* alkyne–cobalt bond closely analogous to the metal–olefin bond in (olefin)$Fe(CO)_4$ complexes. In total the triple bond has been essentially reduced to a double bond. However the reduced triple bond does not appear, from chemical studies, to exhibit the behavior and reactivity expected of an olefin because of very different electronic distribution on the carbon atom in these two cases.

3. The complexation of an acetylene by the $Co_2(CO)_6$ entity leads not only to temporary protection of the triple bond[31] but also to an interesting stabilization of the unsaturated.[32] Therefore, the existence of straight-line relationships and zones of similarity between compounds, according to the nature of the substituents on the complexed alkyne, ought to permit the determination of the following unknowns: (a) the vibrational frequency of $\nu(C{\equiv}C)_a$ in an unsymmetrical free ligand; (b) the $\nu(C{\equiv}C)_a$ frequency in a symmetrical acetylene normally inactive in the IR; (c) the $\nu(C{\equiv}C)_a$ frequency in an unknown and unstable free ligand; (d) the $\nu(C{\equiv}C)_c$ frequency of a complex involving a phenyl group that can give rise to bands overlapping. Thus, an examination of $\nu(C{\equiv}C)_c$ in the complex together with $\nu(C{\equiv}O)_{av}$ identifies clearly the straight line and the zone to which the compound belongs.

For example, the derivative $(HC{\equiv}CCF_3)Co_2(CO)_6$ having the $\nu(C{\equiv}O)$ frequencies 2112, 2072, and 2040 cm^{-1}, i.e., $\nu(C{\equiv}O)_{av} = 2075$ cm^{-1}, belongs to y_1 (Figure 3). The experimental value of $\nu(C{\equiv}C)_c$ at 1533 cm^{-1} indicates that it should have a free $\nu(C{\equiv}C)_a$ frequency close to 2162 cm^{-1} (Figure 1). The experimental frequency for this free ligand is 2159 cm^{-1}.[33] In the same way, the complex $(PhC{\equiv}CCOCH_3)Co_2(CO)_6$ having $\nu(C{\equiv}O)_{av}$ at 2065 cm^{-1} and $\nu(C{\equiv}C)_c$ at 1580 cm^{-1} belongs to line y_1 (Figure 3) and zone E (Figure 1). The corresponding $\nu(C{\equiv}C)_a$ frequency is of the order of 2247 cm^{-1}, close to the experimental value of 2250 cm^{-1}. This is significant because the IR band is actually weak and very close to an intense band at 2202 cm^{-1} due to the first harmonic of $\nu(C{-}C)$. Indeed it would be difficult to correctly assign $\nu(C{\equiv}C)_a$ in this compound simply on the basis of frequency and intensity. Thus, the ambiguity of band overlapping can be solved by complexation without suffering from too much confusion with other bands. Furthermore, if there is some doubt concerning the nature of substituents on the alkyne after reaction or possible modification and if after complexation the $\nu(C{\equiv}C)_c$ frequency is known precisely, then examination of Figures 3 and 1 will remove this doubt. A $\nu(C{\equiv}O)_{av}$ frequency at 2065 cm^{-1} corresponding to y_1 leads to either complexes D or to complexes E; carrying $\nu(C{\equiv}C)_c$ onto Figure 1 (either 1500 or 1570 cm^{-1}) provides knowledge of the electronic nature of the substituent on the alkyne.

Finally, the linear relationships of Figure 1 allow one to find easily the $\nu(C{\equiv}C)_c$ frequency in some particularly complicated stretching regions of metal complexes involving a phenyl group. For example, the free ligand $PhC{\equiv}CCHO$ exhibits a $\nu(C{\equiv}C)_a$ frequency at 2239 cm^{-1} and the complex a $\nu(C{\equiv}O)_{av}$ frequency at 2063 cm^{-1}. Correlating $\nu(C{\equiv}C)_a$ and $\nu(C{\equiv}C)_c$ on line y_1 of Figure 1 leads to a $\nu(C{\equiv}C)_c$ at 1576 cm^{-1}. By examining the IR spectrum that shows three overlapping bands at 1596, 1578, and 1569 cm^{-1}, a clear choice of the $\nu(C{\equiv}C)_c$ at 1578 cm^{-1} can be made, the bands at 1596 and 1569 cm^{-1} resulting from the $\nu(C{=}C)$ frequency of the phenyl group.

Experimental Section

All reactions and manipulations with dicobalt octacarbonyl were carried out under a dry, oxygen-free, nitrogen atmosphere. Solvents (benzene, tetrahydrofuran, pentane, and *n*-hexane) were dried over sodium benzophenone and distilled under dry nitrogen just prior to use. Dicobalt octacarbonyl was purchased from Strem Chemical Co. Most of the free acetylene derivatives were commercial samples used without further purification, and the remaining were prepared according to literature procedures. Trimethylphosphine was prepared as previously described.

Preparation of $(RC{\equiv}CR')Co_2(CO)_6$. The (alkyne)cobalt complexes were prepared by the well-known method[34] by treating $Co_2(CO)_8$ with the appropriate alkyne (small excess) in dry deoxygenated pentane or THF (use of syringes), under a nitrogen atmosphere, at room temperature. After gas evolution has vanished, the reaction mixture was stirred for 1 or 2 h and purity was followed by thin-layer chromatography (silica gel 60 F 254). Pure complexes were obtained, after preparative chromatography on silica gel (plates or short columns), either by low-temperature crystallization (solids) or by removal of the solvent under vacuum (liquids).

Preparation of $(RC{\equiv}CR')Co_2(CO)_{6-n}(PR_3)_n$. Monophosphine derivatives ($n = 1$) were prepared by the methods described in the literature, e.g., ref 18, 34, and 35. Disubstitution products ($n = 2$) were obtained by using an excess of PR_3, at a temperature of 40 °C.

Preparation of α-Acetylenic Dialdehydes Acetals Deuterated on the Aldehyde Function and Their Complexes. First triethylorthoformate-α-d_1 (D–C(OEt)$_3$) was prepared from deuterium cyanide, deuterium chloride, and ethanol-d_1 according to a procedure previously described[36] and purity was checked by ^1H NMR.

Second, the deuterated acetal $(EtO)_2DCC{\equiv}CCD(OEt)_2$ was prepared by the same method as for the hydrogenated acetal[37] using D–C(OEt)$_3$ instead of H–C(OEt)$_3$, i.e., preparation of the disubstituted Grignard derivative of acetylene and reaction with D–C(OEt)$_3$. Purity and absence of aldehydic hydrogen were followed by ^1H NMR. Finally, treatment of this acetal with $Co_2(CO)_8$ and chromatographic purification gave rise to the deuterated complex $[(EtO)_2DCC{\equiv}CCD(OEt)_2]Co_2(CO)_6$ that was the starting material for the α-acetylenic deuterated dialdehyde XIII (by pure formic acid formolysis) and for the phosphine derivatives XIV–XVI (mono- or disubstituted by PR_3 followed by formolysis).

Spectral Measurements. Infrared spectra were recorded on a Perkin-Elmer 225 spectrophotometer in the spectral region of 4000–200 cm^{-1}. Calibration in wavelength of the spectra was made by using as standards the absorption lines of H_2O, CO_2, and CO. In multiple bond stretching regions, several thicknesses (neat sample or in a solvent) or concentrations (solids in dry KBr) were studied, so as to obtain optimal intensities and good band separations. ^1H NMR spectra were recorded on a 60-MHz Varian EM 360 spectrometer with an internal Me_4Si standard.

Acknowledgment. We are indebted to Prof. A. J. Carty (Waterloo) for helpful discussions concerning this paper as well as Dr. F. Petillon (Brest) for providing samples of $(F_3CC{\equiv}CCF_3)$- and $(F_3CC{\equiv}CH)Co_2(CO)_6$.

Registry No. **1**, 12154-91-5; **2**, 59954-60-8; **3**, 40698-46-2; **4**, 56792-69-9; **5**, 12264-12-9; **6**, 41626-24-8; **7**, 53556-74-4; **8**, 14515-69-6; **9**, 90108-95-5; **10**, 37726-81-1; **11**, 41626-27-1; **12**, 90108-86-4; **13**, 90108-96-6; **14**, 90108-97-7; **15**, 90108-98-8; **16**, 90108-99-9; **17**, 37685-64-6; **18**, 82659-43-6; **19**, 90109-00-5; **20**,

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Communications

Crystal Structure of (μ-Trithio)bis[tricyclohexylgermanium(IV)]: Corrigendum[†]

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Summary: The crystal structure of $[(C_6H_{11})_3Ge]_2S_3$, which has been described and refined[1] in the triclinic space group $P1$, can be better described in space group $P\bar{1}$. Least-squares refinement in $P\bar{1}$ led to an R of 0.052 for 3394 reflections, compared to an R of 0.070 obtained for the $P1$ refinement. In the $P\bar{1}$ description, the central S atom is disordered between two centrosymmetrically related sites; as a result of this disorder, the S–S distances, which are calculated at 1.973 (3) and 2.051 (3) Å, may well be equal at about 2.01 Å. Other distances and angles are now normal.

The crystal structure of $[(C_6H_{11})_3Ge]_2S_3$ has been described[1] in the triclinic space group $P1$ (a = 9.004 (7), b = 9.808 (4), c = 11.815 (5) Å; α = 83.14 (3), β = 84.64 (5), γ = 66.92 (5)°; Z = 1) and refined to an R of 0.063 for 3185 reflections with $I > 1.9\sigma(I)$, R = 0.070 for all 3395 measured reflections. Three considerations led us to investigate the possibility of higher symmetry: (1) the molecule has potential symmetry that space group $P1$ cannot satisfy; (2) averaging the coordinates (Table I[1]) of the two pairs of chemically equivalent heavy atoms Ge(1), Ge(2) and S(1), S(3) gives nearly identical values ($\bar{x}$ = 0.193, $\bar{y}$ = 0.128, $\bar{z}$ = −0.197); (3) most convincing of all, the authors noted that the highest peak in a final difference map (1.2 e·Å^{-3}) "was in the vicinity of the sulfur atoms, at 1.92, 2.21, and 2.04 Å from the S(1), S(2) and S(3) atoms, respectively". By triangulation, this peak must be related to the central atom S(2) by the same point that relates Ge(1) to Ge(2) and S(1) to S(3), suggesting that the space group might be $P\bar{1}$ with S(2) disordered between two centrosymmetrically related sites. Further study showed that every remaining atom in Table I[1] has a chemically equivalent mate approximately related by the same center of symmetry.

Table I. Coordinates (×10^5 for Ge; ×10^4 for S and C) and U_{eq} Values (×10^4) (Space Group $P\bar{1}$)

	x	y	z	U_{eq}, Å^2
Ge(1,2)	19399 (6)	12777 (5)	−19726 (4)	419 (1)
S(1,3)	1903 (2)	−226 (2)	−351 (1)	656 (3)
S(2)[a]	73 (3)	−920 (3)	−537 (2)	575 (5)
C(11,61)	95 (5)	1635 (5)	−2894 (4)	481 (10)
C(12,66)	−1465 (6)	2863 (6)	−2494 (4)	604 (13)
C(13,65)	−2858 (6)	3163 (6)	−3258 (5)	737 (16)
C(14,64)	−2440 (7)	3511 (6)	−4499 (5)	734 (15)
C(15,63)	−921 (7)	2272 (7)	−4906 (5)	758 (16)
C(16,62)	475 (6)	2000 (6)	−4162 (4)	611 (13)
C(21,41)	1884 (5)	3155 (5)	−1489 (4)	491 (10)
C(22,46)	2355 (7)	4078 (6)	−2466 (4)	640 (13)
C(24,45)	2280 (9)	5532 (6)	−2093 (6)	906 (18)
C(23,44)	3248 (8)	5318 (6)	−1069 (5)	756 (15)
C(25,43)	2770 (7)	4430 (7)	−103 (5)	742 (14)
C(26,42)	2876 (7)	2948 (6)	−456 (4)	672 (13)
C(31,51)	3981 (5)	112 (5)	−2785 (4)	448 (9)
C(32,56)	5483 (6)	−174 (6)	−2160 (4)	595 (12)
C(33,55)	7031 (6)	−1081 (7)	−2830 (5)	741 (16)
C(34,54)	6989 (7)	−2521 (6)	−3142 (5)	715 (15)
C(35,53)	5488 (7)	−2238 (6)	−3767 (5)	733 (15)
C(36,52)	3952 (6)	−1366 (5)	−3087 (5)	643 (13)

[a] Half-populated site.

Table II. 206 Reflections, $I \leqslant 1.9\sigma(I)$

	$P\bar{1}$	$P1$
ΣF_o	222.4	218.4
$\Sigma \lvert F_c \rvert$	186.0	463.7
$\Sigma \lvert \Delta F \rvert$	99.4	270.8
R	0.45	1.24

Reformulating the structure in $P\bar{1}$ required a shift of origin to x = 0.19, y = 0.13, and z = −0.20 and an averaging of symmetry-related coordinates. (This averaging was confusing because of inconsistencies in the atom numbering system, which does not conform to Figure 1 of ref 1.) Atom S(2) was assigned a population parameter of 0.5. The hydrogen atoms were placed in assumed positions so as to complete tetrahedra with C–H = 0.95 Å, as in ref 1, and were not further adjusted. Initial least-squares refinement led to an R of 0.065 for the 3395 reflections in the supplementary table, but one reflection (70$\bar{2}$) was a statistical outlier; when it was removed from the refinement, convergence was reached at R = 0.052 for all 3394 reflections and R = 0.050 for 3188 reflections with $I > 1.9\sigma(I)$, compared to 0.070 and 0.063 for the $P1$ refinement.[1] The principal features of a final difference map were about 0.5 and −0.9 e·Å^{-3} in height and formed a familiar clover-leaf pattern about the Ge atom, suggesting that the U_{ij} terms were not able to completely compensate for systematic errors such as absorption. There were similar but smaller features about S(1,3), but no indications of additional disorder. The final $P\bar{1}$ coordinates are given in Table I. Coordinates assigned to the H atoms and U_{ij}

[†] Contribution No. 6978.

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