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(18) The designation η^6 will be used here to designate coordination to one six-membered ring of the fluorenyl ligand. The actual structure as a η^6 compound is a simplification; see text to follow.

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Raman Spectra of the Cobalt Carbonyl Acetylene Complexes $Co_2(CO)_6C_2R_2$

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Raman spectra are reported and discussed for $Co_2(CO)_8C_2R_2$ species (R = H, CF_3, CH_3, $COOCH_3$, C_6H_5) and for $Fe_2(CO)_6S_2$. In the 2000-cm^{-1} region a definite assignment of $\nu_5(B_1)$ is achieved and a dependence of the separation between $\nu_2(A_1)$ and $\nu_6(B_2)$ in the electronegativity of R is revealed and explored in a simple normal-coordinate treatment. For the low-frequency spectral region the data for $Fe_2(CO)_6S_2$ facilitate the interpretation of the data for the cobalt species. This interpretation differs at several points from that of previous workers.

The relative ease of preparation of complexes of general formulation $Co_2(CO)_6RC{=}CR'$ has led to several studies aimed, at least in part, at comparing the vibrational characteristics of the coordinated and free alkyne.[1-4] By systematic variation of the ligand and by isotopic substitution it has proved possible to identify, with a fair degree of certainty, most of the internal vibrations of simple alkynes and to discuss the origin of the frequency changes observed.

In addition to studies on the alkynes there has also been interest in the vibrational spectra in the ν(CO) region although, again, almost all of the relevant reports have been concerned solely with infrared studies. As is well known, the coupling of the individual CO vibrators gives rise to well separated peaks, thus, in the present case for instance, offering the hope that the extent of coupling between the two $Co(CO)_3$ groups can be determined. Much of the work in this area on these compounds is that of Bor and his co-workers.[5-7] Their work has clearly shown that the interaction between CO groups of different $Co(CO)_3$ units may be comparable with the interactions between CO groups of the same unit.[7] In view of this wealth of information it might be supposed that Raman data would be superfluous. This is not the case for several reasons. First, there is a frequent uncertainty in the infrared spectrum over the assignment of $\nu_2(A_1)$ and $\nu_6(B_2)$. Raman depolarization data could enable a clear distinction. Second, a rather weak peak has been assigned to the $\nu_5(B_1)$ fundamental mode. A confirmation of this assignment from Raman studies is desirable. In practice, we have been able to achieve the latter demonstration. However, only in the complex of $C_2(CH_3)_2$ were the $\nu_2(A_1)$ and $\nu_6(B_2)$ modes sufficiently well resolved to make an unambiguous assignment possible on the basis of our Raman spectra.

Solid $Co_2(CO)_6C_2RR'$ species are reasonably stable in air but in solution or in the liquid state all decompose quite rapidly. Further, most are readily photodecomposed. In our Raman studies we have found that such decomposition could frequently only be avoided when the deep red krypton laser line (6764 Å) was used for excitation. Even at a low incident power, the 6471-Å line sometimes caused appreciable decomposition. In all cases, therefore, we have deemed it advisable to repurify all samples used in our Raman studies before reuse. In the present work we have studied species with R = R' = COOH, $COOCH_3$, C_6H_5, and $Fe_2(CO)_6S_2$. Only for the latter compound are we aware of previous Raman data;[8] for the ν(CO) region this work was on solid samples and at a lower resolution than the solution data reported in this paper.

Results and Discussion

We were successful in obtaining good-quality Raman spectra of the species with R = R' = H, CF_3, CH_3, and $COOCH_3$ and of $Fe_2(CO)_6S_2$, all in CCl_4 solution, in the ν(CO) region. A spectrum was similarly obtained for R = R' = C_6H_5 but this was of a rather lower quality. These spectra all show a common pattern. There is a high-frequency band and a lower frequency set of three bands, the separation between the three components being rather variable so that while those bands are clearly resolved for R = R = CF_3 (Figure 1) for $Fe_2(CO)_6S_2$ (Figure 2), one band is little more than a shoulder and in the case of R = R' = H (Figure 3) there are only two resolved bands.

Comparison with the infrared frequency data and our polarization measurements make it quite clear that even when three bands are observed they should not be necessarily assigned in the same way in all compounds. In the case of R = R' = CH_3, for instance, it is clear from such considerations that $\nu_2(A_1)$ and $\nu_6(B_2)$ are resolved. The normal pattern is that ν_6 appears at a higher frequency than ν_2. However, as the electronegativity of R (=R') increases, this separation decreases and for the most electronegative substituents the frequency order is actually reversed. Confirmatory evidence for this comes from two additional sources: first, from the relative infrared intensities of the two bands ($I(\nu_6) > I(\nu_2)$); second, from the observation of a correlation between the separation ($\nu_6 - \nu_2$) and the Taft parameter σ^{*}[9] (Figure 4). The extrapolation to the cases R = R' = CF_3 or $COOCH_3$ clearly requires that $\nu_6 - \nu_2$ be negative. The Raman spectral data are collected in Table I where they are compared with infrared data for the corresponding compounds. In making this comparison it must be remembered that the infrared data were obtained using hexane as a solvent so that small differences in solvent effects are to be expected. Unfortunately, paraffinic hydrocarbons do not prove to be generally suitable as solvents for these compounds in a Raman study. Our assignments, also given in Table I, generally concur with those of Bor.[7] In particular, our measurements of depolarization ratios clearly confirm the A_1 symmetry species of the highest

Table I. IR (*n*-Hexane) and Raman (CCl_4) CO Stretching Frequencies (cm^{-1}) of $Co_2(CO)_6(RC_2R')$ and $Fe_2(CO)_6S_2$ Complexes

Complex	Spectrum	$\nu_1(A_1)$	$\nu_4(B_1)$	$\nu_6(B_2)$	$\nu_2(A_1)$	$\nu_5(B_1)$	$\nu_3(A_2)$
$Co_2(CO)_6(HC_2H)$	IR	2098.8	2059.6	2034.6	2028.9	2017.0	Inact
	R	2102	2062	2032		2017	
$Co_2(CO)_6(CH_3C_2CH_3)$	IR	2089.6	2048.7	2026.2	2015.6	2005.0	Inact
	R	2093	2053	2028	2017	2007	
$Co_2(CO)_6(C_6H_5C_2C_6H_5)$	IR	2090.7	2056.1	2030.6	2026.4	2013.7	2010.6
	R	2092	Not obsd	2030		2014	
$Co_2(CO)_6(COOCH_3C_2COOCH_3)$	IR	2110.5	2079.8	2048.8	2053.8	not obs.	Inact
	R	2115	2084	2054		2042	2034
$Co_2(CO)_6(CF_3C_2CF_3)$	IR	2120.9	2089.1	2062.7	2064.6	2052.2	Inact
	R	2125	2093	2063		2054	2048
$Fe_2(CO)_6S_2$	IR	2084.0	2044.4	2008.3		1993.0	Inact
	R	2087	2048	2008		1994	1987
$Co_2(CO)_6(n\text{-}C_3H_7C_2nC_3H_7)$	IR	2087.0	2046.9	2025.0	2013.7	2002.7	Inact
$Co_2(CO)_6(CH_2N(C_2H_5)_2C_2CH_2N(C_2H_5)_2)$	IR	2088.3	2049.6	2026.7	2017.1	2007.0	2002.6
$Co_2(CO)_6(CH_3C_2C_6H_5)$	IR	2090.1	2052.9	2028.1	2022.0	2010.0	Inact

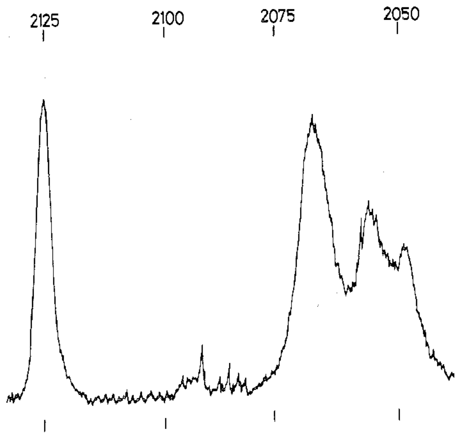

Figure 1. Raman spectra of $Co_2(CO)_6C_2(CF_3)_2$ in CCl_4 solution in the 2000-cm^{-1} region.

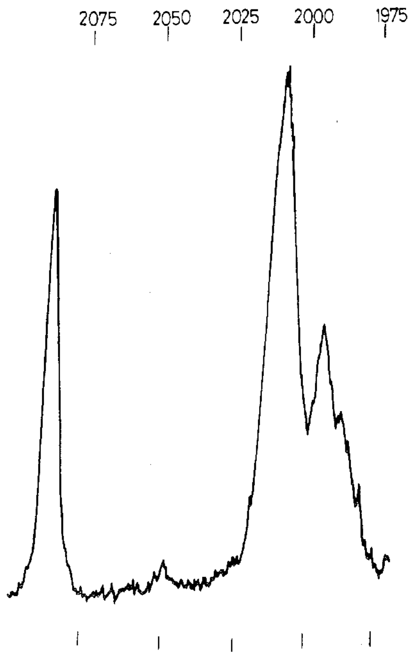

Figure 2. Raman spectra of $Fe_2(CO)_6S_2$ in CCl_4 solution in the 2000-cm^{-1} region.

frequency band. As would be expected from general considerations,[10] the high degree of polarization associated with this band means that the second, lower frequency, A_1 band is not strongly polarized. Two features clearly emerge from our spectra. First, the lowest of the set of three bands of the lower frequency group is clearly a fundamental, confirming the suggestion of Bor.[7] Second, the shoulder mentioned above on the spectrum of $Fe_2(CO)_6S_2$ is not one of the threee bands seen in some other species but is more probably the infrared-inactive A_2 mode. A close inspection of the spectra of the cobalt species in this region suggests that they too may contain an unresolved shoulder in a similar position. Table I also contains infrared frequencies for compounds for which we have been unable to obtain Raman data.

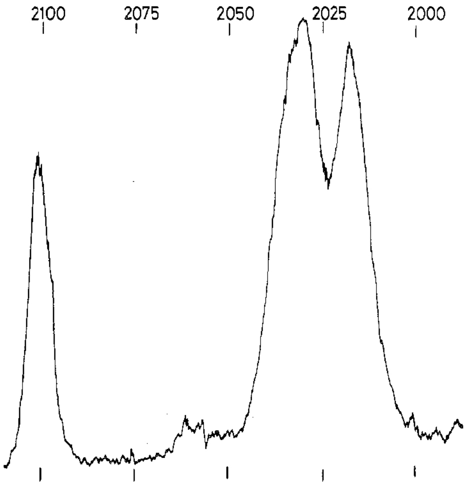

Figure 3. Raman spectra of $Co_2(CO)_6C_2H_2$ in CCl_4 solution in the 2000-cm^{-1} region.

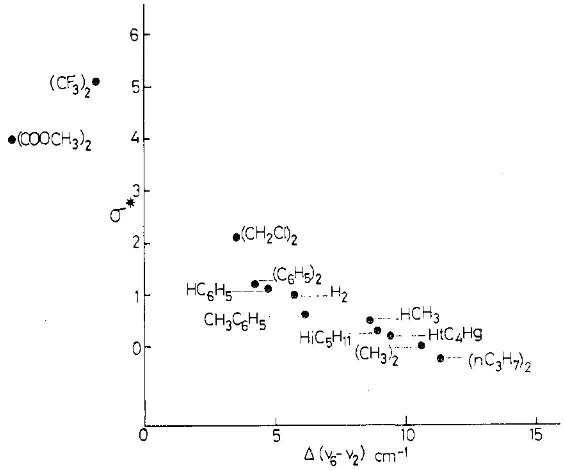

Figure 4. Plot of the Taft parameter σ^* against $\nu_6 - \nu_2$ for $Co_2(CO)_6C_2R_2$ species.

There are several interesting points which arise from a study of the infrared and Raman spectra. Although the C_{2v} point group is generally taken as that appropriate to a vibrational analysis of the $M_2(CO)_6$ unit, a simpler alternative is the D_{3h}

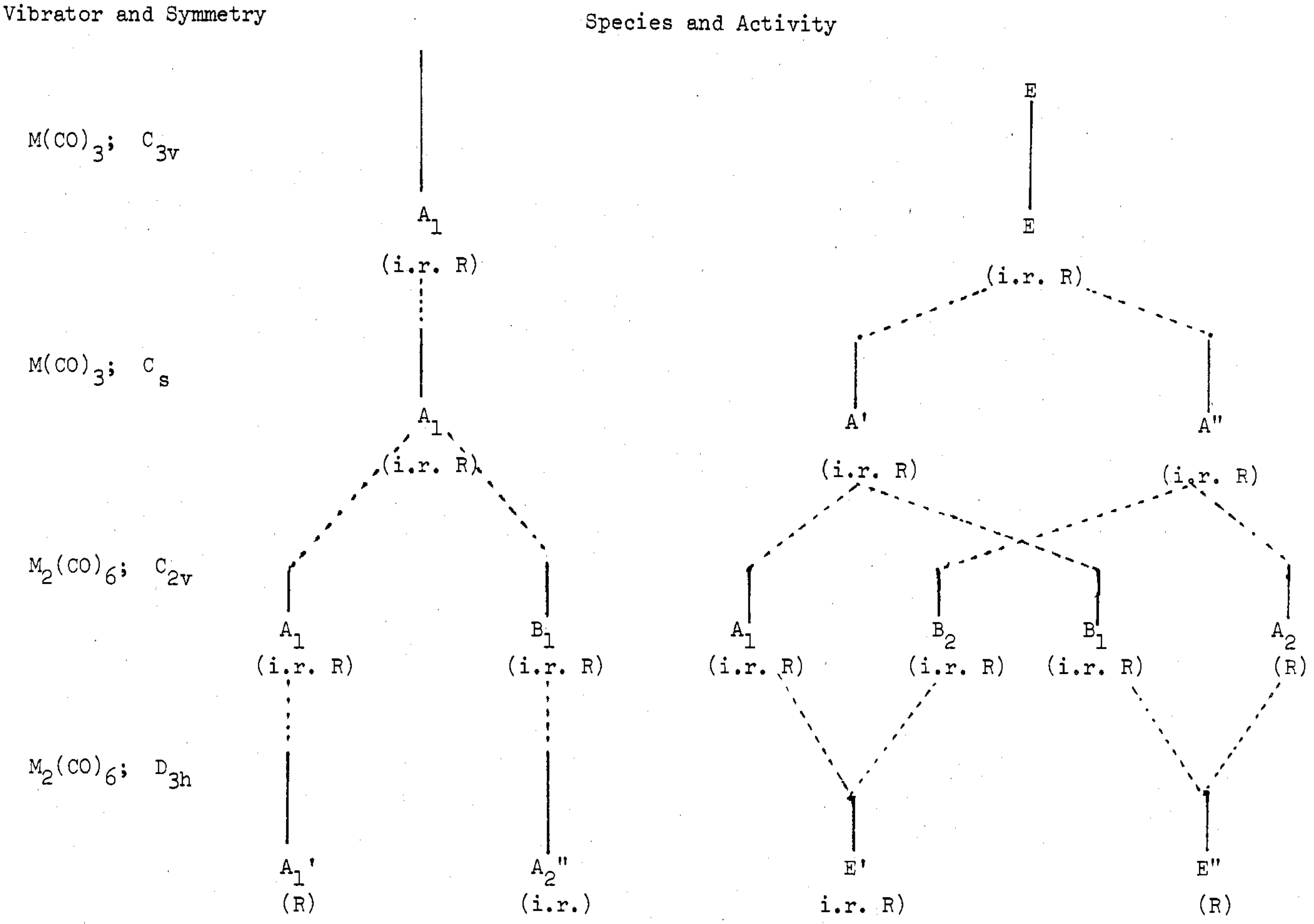

Figure 5. Symmetry correlations and spectral activities for the ν(CO) modes in $M_2(CO)_6$ species.

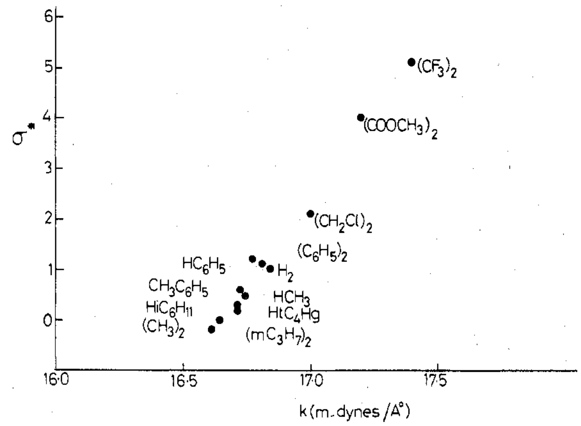

Figure 6. Plot of the Taft parameter σ^* against the C–O bond stretching force constant for $Co_2(CO)_6C_2R_2$ species.

point group. A qualitiative survey of the band intensities in the infrared and Raman spectra provides some insight into the relative applicability of C_{2v} and D_{3h}. Thus, a weak peak in the ν(CO) Raman spectra appearing in the region between the two main sets of spectral features is assigned to a mode of B_1 symmetry and is strong in the infrared region. This mode correlates with A_2'' in D_{3h}, which would be Raman forbidden. The second B_1 peak appears only weakly in the infrared but strongly in the Raman. This mode correlates with one component of E″ in D_{3h}, where it would be Raman allowed and infrared forbidden. It is evident that the C_{2v}–D_{3h} correlation may be usefully used in the present context; indeed, the way that it provides a good general account of the spectra is shown in Figure 5.

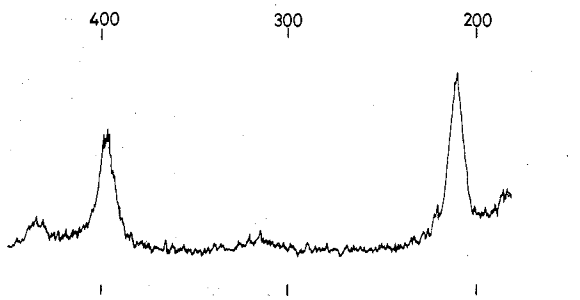

Figure 7. Raman spectra of $Co_2(CO)_6C_2H_2$ in C_6H_6 solution in the 300-cm^{-1} region.

The frequencies of all the bands increase as the electron-attracting powers of R and R′ increase. Interestingly, in confirmation of the work of Cetini et al.,[11] we find that a plot of the frequency of the highest A_1 band against the Taft parameter σ^* is linear. Bor has reported normal-coordinate analyses on the CO vibrators in some $Co_2(CO)_6C_2R_2$ species.[7] A preliminary study suggested that the correlation noted above exists between the bond stretching force constants and not with any of the interaction constants. Unfortunately, Bor has not carried out analyses on all of the compounds we have studied; in particular he has not studied compounds with electronegative alkyne substituents. We have therefore carried out normal-coordinate analyses using a D_{3h} model. As noted above, this gives a good approximate account of many aspects of the spectra and has the advantage that the number of unknowns does not exceed the observables. The bond stretching force constants obtained by us are very similar to those reported by Bor.[7] A good correlation between σ^* values

Table II

Compd	Raman data (benzene), cm^{-1}	IR data (*n*-hexane), cm^{-1}	Assignments
$Co_2(CO)_6(HC_2H)$	~610 w (CCl_4)	605 m	δ(C-H)
		580 w	Co-CO str + Co-C-O bend
	556 m, p	554 m	
	~520 w	522 s	
		~512 m, sh	
	490 w	495 m	
		~485 w, sh	
		452 m	
	435 m, p	427 w	
	395 s, p	392 w	Co_2-alkyne str
		380 w	
		360 w	
	310 m, p		?
	210 vs, p		Co-Co str
$Co_2(CO)_6(CH_3C_2CH_3)$	565 w	556 m	Co-CO str + Co-C-O bend
		520 s	
	510 w	505 s	
		478 m	
	460 w	455 m	
	430 m, p(?)	430 w	
	380 vs, p	385 vw	Co_2-alkyne str
	215 vs, p		Co-Co str
$Co_2(CO)_6(CF_3C_2CF_3)$	530 w	530 s	Co-CO str + Co-C-O bend + CF_3 rock
		510 s	
	495 w, np	495 s	
	460 w, np	455 w, sh	
		445 m	
	430 m, p		
		394 m	
	320 w, np		Co_2-alkyne asym str
	302 w, np	295 vw	
	275 vs, p	272 w	Co_2-alkyne sym str
	255 w, np	252 w	Co_2-alkyne asym str
	190 m, p		Co-Co str
$Fe_2(CO)_6S_2$		624 w	
		614 m	
		590 w	Fe-CO str + Fe-C-O bend
		570 m	
		560 s	
	555 s, p	555 m, sh	S-S str
	494 m, p	490 w	
	480 m, p	470 w	
		462 vw	Fe-CO str + Fe-C-O bend
	450 m, p	446 w	
	405 w	405 w, br	
	332 vs, p		Fe_2-S_2 sym str
	320 w, np	325 w	
	310 w, np		Fe_2-S_2 asym str
	265 m, np		
	195 vs, p		Fe-Fe str

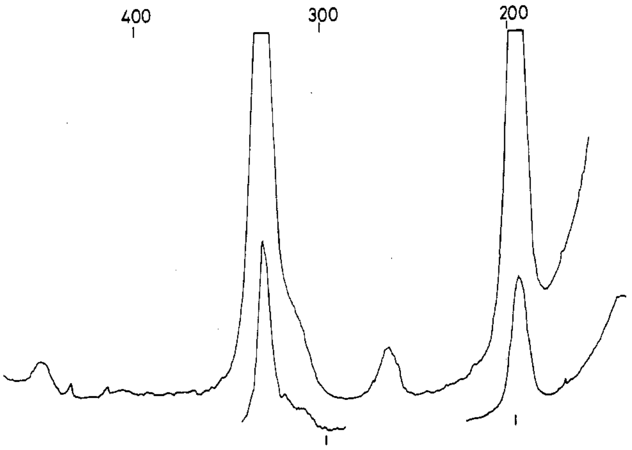

Figure 8. Raman spectra of $Fe_2(CO)_6S_2$ in C_6H_6 solution in the 300-cm^{-1} region.

and the bond stretching force constants was obtained and is shown in Figure 6. Details of our analysis are deposited as supplementary material.

Of the other spectral regions that below ca. 600 cm^{-1} is of particular interest. In this region, in addition to ν(M-C) and ν(M-C-O) modes, are expected any features which correspond to ν(M-M) and ν(M-C_2RR′-M) modes.

Complete data for this region are available only for the compounds where R = R′, H, CH_3, and CF_3 (Figures 7and 8 show the spectra for R = R′ = H and for $Fe_2(CO)_6S_2$, respectively). Additionally, infrared data are available in the literature for the compounds with R = R′ = D, R = H, and R′ = D.[2] Two strong Raman peaks are invariably observed in addition to numerous weaker peaks (Table II). Although the observed weak peaks are not sufficiently well resolved to allow us to attempt a detailed assignment, the existence of common band patterns in the 400–580-cm^{-1} region, together with the recognition that the ν(M-C) and δ(M-C-O) modes commonly appear in this region, leads to a rather firm assignment. In one important respect this assignment differs from that of Iwashita, Tamura, and Nakamura,[2] who attributed a band at 550–560 cm^{-1} to a cobalt–acetylene stretching vibration. Their assignment is not in accord with our Raman data and fails to explain a rather similar band pattern in the infrared spectrum of $Fe_2(CO)_6S_2$ and, in particular, its strong band at 560 cm^{-1}.

The Raman spectra are of particular value in this spectral region, since two strong bands, both polarized, are observed. That at ca. 200 cm^{-1} appears to be characteristic of a situation in which two metal atoms are attached to a pair of bridging atoms. It is found in the present work in the cobalt alkyne series, in $Fe_2(CO)_6S_2$, and has been reported in a variety of other compounds.[12-15] This band (which may also appear in the infrared spectrum) we assign, as a first approximation, to ν(M–M). The other strongly polarized Raman band is more variable in position. It appears that the more electronegative the alkyne substituent (or, equally, the greater the mass of the substituent) the lower the frequency of this band. This correlation leads us to attribute it to the totally symmetric Co_2–alkyne stretching mode. It is evident, from their common symmetry, that mixing between these two modes may occur. This is the more likely in our assignment since both are associated with vibrations involving the same atoms. We therefore regard the change of relative intensity of these two bands in $Co_2(CO)_6C_2(CF_3)_2$, where they are closer together than in any other species which we have studied, as indicative of mixing and strong corroborative support for our assignment.

In the above discussion we have modified one assignment of Iwashita et al. There are several consequent reassignments. In the particular case of $Co_2(CO)_6C_2H_2$, having reassigned the 551-cm^{-1} band, we attribute the 605-cm^{-1} band in their infrared spectrum to δ(C–H). This band is also observed in the Raman spectra where it is found to be depolarized, so that a symmetry species of B_1 is indicated. Iwashita et al. assigned the 605-cm^{-1} band to $\nu(Co–C_2)$ because of the appearance of a rather weaker band at 587 cm^{-1} in $Co_2(CO)_6C_2D_2$. However, we believe that the isotopic shift of the 605-cm^{-1} band is much larger than this and has led to the band being lost under the strong absorption in the 470–570-cm^{-1} region. Rather, we suspect that the 587-cm^{-1} band is a combination of the bands corresponding to those observed in the Raman spectra at 210 and 395 cm^{-1} in the H_2 analogue, shifted and strengthened by Fermi resonance with the band at 602 cm^{-1}. The latter has its counterpart at 768 cm^{-1} in the H_2 compound and is almost certainly to be attributed to the totally symmetric δ(C–H) mode.

We have found no band which can clearly be assigned to the asymmetric metal–alkyne stretching mode, in either the infrared or Raman spectra, although a number of weak features remain unassigned in each. One rather puzzling band is observed weakly at 310 cm^{-1} in the Raman spectra of $Co_2(CO)_6C_2H_2$. It has no counterpart in the more stable compounds and is found to be strongly polarized. This is puzzling since this means that there appear to be more polarized bands than there are totally symmetric modes! These considerations together with the recognized difficulty of obtaining the compound in a pure state lead us to attribute this band to an impurity.

The general aspects of the above discussion hold for all of the compounds which have been the subject of the present study. Additional features also appear, characteristic of the individual compounds. Thus, in $Fe_2(CO)_6S_2$, the S–S stretching mode gives rise to a band at 555 cm^{-1} in both infrared and Raman spectra.

In the case of the iron compound, the assignment of ν(S–S) completes the discussion of the Raman spectrum. For the other compounds other features occur, originating, essentially, in ligand-only vibrations. Interestingly, there is no band corresponding to ν(C≡C) in many of our spectra, notwithstanding its rather clear assignment in the infrared. An exception is the parent compound (R = R′ = H), where a medium-intensity, strongly polarized band at ~1405 cm^{-1} is assigned to this mode.

Table III[a]

Assignment	Ligand[a]		Complex
C–H str	2920	$A_1' \rightarrow A_1$	2903 (IR), 2905 (R, p)
	2975	$A_2'' \rightarrow B_1$	2970 (R), 2963 (IR), 2944 (R, p?), 2938 (IR)
	2975	$E' \rightarrow A_1 + B_2$	
	2961	$E'' \rightarrow A_2 + B_1$	
C=C str	2313	$A_1' \rightarrow A_1$	1630 (IR) (R not obsd)
C–H bend	1379	$A_1' \rightarrow A_1$	1362 (IR), 1360 (R)
	1380	$A_2'' \rightarrow B_1$	
	1468	$E' \rightarrow A_1 + B_2$	1427 (IR), 1440 (IR)
	1447	$E'' \rightarrow A_2 + B_1$	1460 (R), 1480 (R)
C–C str	697	$A_1' \rightarrow A_1$	764 (IR)
	1126	$A_2'' \rightarrow B_1$	1125 (IR)
CH_3 rock	1050	$E' \rightarrow A_1 + B_2$	1060 (IR), 1040 (IR), 1010 (IR)
	1029	$E'' \rightarrow A_2 + B_1$	

[a] Values in cm^{-1}. [b] D_{3h} symmetry; values from G. Hertzberg, "Infrared and Raman Spectra", Van Nostrand, New York, N.Y., 1945, p 358.

In this compound our Raman data again lead us to change an assignment of Iwashita et al. A weak band at ~3115 cm^{-1} is clearly depolarized and so is assigned to the antisymmetric C–H stretch. This reverses the previous assignment of the two strong infrared-active bands seen in this region (the second peak is not Raman active). If our conclusion is correct, this would be a rather novel aspect of coordination of the acetylene ligand.

For $Co_2(CO)_6C_2(CH_3)_2$ the interpretation of the Raman spectra in the ν(C–H) and δ(C–H) regions is relatively clear and is detailed in Table III, where a comparison with the free-ligand values is given. However, there are no features which can be associated with ν(C–C) or $\rho(CH_3)$ in the Raman. For the compounds with R = R′ = CF_3, it may well be that a band at 1640 cm^{-1} is related to ν(C≡C), although the similar assignment of a strong band at ~1600 cm^{-1} in the infrared spectrum suggests that it may be necessary to find an alternative explanation for the 1640-cm^{-1} Raman peak. In this compound there is a series of bands between 660 and 820 cm^{-1} which, no doubt, correlate with ν(C–C) and $\delta(CF_3)$ frequencies in the free ligand between 603 and 900 cm^{-1}.[16]

Experimental Section

Compounds were generally prepared by the well-known method involving the reaction of $Co_2(CO)_8$ with a small excess (5–10%) of the appropriate alkyne in petroleum ether under an inert atmosphere.[17] Although the reaction subsides after 2–3 h, the reaction mixtures were left for 1 day before separation was attempted.

Gaseous alkynes were condensed in evacuated liquid N_2 cooled thick-walled glass vials which contained the carbonyl solutions. The vials were sealed and allowed to stand overnight at room temperature. The preparation of $Co_2(CO)_6C_2(CF_3)_2$ requires rather more drastic conditions.[18] Reaction mixtures were first filtered and the solutions chromotographed on alumina with petroleum ether or eluent. Products were obtained either by low-temperature crystallization or, more simply, by removal of the solvent. $Co_2(CO)_6C_2(CF_3)_2$ was sublimed and $Co_2(CO)_6C_2H_2$ was distilled under vacuum just before use. Purity was checked by analysis and thin-layer chromotography (adsorbant silica gel G according to Stahl; eluent petroleum ether).

$Co_2(CO)_6C_2(COOH)_2$ is insoluble in petroleum ether and the above procedure could not be used. It was collected as precipitate from the reaction mixture, dissolved in diethyl ether, and crystallized at low temperature.

Infrared spectra were recorded on a Perkin-Elmer 325 spectrometer. KBr and CsI cells were used. Raman spectra were obtained by a Spex 1401 spectrometer equipped with a Spectra Physics 165 mixed-gas laser. Solid-state spectra were recorded by using sealed capillary tubes and solution spectra using a small closed cell, purged of air with CO.

Acknowledgment. P.L.S. is indebted to the British Council for partial financial support.

Registry No. $Co_2(CO)_6(HC_2H)$, 12264-05-0; $Co_2(CO)_6(CH_3C_2CH_3)$, 12282-08-5; $Co_2(CO)_6(C_6H_5C_2C_6H_5)$, 14515-69-6; $Co_2(CO)_6(COOCH_3C_2COOCH_3)$, 37685-64-6; $Co_2(CO)_6(CF_3C_2CF_3)$, 12557-89-0; $Fe_2(CO)_6S_2$, 58500-79-1; $Co_2(CO)_6(n\text{-}C_3H_7C_2\text{-}n\text{-}C_3H_7)$, 34766-99-9; $Co_2(CO)_6(CH_2N(C_2H_5)_2C_2CH_2N(C_2H_5)_2)$, 61395-31-1; $Co_2(CO)_6(CH_3C_2C_6H_5)$, 53556-74-4; $Co_2(CO)_6(HC_2\text{-}t\text{-}C_4H_9)$, 56792-69-9; $Co_2(CO)_6(HC_2\text{-}i\text{-}C_5H_{11})$, 61395-32-2; $Co_2(CO)_6(HC_2C_6H_5)$, 12154-91-5; $Co_2(CO)_6(CH_2ClC_2CH_2Cl)$, 37685-62-4.

Supplementary Material Available: Normal-coordinate calculations on CO vibrators and tables of force and interaction constants of $Co_2(CO)_6(RC_2R')$ species and of $Fe_2(CO)_6S_2$ (5 pages). Ordering information is given on any current masthead page.

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Organocobalt Cluster Complexes. 21. Conversion of Halomethylidynetricobalt Nonacarbonyl Complexes to the Tricobaltcarbon Decacarbonyl Cation by the Action of Aluminum Halides. A New and Useful Route to α-Functional Alkylidynetricobalt Nonacarbonyl Complexes[1,2]

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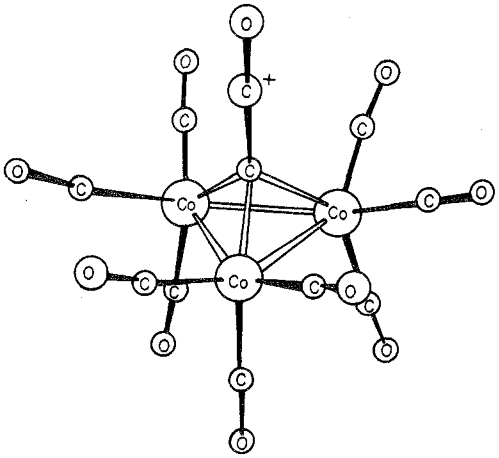
The action of aluminum halides, AlX_3 (X = Cl, Br, I), on halomethylidynetricobalt nonacarbonyl complexes, $XCCo_3(CO)_9$ (X = Cl, Br), results in formation of the acylium haloaluminate salt $(OC)_9Co_3CCO^+[AlX_4{\cdot}AlX_3^-]$, even when the reaction is carried out under nitrogen. Addition of a diversity of nucleophiles (alcohols, phenols, amines, thiols, R_4Sn compounds, reactive aromatics, silicon hydrides) to such reagents produces cluster complexes of type $YC(O)CCo_3(CO)_9$ with Y = RO, ArO, RR′N, RS, R, Ar, H) in moderate to good yields. The possible mechanism of this novel Co-to-C carbon monoxide transfer is discussed.

Introduction

We have reported recently the preparation (eq 1) and chemistry of the hexafluorophosphate salt of the tricobaltcarbon decacarbonyl cation, I.[3] The reaction of this salt with a broad spectrum of nucleophiles provided access to many new functionally α-substituted alkylidynetricobalt nonacarbonyl complexes. We report here a new route to reagent I, the discovery of which, in contrast to that shown in eq 1, was entirely serendipitous.

$$(OC)_9Co_3CCO_2R + (EtCO)_2O + H^+PF_6^- \rightarrow (OC)_9Co_3CCO^+PF_6^- + EtCO_2R + EtCO_2H \qquad (1)$$



I

In 1970, Dolby and Robinson[4] described a new, general synthesis of benzylidynetricobalt nonacarbonyl complexes from chloro- or bromomethylidynetricobalt nonacarbonyl (eq 2).

$$ClCCo_3(CO)_9 + ArH \xrightarrow{AlCl_3/CH_2Cl_2} ArCCo_3(CO)_9 \qquad (2)$$

At that time we were particularly interested in developing new routes to alkylidynetricobalt nonacarbonyls, $RCCo_3(CO)_9$ (R = alkyl), and the fact that the halomethylidynetricobalt nonacarbonyls were reactive Friedel–Crafts halides suggested to us a possible route to such compounds based on known organotin chemistry.

Tetramethyltin reacts with acyl chlorides in the presence of aluminum chloride as shown in eq 3.[5] It therefore might have been expected that the reaction of tetramethyltin with $ClCCo_3(CO)_9$ in the presence of aluminum chloride would give the methylated complex $CH_3CCo_3(CO)_9$. However, when this reaction was carried out in dichloromethane solution under a nitrogen atmosphere, the product which was isolated (in 26%

$$(CH_3)_4Sn + RC(O)Cl \xrightarrow{AlCl_3} RC(O)CH_3 + (CH_3)_3SnCl \qquad (3)$$