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^{13}C NMR Study of Methynyltricobalt Enneacarbonyls

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The ^{13}C NMR apical carbon resonances for a series of $Co_3(CO)_9CY$ complexes have been observed to be in the lowfield region (310–230 ppm). Variable temperature spectra have shown "thermal decoupling" of carbon from cobalt and scrambling of the carbonyls.

Introduction

Since the discovery of the very stable organometallic compounds $Co_3(CO)_9CY$[1], the unique feature of an aliphatic carbon bonded to three transition metals has prompted the investigation of their electronic structure by spectroscopic techniques and reactivity tests. Their high stability is noteworthy as indicated by the numerous and facile synthetic routes[2] and by the fragmentation pattern detected in their mass spectra[3]. I.r.[4] and X-ray[5] results allowed to describe these complexes in a valence bond language as constituted by the roughly octahedral cobalt environments, constricted in order to direct their axial orbitals towards the three tetrahedral-like orbitals of the apical carbon thereby giving the Co_3C moiety a trigonal pyramidal geometry. Furthermore it has been pointed out that the Co–C apical bond length (1.90 Å) could represent a shortening of this bond relative to the predicted value calculated on covalent radii. NMR spectroscopy has provided evidence of a high stabilization of the carbonium ions $Co_3(CO)_9CCHY^+$ [6]. For a better understanding of the nature of the apical carbon ^{13}C NMR has a unique potential; quite recently two papers on ^{13}C NMR studies of $Co_3(CO)_9CCHY^+$ [6] and $Co_3(CO)_8LCY$[7] have been published, but the apical carbon resonance was not reported.*

Results and Discussion

The ^{13}C chemical shifts are reported in Table I. The resonances of the apical carbon are in the downfield region in a range of ~75 ppm. These signals were quite difficult to detect because of the line broadening owing to the spin–spin coupling with the three cobalt atoms which are undergoing moderately rapid quadrupole induced relaxation (^{59}Co: I = 7/2). Low temperature spectra did improve the observation of these resonances but solubility prevented runs at such temperatures where thermal decoupling is completely efficient. At –40° C $W_{1/2}$ was still 45 Hz for II. The observed δ are difficult to reconcile with the formally sp^3 hybridization of CY. Some doubts, however, have already been cast on this hypothesis[2,8]. In order to understand the large downfield shift we may consider that CY is vividly reminiscent of triply bridging carbonyls, whose absorptions are the more downfield in the range of metal bonded carbonyls for each metal.** Relevant are

TABLE I. ^{13}C Chemical Shifts for $Co_3(CO)_9CY$ Complexes.

	Y	C–Y	CO	Others
I	H	263	200.2	
II	CH_3	296	200.3	CH_3 46.0
III	C_6H_5	286	200.9	C_6H_5: C_1 167.4, $C_{2,5}$ 130.1, $C_{3,6}$ 129.1, C_4 133.8
IV	CF_3	255	198.5	CF_3 133.2 (273)^a
V	$COOCH_3$	268	198.2	CO 198^b; CH_3 52.0
VI	F	309 (498)^a	199.1	
VII	Cl	276	198.5	
VIII	Br	269	199.0	
IX	I	234	198.6	

^{a} $^1J_{^{13}C-^{19}F}$. ^{b}Superimposed to the Co–CO signal.

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* Since the submission of this paper ^{13}C resonance for the apical carbon has been reported for neutral $Co_3(CO)_9CY$ and ions $Co_3(CO)_9CCHY^+$ (D. Seyferth, C.S. Eschbach, and M.O. Nestle, *J. Organomet. Chem.*, *97* C11 (1975)) and for $[(C_2H_5)_2N]_2C_2M_3(C_5H_5)_3$ (M = Co, Rh) (R.B. King, and C.A. Harmon, *VII ICOMC, Venice, September 1975).*

** Triply bridging carbonyl chemical shifts were reported for $(\eta^5\text{-}C_5H_5)_3Rh(CO)(C_6H_5C_2C_6H_5)$ (241.6 ppm)[9] and for $Rh_{12}(CO)_{30}^{2-}$ (237.4 ppm)[10]. δ's of doubly bridging carbonyls in cobalt complexes are reported at 243.1 ppm in $Co_4(CO)_{12}$[11] and at 251.2 ppm in $RhCo_3(CO)_{12}$[12].

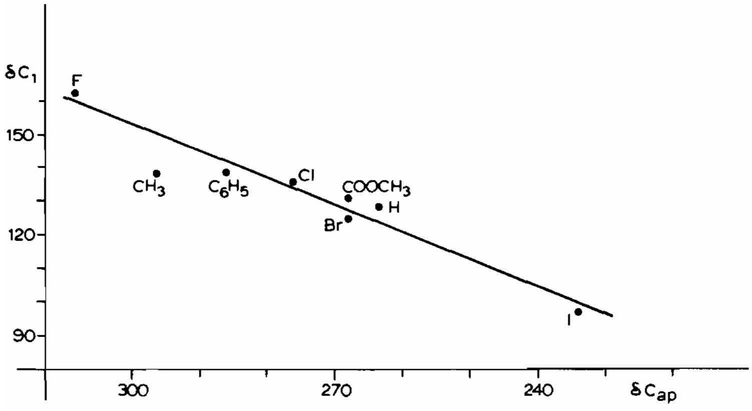

Fig. 1. Plot of δ C_1 of C_6H_5X *vs.* δC_{ap}(ppm).

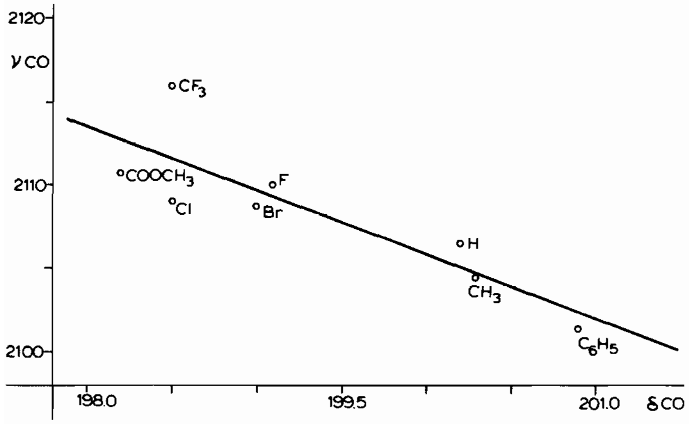

Fig. 2. Plot of νCO (cm^{-1}) *vs.* δCO (ppm).

also the δ's observed for the carbyne in $XW(CO)_4CCH_3$ (288.8, 288.1, 286.3; X = Cl, Br, I)[13] and for the carbide in $[Rh_6(CO)_{15}C]^{2-}$ (264.7 ppm)[14].

I.r. observations on the effect of the substituent on the C–Y stretching frequencies[2] suggested that the $Co_3(CO)_9C$ cluster behaves as an electron sink capable of π interaction with the substituent. The above argument is supported by the dependence of the chemical shift of the apical carbon on the substituent; the chemical shift of C_1 in monosubstituted benzenes[15] is plotted *vs.* δ of C_{ap} showing a good linear relationship (Figure 1).

The chemical shift of the substituents is a probe of the electron deficiency of the apical carbon; quite remarkable at this purpose is the observation of the signal at τ –2.14 in the ^1H NMR spectrum of I ($CDCl_3$ solution) although other contributions cannot be excluded as determining this dramatic downfield shift. The ^1H chemical shift and chemical evidence led to the suggestion of an acidic nature of the hydrogen atom[16].

From these results a picture of the Co_3C cluster as an electron reservoir analogous to an aromatic system appears to be the more satisfactory.

The highest νCO (totally symmetric)[2] are plotted in Figure 2 *vs.* the carbonyl chemical shifts. The effect of the substituent is transmitted through the carbon–cobalt bond to the carbonyls with an upfield shift for electron withdrawing substituents. Similar correlations have been reported for other metal carbonyl derivatives[17]. Moderately rapid quadrupole induced relaxation of cobalt influences the linewidth of the carbonyls which appear as broad signals. Whereas solubility prevented the observation of the apical carbon in the low temperature spectra, ^{13}CO enriched samples of II, III, VI were run up to –90° C allowing the observation of the CO signals with significant narrowing ($W_{1/2}$ 7Hz at –90° C). The $W_{1/2}$ in the room temperature spectra of the complexes are quite different ranging from 40 to 60 Hz. The thermal decoupling has been reported for cobalt and manganese carbonyl derivatives as an experimental technique allowing the sharpening of broad resonances[18]. Quadrupole effects have been more deeply investigated in the ^1H NMR spectra of boron derivatives[19]; several examples of well resolved multiplets and decoupled spectra have been reported for the same compound at different temperatures[20]. In order to determine the $J_{^{13}C-^{59}Co}$ and evaluate its influence on the different linewidths observed we have run spectra at high temperature, *i.e.* in a condition where the inefficient quadrupole induced relaxation should allow the observation of resolved multiplets. A progressive broadening of the resonances has been observed but unfortunately the high rate of decomposition above 120° C prevented the determination of J_{C-Co}.

Two resonances were expected for the carbonyls in the ratio 2:1 on the ground of the X-ray results[5]; the observation of one single sharp CO signal in the low temperature spectra is therefore indicating that an intramolecular exchange process is operating if considerations on accidental superposition are avoided.

Experimental

$Co_3(CO)_9CY$ were prepared by published methods[21]. Deuterated solvents were purchased from NMR Ltd. and were used directly after drying over molecular sieves. The complexes were enriched 50–60% by stirring for three days at 45° C in the presence of <1 atmosphere of 90% enriched ^{13}CO (Stohler Isotope Chemicals). Sample purity after enrichment was confirmed by mass spectroscopy. Solutions 0.1–0.2*M* were sealed under vacuum in 10 mm tubes with the addition of 0.05*M* $Cr(acac)_3$ as an inert relaxation reagent and tetramethylsilane as an internal standard. Pmr spectra were recorded on a Jeol C60-HL and ^{13}C NMR 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 each temperature for resonances others than apical carbon for which 80,000–120,000 transients were necessary. For long runs block accumulations of 100 transients before transformation, $\pi/5$ flipping angle, 10,000 Hz spectral width and 0.5 sec repetition time were used. The temperature was monitored by a Jeol JNM-DBT-P-5-H 100E temperature control unit with a thermocouple approximately 1 cm above the sample (outside of the RF and decoupling coils).

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