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^{1}H and ^{13}C NMR Studies of Acetylenic Complexes of $Co_2(CO)_8$

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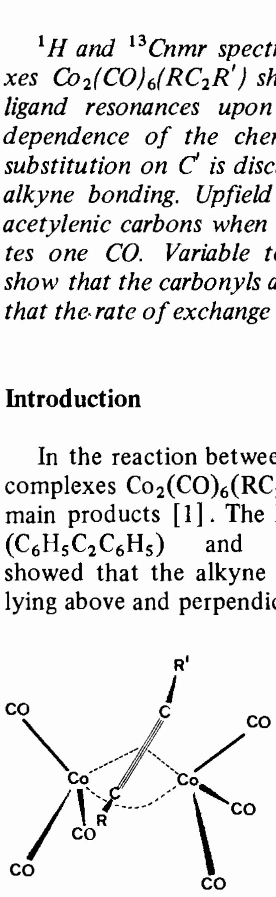
^{1}H and ^{13}Cnmr spectra of the acetylenic complexes $Co_2(CO)_6(RC_2R')$ show downfield shifts of the ligand resonances upon complexation. The slight dependence of the chemical shift of C from the substitution on C' is discussed in terms of the metal–alkyne bonding. Upfield shifts are observed for the acetylenic carbons when L (P- or As-ligand) substitutes one CO. Variable temperature ^{13}Cnmr spectra show that the carbonyls are rapidly interchanging and that the rate of exchange depends on R and R'.

Introduction

In the reaction between $Co_2(CO)_8$ and alkynes the complexes $Co_2(CO)_6(RC_2R')$ (1) are easily formed as main products [1]. The X-ray analysis of $Co_2(CO)_6(C_6H_5C_2C_6H_5)$ and $Co_2(CO)_6(t\text{-}C_4H_9C_2t\text{-}C_4H_9)$ showed that the alkyne is bridging the cobalt atoms lying above and perpendicular to their axis [2].



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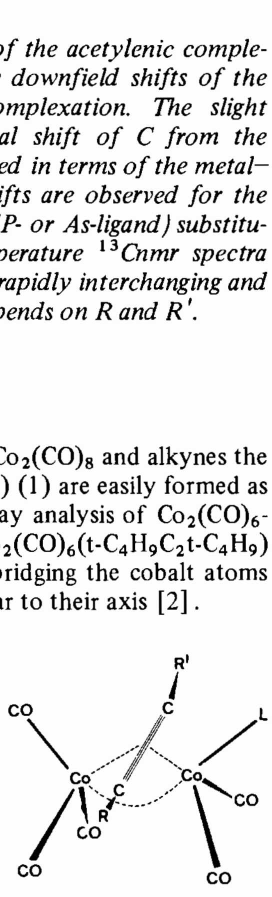

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A model considering the alkyne as a monodentate ligand with each cobalt in a dsp^3 trigonal bipyramidal state was adopted for a simple MO claculation [3]. Spectroscopic studies in order to understand the particular nature of the acetylene upon complexation have shown the similarity in the geometry of electronically excited acetylenes and of the coordinated alkynes [4]. Hybridization of the acetylenic carbons intermediate between sp and sp^2 has been suggested by the determination of the $^1J_{C-H}$ in a ^{13}C enriched acetylene sample of $Co_2(CO)_6(HC_2H)$ [5]. More recently a detailed Raman investigation has assigned the fundamental modes of the "core" $Co_2(RC_2R')$ of some complexes and the six modes of CO stretching. Approximate values of the force constants calculated on the basis of a distorted D_{3h} model have been easily correlated with the properties of the R groups [6]. In another study the IR-inactive A_2 frequencies have been obtained from the ^{13}CO isotopic satellites, and the force constants have been calculated, on the basis of the C_{2v} symmetry, by the "cosβ method" [7].

We have undertaken a ^{1}H and ^{13}C NMR investigation of (1) and of $Co_2CO)_5L(RC_2R')$ (2) to study their dynamic behaviour and the coordination shifts in acetylenic complexes.

Experimental

The $Co_2(CO)_6$(alkyne) complexes were synthesized according to the literature methods [1]; purity was checked by TLC, IR and mass spectrometry.

$Co_2(CO)_5[As(C_6H_5)_3](HC_2H)$ and $Co_2(CO)_5[P(nC_4H_9)_3](C_6H_5C_2C_6H_5)$ were already reported [8]. $Co_2(CO)_5[P(C_2H_5)_2C_6H_5](HC_2H)$ and $Co_2(CO)_5[P(C_2H_5)_2C_6H_5](HC_2tC_4H_9)$ have been prepared and characterised as follows.

$Co_2(CO)_5[P(C_2H_5)_2C_6H_5](HC_2H)$

1.5 g (~9 mmol) of diethylphenylphosphine was added with stirring to an n-heptane solution of 1.4 g. (4.4 mmol) of $Co_2(CO)_6(HC_2H)$. The mixture was allowed to react at 50 °C for 3 hr under nitrogen. The filtered solution was concentrated under vacuum and the residue chromatographed on a silica gel column. Elution with petroleum ether gave the unreacted complex first, followed by $Co_2(CO)_5[P(C_2H_5)_2C_6H_5](HC_2H)$ as a dark red band, which was collected and evaporated to give 0.9 g. of viscous oil (yield 45%). *Anal.* Calcd. for $C_{17}H_{17}Co_2O_5P$: C 45.36; H 3.81; Co 26.19; O 17.77; P 6.88%. Found: C 45.1; H 3.9; Co 26.4%. IR (n-heptane) 2068 (s), 2014 (s), 2007 (s), 1995 (m) cm^{-1}.

$Co_2(CO)_5[P(C_2H_5)_2C_6H_5](HC_2tC_4H_9)$

Similarly, 1.7 g (~10 mmol) of diethylphenylphosphine and 1.8 g (5 mmol) of $Co_2(CO)_6(HC_2tC_4$-

H_9) were reacted at 30 °C for 4 hr in n-heptane. The reaction gave 1.5 g of $Co_2(CO)_5[P(C_2H_5)_2C_6H_5](HC_2tC_4H_9)$ as dark red viscous oil (yield 60%). *Anal.* Calcd. for $C_{21}H_{25}Co_2O_5P$: C 49.82; H 4.98; Co 23.28; O 15.80; P 6.12%. Found: C 50.0; H 5.1; Co 22.9%. IR (n-heptane) 2062 (s), 2010 (s), 2003 (s), 1995 (m) cm^{-1}.

Dicobaltoctacarbonyl, alkynes and P- and As-ligands were obtained commercially. Solvents, as reagent grade, were dried and purified by the usual methods.

Deuterated solvents were purchased from NMR Ltd. and were used directly after drying over molecular sieves. Solutions were sealed under vacuum in 10 mm tubes with addition of 0.05 *M* $Cr(acac)_3$ as an inert relaxation reagent and TMS as an internal standard. $CDCl_3$, CD_2Cl_2,CD_2Cl_2/CF_2Cl_2 and C_6D_5-CD_3 were the solvents in the temperature study. CD_3OD was used for IX, owing to its low solubility in common solvents.

^{1}Hnmr spectra were recorded on a Jeol–C60–HL and ^{13}Cnmr spectra on a Jeol–PFT–100 operating at 25.1 MHz in the Fourier transform mode. Chemical shifts are reported downfield positive with respect to internal TMS. Accumulations of 2,000–10,000 transients were performed at a spectral width of 5,000 Hz. The temperature was monitored by a Jeol JNM-DBT-P-5-H 100 E temperature control unit with a thermocouple approximately 1 cm above the sample (outside of the RF and decoupling coils).

Infrared spectra were measured by a Beckman Spectrophotometer IR 12; mass spectra were recorded with a Hitachi RMU-6H single focusing mass spectrometer. Elemental analysis (C, H) was carried out with a Model 185 C, H and N analyser (F and M Scientific Co.); cobalt was determined by a Perkin–Elmer Model 303 atomic absorption spectrophotometer with DCR 1.

Results and Discussion

^{1}H and ^{13}C Chemical Shifts

The ^{1}H chemical shifts of the proton bearing acetylenes and the ^{13}C chemical shifts of the carbonyls and of the acetylenic carbons (C and C′) are reported in the Table for (1) and (2). The large ^{1}H downfield shift upon complexation and the magnitude of $^4J_{H-H}$ in III suggest a reduction in the triple bond character and increase of double bond character consistent with our previous observations on the isoelectronic complexes $Cp_2Ni_2(RC_2R')$ [9].

In the majority of cases the ^{13}C chemical shifts of C and C′ show deshielding if compared with the chemical shifts of the free alkynes. The nature of the coordination shift of the unsatured ligands has not yet been completely clarified and it has given rise to some controversies [10]. First of all, the diamagnetic correction of the chemical shift, σ_d', should be taken into account as has been recently suggested [11]. Its absolute value should be fairly large in compounds involving Co–C bond, owing to its dependence on the atomic number, but it is expected to be almost constant in a homologue series. The downfield shift observed upon complexation means that the σ_p term cancels the upfield contribution of σ_d' to the shielding tensor. Changes in ΔE and in the ring currents of the Co_2C_2 entity can contribute to the deshielding of the coordinated acetylenic carbon, as well as the increase of $\langle Q_{AB} \rangle$ which is zero in the free alkyne [12]. Finally, the π-electron density of the ligand can play a non negligible role, as its decrease causes a downfield shift. According to the DewarnChatt–Duncanson model [13] the π-electron density decreases as the ligand-to-metal donation increases and the metal-to-ligand back-donation decreases. Electron releasing groups (*e.g.* CH_3; VI) show a large downfield shift, whereas electron withdrawing groups (*e.g.* COOH; IX) show a smaller one. The importance of the reduction in the multiple bond order to the net deshielding is also consistent with the $^1J_{C-H}$ value observed in I–IV and X.

In the asymmetrically substituted complexes the ^{13}C chemical shift of C is rather less sensitive to the nature of the substituent on C′ than it is in the free ligand; this behaviour is confirmed by the little variation (0.5 ppm) of the corresponding ^{1}H chemical shift. These observations suggest that the inductive effect of the substituent on C′ is hardly transmitted to C via multiple bond. The former triple bond is modified by the coordination of the alkyne to the metal in such a way that each carbon behaves nearly as an independent entity, sensitive only to the substituent directly bonded to it. Such behaviour can give rise to some "electronic asymmetry" inside the Co_2-C_2 core: this is confirmed by a recent report [14], which suggests that an electronic distortion due to the ligand in $Co_2(CO)_6(HC_2R)$ complexes is responsible for the slight infrared intensity of the $\nu(A_2)$ C–O stretching mode, which is IR inactive with the C_{2v} symmetry. The complexes (2) exhibit upfield shifts of both C and C′, if compared with the corresponding (1). An increase of the negative charge on the metal, owing to the better σ-donor properties of L, reinforces the metal-to-alkyne back-donation causing the shielding of the acetylenic carbons.

The chemical shifts of the carbonyls are in the range of 6 ppm. This small variation does not permit a good correlation between the value of δ_{CO} and some other CO parameter, *e.g.* the CO stretching force constants [6–7]. However, the qualitative dependence of δ_{CO} from the properties of the R and R′ groups is clearly established, as the resonances are shifted to the downfield side of the range with electron donor groups and to the upfield side with

TABLE 1. ^1H and ^{13}C Chemical Shifts of $Co_2(CO)_6(RC_2R')$ (1) and $Co_2(CO)_5L(RC_2R')$ (2) Complexes.

Complex	R	R′	L	$\delta_{^1H}$ (CH)[a,b]		$\delta_{^{13}C}$ CO		C		C′
I	H	H	–	5.97 (1.80)		199.5			70.8	
II	H	C_6H_5	–	6.28 (2.93)		200.0		72.7 (77.7)		90.0 (83.3)
III	H	CH_3	–	6.02[c] (1.88)		199.5		73.0		90.8
IV	H	iC_5H_{11}	–	6.04		201.5		74.0 (67.8)		99.0 (84.4)
V	H	tC_4H_9	–	6.03 (1.98)		201.7		73.4 (66.8)		112.0 (93.6)
VI	CH_3	CH_3	–	–		200.9			94.4 (73.9)	
VII	CH_3	C_6H_5	–	–		200.2		94.2 (85.7)		91.6 (79.8)
VIII	C_6H_5	C_6H_5	–	–		199.3			91.0 (88.9)	
IX	COOH	COOH	–	–		199.5			81.0 (74.0)	
X	H	$COOCH_3$	–	5.82 (1.74)		199.7		73.5 (74.8)		76.9 (74.1)
XI	$COOCH_3$	$COOCH_3$	–	–		198.2			79.0 (75.1)	
					199.2 (2)[d]		195.7 (1)[d]			
XII	CF_3	CF_3	–	–		195.6			29.4	
					196.5 (2)[e]		192.8 (1)[e]			
XIII	H	H	$As(C_6H_5)_3$	–	207.0 (2)		202.9 (3)		70.2	
XIV	H	H	$P(C_2H_5)_2C_6H_5$	–	207.4 (2)		204.6 (3)		69.6	
XV	H	tC_4H_9	$P(C_2H_5)_2C_6H_5$	–	208.0 (2)		203.6 (3)	71.2 (66.8)		108.7 (93.6)
XVI	C_6H_5	C_6H_5	$P(nC_4H_9)_3$	–	207.3 (2)		203.5 (3)		89.2 (88.9)	

[a] In parenthesis, values of the free ligand.. [b] J_{C-H} (±5 Hz): 223 (I), 220 (II), 222 (IV), 221 (V), 225 (X). [c] $^4J_{H-H}$ ~1.5 Hz. [d] At −106 °C. [e] At −92 °C.

electron withdrawing groups. Changes in the electron density on the metal reflect in variations of the C–O π bond order and hence of the shielding [15]. The same argument holds for the observed downfield shift of the carbonyls when one carbonyl is substituted by L. The effect is transmitted to less extent to the carbonyls bonded to the cobalt where the substitution does not occur. This feature is consistent with the observations in the monophopshine derivative of $C_{10}H_{12}Fe_2(CO)_6$ [16], and in the phosphine derivatives of $Os_3(CO)_{12}$ [17] and of $FeCo_2(CO)_9S$ [18].

Dynamic Behaviour

In the symmetrically substituted complexes (1) two resonances are expected for the carbonyls in the ratio 1:2 for the apical and basal carbonyls; three resonances are predictable for the unsymmetrically substituted ones. Variable temperature ^{19}F nmr spectra of the structurally related $Rh_2(PF_3)_6(RC_2R')$ have shown these complexes to be stereochemically nonrigid and a critical dependence of the activation energy on the nature of the substituent [19]. In the room temperature spectra of I–XII a unique broad signal is observed for the carbonyls. The lowering of the temperature down to –80 °C results in a progressive sharpening of that resonance. In that range of temperature the broadening is therefore due to the spin–spin coupling of the carbonyls with the cobalt ($I = 7/2$) [20, 21], and not to exchange.

Spectra at lower temperature are difficult to obtain for the limited solubility of some samples. However spectra down to –110 °C were recorded except that for IX and X (their solutions freeze at –85 °C and –95 °C respectively). One sharp signal is observed for the complexes I–VIII, whereas two signals with integrated intensities 2:1 are present in the limiting spectrum of XI and XII [T_c –101 °C (XI), –87 °C (XII)]. The higher energy of activation for the intramolecular exchange of the carbonyls in XII compared with that in XI and in the other complexes indicates that strongly electron withdrawing substituents on the alkyne increase the barrier to the scrambling of the carbonyls. These qualitative observations are in accord with those reported for the isostructural $Rh_2(PF_3)_6(RC_2R')$ [19] and for the $Fe(CO)_3$ olefin complexes [22]. The geometry of (1) is such that these results do not allow any distinction between localised or delocalised scrambling of the CO. We have then examined the ^{13}C spectra of (2) in which the $Co_2(CO)_6$ moiety is no longer symmetric and in which recent infrared studies have shown that L is substituting one carbonyl in an apical position [23]. In this case two signals are present even in the room temperature spectra with integrated intensities 2:3; the peaks are broad as a result of the quadrupolar coupling as confirmed by the observation of two narrow doublets when the spectra are obtained in a viscous solvent [24]. Therefore in (2) the interchange of the carbonyls is localised at each cobalt and we suggest that this is the case also in (1). Further support to this idea comes both from the facile internuclear CO scrambling observed in several phosphine derivatives of $Os_3(CO)_{12}$ [17] and of $FeCo_2(CO)_9S$ [18] and from variable temperature ^{13}Cnmr studies on several binuclear complexes without bridging carbonyls that have shown that the exchange of CO is localised on each metal: $Fe_2(CO)_6(RC_2R')_2$ [25], $Fe_2(CO)_5$(acenaphthylene) [26], $Fe_2(CO)_6C_8H_{10}$ [27], $Fe_2(CO)_5(PEt_3)C_{10}H_{12}$ [16], $Mo_2(CO)_6$(guaiazulene) [28].

Several mechanisms may account for the localised site exchange of the carbonyls in (1) and (2): rotation about the Co–Co bond of one $Co(CO)_3$ moiety, polytopal rearrangement within each $Co(CO)_3$ moiety (the Berry mechanism) [29], fast rotation of the alkyne. The latter may be an independent motion or a concerted one with the motion of the CO. On the basis of the experimental results we have no way of distinguishing among the previous hypotheses. However, the intramolecular and intermolecular [30] CO exchange in the $Co_2(CO)_6(RC_2R')$ complexes exhibit a similar behaviour, *i.e.* the value of the activation energy increases with the electron withdrawing ability of the acetylene. Therefore the fairly good correlation established between the intermolecular exchange and the strength of the metal alkyne bond [30] suggests that this bond plays an important role also in the intramolecular exchange process.

High temperature spectra of (1) were observed in order to evaluate the cobalt–carbon coupling constant; severe decomposition occurred above 90 °C, at which the cobalt relaxation time is still too fast to allow the observation of well resolved multiplets [17, 24].

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