

terms involving NaAlCl_4 and AlCl_4^- (which partially cancel one another) were neglected. From the heats of formation of the gaseous chloride ion (-58.0 kcal/mole) and the gaseous, monomeric aluminum chloride molecule (-140.42 kcal/mole),¹⁶ the dissociation energy of the $\text{AlCl}_3\text{-Cl}^-$ bond is calculated to be 78 ± 7 kcal/mole.

The heat of breaking a single Al-Cl-Al bridge in Al_2Cl_6 is 14.5 kcal/mole^{17,18} which is 63 kcal/mole weaker than the $\text{AlCl}_3\text{-Cl}^-$ bond. This is in accord with the electron diffraction data of Palmer and Elliott,¹⁹ who found that the bond distance of the bridging chloride in Al_2Cl_6 (2.21 ± 0.04) was larger than for terminal chlorine in Al_2Cl_6 (2.06 ± 0.04) and larger than the Al-Cl distance in the NaAlCl_4 (2.13 ± 0.03). Similarly, Klemperer²⁰ found that the force constants for bridging and terminal chlorines in Al_2Cl_6 are approximately 1.3 and 2.5×10^5 dynes/cm, respectively.

The donor strength of the chloride ion toward aluminum chloride as reference acceptor cannot be compared with other donors since the data are lacking. The most extensive series of measurements give only the heat of forming the solid complex,^{21,22} and it will be necessary to have many more gas phase heats of complexing before achieving real understanding of the contributions of steric effects and reorganization energy to the bond strength.

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CONTRIBUTION FROM THE MELLON INSTITUTE,
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A Tetranuclear Nickel Atom Cluster Derived from Hexafluorobut-2-yne and Nickel Carbonyl^{1,2}

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Reactions between hexafluorobut-2-yne ($\text{CF}_3\text{C}\equiv\text{CCF}_3$) and several metal carbonyl derivatives have been

(1) The initial phases of this work were carried out at Harvard University, Cambridge, Mass., and are described in the Ph.D. thesis (1962) of J. R. Phillips.

(2) The present note constitutes part XXXIV of the series "Chemistry of the Metal Carbonyls" [for part XXXIII see A. Forster, J. B. Wilford, and F. G. A. Stone, *J. Chem. Soc.*, 6519 (1965)] and part XIV of the series "Organometallic Chemistry of the Transition Metals" [for part XIII, see R. B. King and A. Fronzaglia, *J. Am. Chem. Soc.*, **88**, 709 (1966)].

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reported. These studies have resulted in the isolation of the mononuclear hexafluorobut-2-yne complexes $\pi\text{-(CF}_3)_2\text{C}_2\text{Mn(CO)}_2(\pi\text{-C}_5\text{H}_5)_5$ and $[(\pi\text{-CF}_3)_2\text{C}_2]_3\text{W(NC-CH}_3)_6$,⁶ the binuclear complexes $\pi\text{-(CF}_3)_2\text{C}_2\text{Co}_2(\text{CO})_6$ and $\pi\text{-(CF}_3)_2\text{C}_2\text{Ni}_2(\pi\text{-C}_5\text{H}_5)_2$,⁷ the mononuclear tetrakis(trifluoromethyl)cyclopentadienone complexes $[\pi\text{-(CF}_3)_4\text{C}_4\text{CO}]\text{Fe(CO)}_3$,⁷ $[\pi\text{-(CF}_3)_4\text{C}_4\text{CO}]\text{Co}(\pi\text{-C}_5\text{H}_5)_5$,⁸ and $[\pi\text{-(CF}_3)_4\text{C}_4\text{CO}]\text{Rh}(\pi\text{-C}_5\text{H}_5)_9$ and the mononuclear hexakis(trifluoromethyl)benzene complex $[\pi\text{-(CF}_3)_6\text{-C}_6]\text{Rh}(\pi\text{-C}_5\text{H}_5)_9$. We now describe a novel nickel complex $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$.

Experimental Section

For the preparation of $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$ a mixture of tetracarbonylnickel and hexafluorobut-2-yne was heated for about 24 hr at 50° in a sealed evacuated stainless steel reaction vessel.¹⁰ After cooling to room temperature the reaction vessel was opened, and the product was washed out with pentane in small portions, until the originally deep red-purple washings were only weakly colored. After removal of pentane (25 mm), the red-violet residue was sublimed at $50\text{--}80^\circ$ ($0.1\text{--}0.5$ mm) to afford $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$, mp $119\text{--}121^\circ$ dec, exploding in air at 174° . In a typical preparation using a reaction vessel of 150-cc capacity, 13.0 ml (17.2 g, 101 mmoles) of tetracarbonylnickel and 8.0 g (49.4 mmoles) of hexafluorobut-2-yne gave 4.13 g (31% yield) of $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$.

The formula $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$ was established most conclusively by high-resolution mass spectrometry (Table I), but was confirmed by elemental analyses.¹¹

Anal. Calcd for $\text{C}_{15}\text{F}_{18}\text{Ni}_4\text{O}_8$: C, 22.4; H, 0.0; F, 42.4; Ni, 29.2. Found: C, 23.2, 22.4; H, 0.3, 0.0; F, 41.7; Ni, 28.5.

The dark purple, pungent-smelling crystals turned brown and became more malodorous upon standing for several days in air. Pentane solutions of the purple solid oxidize in air within several hours, giving a trimer of hexafluorobut-2-yne (parent molecular ion C_6F_8^+) as the main volatile component. Degradation of $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$ with HCl gas at $40\text{--}50^\circ$ for 46 hr in an evacuated bulb afforded 1,1,1,4,4,4-hexafluoro-2-butene (64% yield), identified by its infrared and mass spectra. As gauged by the color of a pentane solution of $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$, no reaction occurred with triphenylphosphine until three equivalents had been added. At this point the solution immediately decolorized with separation of a pale brown precipitate, which was not characterized.

The infrared spectrum of $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$ (cyclohexane solution, high-resolution conditions¹²) showed the following absorptions (cm^{-1}) in the regions of interest: ν_{CO} : 2115 (vs), 2103 (vs); $\nu_{\text{C-C}}$: 1565 (w), 1550 (w); $\nu_{\text{C-F}}$: 1235 (w), 1220 (m), 1205 (s), 1165 (m), 1153 (m). The ^{19}F nmr spectrum of $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$ exhibited two groups of absorptions of equal intensity at 50.3 and 54.5 ppm, upfield from internal CCl_3F in dichloromethane solutions.

Discussion

Consideration of a structure for $[\pi\text{-(CF}_3)_2\text{C}_2]_3\text{Ni}_4(\text{CO})_8$ must be guided by the following requirements: (1) Degradation with hydrogen chloride affords $\text{CF}_3\text{-CH=CHCF}_3$, indicating that the $\text{CF}_3\text{C}\equiv\text{CCF}_3$ ligands have not condensed to a ring system, as in previously

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(11) Owing to the presence of carbon, nickel, and especially fluorine, a direct oxygen analysis could not be performed.

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TABLE I
MASS SPECTRUM OF $[\pi-(CF_3)_2C_2]_3Ni_4(CO)_3$:
PRINCIPAL PEAKS ABOVE m/e 300^a

m/e	Relative intensity ^b	Assignment	m/e	Relative intensity ^b	Assignment
810	25 ± 2	C ₁₈ F ₁₈ Ni ₄ O ₃ ⁺	705	2.5 ± 0.5	C ₁₂ F ₁₇ Ni ₄ ⁺
808	60 ± 3		703	4 ± 1	
806	120 ± 6		701	5 ± 1	
804	154 ± 5		699	4 ± 1	
802	100				
789	16 ± 2	C ₁₈ F ₁₇ Ni ₄ O ₃ ⁺	618	10 ± 2	C ₁₀ F ₁₂ Ni ₄ O ₂ ⁺
787	29 ± 4		616	19 ± 3	
785	40 ± 6		614	25 ± 4	
783	27 ± 3		612	17 ± 3	
780	20 ± 3	C ₁₄ F ₁₈ Ni ₄ O ₂ ⁺	590	15 ± 3	C ₆ F ₁₂ Ni ₄ O ⁺
778	35 ± 8		588	28 ± 5	
776	48 ± 11		586	37 ± 4	
774	31 ± 6		584	28 ± 5	
752	10 ± 3	C ₁₈ F ₁₈ Ni ₄ O ⁺	562	27 ± 2	C ₈ F ₁₂ Ni ₄ ⁺
750	20 ± 4		560	60 ± 6	
748	25 ± 5		558	81 ± 7	
746	15 ± 3		556	54 ± 5	
724	10 ± 3	C ₁₂ F ₁₈ Ni ₄ ⁺	464	90 ± 12	C ₃ F ₁₀ Ni ₃ ⁺
722	18 ± 6		462	170 ± 16	
720	25 ± 7		460	150 ± 17	
718	16 ± 4				
		C ₄ F ₆ Ni ₄ ⁺	400	45 ± 13	C ₃ F ₈ Ni ₂ ⁺
			398	95 ± 25	
			396	135 ± 35	
			394	90 ± 25	
		C ₄ F ₄ Ni ₃ ⁺	368	50 ± 7	C ₄ F ₄ Ni ₃ ⁺
			366	130 ± 16	
			364	165 ± 22	
		C ₄ F ₄ Ni ₃ ⁺	302	80 ± 10	C ₄ F ₄ Ni ₃ ⁺
			300	160 ± 30	
			298	140 ± 20	

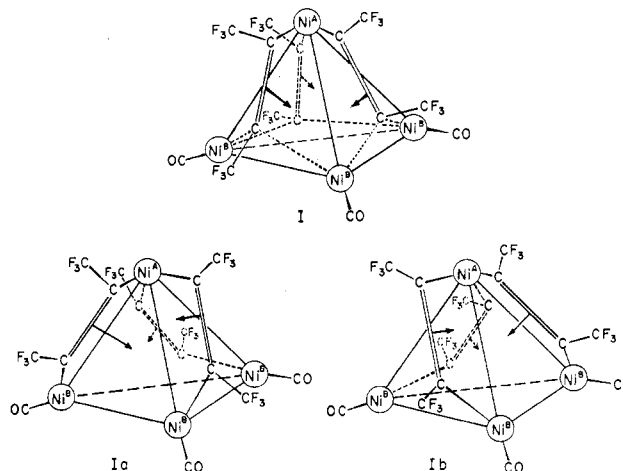
^a Spectra were taken at 70 eV IP using an AEI Industries Ltd. MS9 spectrometer. ^b These intensities are reported relative to m/e 802 = 100. Ranges are given based on spectra of independent samples prepared in three different laboratories.

cited complexes.^{7,9} (2) The high-resolution ¹⁹F nmr spectrum with reasonable chemical shift shows that the compound is diamagnetic. The two resonances of equal relative intensities suggest that all three hexafluorobutene ligands are equivalent but that the two ends of each hexafluorobutene unit are nonequivalent. This situation corresponds exactly to that present in the tungsten-acetylene complexes (RC₂R')₃WL [R and R' = C₆H₅ or C₂H₅, L = CO,¹³ R = R' = CF₃, L = CH₃CN⁶]. (3) The infrared spectrum exhibits two strong terminal metal carbonyl bands in accord with a distribution of the three carbonyl groups about a C₃ axis. There are no bands in the regions for bridging acyl or ketonic carbonyl groups. (4) The unusually high volatility of $[\pi-(CF_3)_2C_2]_3Ni_4(CO)_3$ for a tetranuclear complex with a molecular weight of 802 makes likely a compact structure. These conditions severely restrict the available structures for the complex.

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We are led to propose the delocalized structure I which may usefully be considered to be a resonance hybrid of the two canonical forms Ia and Ib. In this structure, the four nickel atoms are arranged in a trigonal pyramid,¹⁴ with the three basal nickel atoms (Ni^B) equivalent but different from the apical nickel atom (Ni^A). Each basal nickel atom Ni^B is bonded to one carbonyl group, two other basal nickel atoms, the apical nickel atom, and one end of each of two C₄F₆ units. The apical nickel atom is bonded to the three basal nickel atoms and to the other ends of the C₄F₆ groups. By the σ bonding, the carbon-carbon triple bonds are reduced to double bonds. The "hexafluorobutene" moieties are each located above one of the Ni^BNi^ANi^B faces of the trigonal pyramid. The equivalent contributions of Ia and Ib to I will make the carbon-carbon multiple bonds of the CF₃C=CCF₃ moieties parallel to the Ni^BNi^ANi^B faces. A model shows that the apical nickel atom Ni^A and the three σ -bonded carbon atoms could be essentially coplanar.

The novelty of this proposed structure for $[\pi-(CF_3)_2C_2]_3Ni_4(CO)_3$ makes valuable a brief qualitative molecular orbital description of its bonding. It is clearest to consider one of the canonical forms Ia, realizing that resonance with other canonical form Ib, with equivalent bonding, will represent the actual structure (I).



The local symmetry of Ni^A is C_{3v}.¹⁵ Representations of bonding orbitals are 2A (d_{z²}, s, p_z) and 2E (p_x and p_y, d_{x²-y²} and d_{xy}, d_{yz} and d_{xz}). To form the two sets of three equivalent bonds, the d_{z²}, d_{x²-y²} and d_{xy}, and s, p_x, and p_y orbitals are used; the d_{xz} and d_{yz} orbitals are filled and nonbonding, and the p_z orbital is vacant. The basal nickel atoms have approximately C_{4v} local symmetry,¹⁵ with representations 2A₁ (d_{z²}, s, p_z), B₁ (d_{x²-y²}), and E (p_x and p_y, d_{xz} and d_{yz}). The various bonds are formed using the d_{x²-y²}sp³ hybrid orbitals, with the d_{xy}, d_{xz}, and d_{yz} orbitals filled but nonbonding

(14) Since the Ni^ANi^B and Ni^BNi^B bonds need not necessarily be of the same length, the configuration of the four nickel atoms in $[\pi-(CF_3)_2C_2]_3Ni_4(CO)_3$ need not necessarily be a regular tetrahedron. To emphasize this point in the discussion, the configuration of the four nickel atoms is described as a trigonal pyramid, although they could be tetrahedrally disposed.

(15) For the apical nickel atom, Ni^A, the z axis is taken perpendicular to the plane of the basal nickel atoms. For a basal nickel atom, Ni^B, the z axis is taken to be collinear with the presumably linear carbonyl group attached to the nickel atom.

and leaving the d_{z^2} orbital vacant. By this procedure, each nickel "receives" 16 electrons.

Within the metal atom cluster, the vacant p_z orbital (A) of Ni^A and the d_{z^2} orbitals (A + E*) of the three Ni^B atoms interact to produce three bonding MO's, which are filled by the six π electrons from the three carbon-carbon double bonds (A + E) of the C_4F_6 groups, which are directed through the middle of the three faces. The metal cluster as a whole has two electrons less than the krypton configuration.

Thus the bonding in $[\pi-(CF_3)_2C_2]_3Ni_4(CO)_3$ is unusual in that the π bonds from the $\pi-(CF_3)_2C_2$ ligands are directed not just to one metal atom as is customary, but to a delocalized system of four metal atoms. It is well established that CO groups can bridge three metal atoms as in $[\pi-C_5H_5Ni]_3(CO)_2$ ¹⁶ and $Rh_3(CO)_{16}$ ¹⁷ and recently it has been established¹⁸ that the diphenylacetylene groups in the violet isomer of $(C_6H_5C\equiv CC_6H_5)_2Fe_3(CO)_8$ are located on opposite sides of a triangle of iron atoms. Species with structural features similar to those proposed for $[\pi-(CF_3)_2C_2]_3Ni_4(CO)_3$ may be intermediates in the metal carbonyl catalyzed trimerization of acetylenes.¹⁹

Acknowledgments.—R. B. K. is indebted to Mr. M. B. Bisnette for experimental assistance. M. I. B. thanks the Scientific Research Council for a predoctoral studentship and Mr. I. Paul for helpful discussions concerning the MO treatment.

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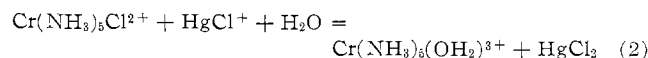
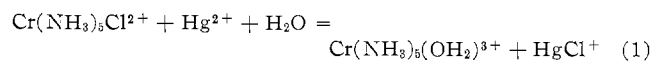
Kinetics and Mechanism of the Reaction of Chloropentaamminechromium(III) Ion and Mercury(II)^{1a}

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The mechanisms of relatively few reactions of halochromium(III) complexes with mercury(II) ion have been reported. The aquation of $Cr(NH_3)_5Cl^{2+}$ appeared quite interesting, for the analogous reactions of $Cr(OH_2)_5Cl^{2+}$ have been studied.² Mercury(II) efficiently accelerates release of chloride ion from the

primary coordination sphere of chromium(III). The reactions taking place are



We have carried out studies on the kinetics and mechanisms of these reactions. Special attention was directed toward the hydrogen ion dependence of the rate and toward a comparison of the rate at which release of chloride ion is increased by mercury(II) relative to spontaneous aquation. A comparison is made of the kinetic effect of those ligands on chromium(III), NH_3 and H_2O , which remain unchanged.

Experimental Section

The compound $[Cr(NH_3)_5Cl]Cl_2$ was prepared according to the method of Schlessinger.³ The perchlorate salt was precipitated from solutions of the chloride by slow addition of a solution of lithium perchlorate or perchloric acid and cooling. The precipitate was washed with ice-cold water, ethanol, and ether and was dried in air. Both the chloride and perchlorate salts were stored in opaque containers to prevent photochemical decomposition which otherwise occurs. The compound $[Cr(NH_3)_5OH_2](ClO_4)_3$ was prepared from the chloro complex by the method of Linhard and Berthold.⁴ The visible and ultraviolet absorption spectra of these complexes agree with published data.^{5,6} Other reagents were prepared and analyzed as described previously. The spectrophotometric rate measurements generally were made at 3760 Å on solutions in thermostated 10-cm silica cells; the procedure was similar to that previously employed.²

The initial concentration of mercury(II) was always at least 20 times that of $Cr(NH_3)_5Cl^{2+}$, and the reaction followed pseudo-first-order kinetics in every experiment. Rate constants were evaluated graphically, usually taking data to at least 90% completion, and generally were reproducible to within 2–5% average deviation. Spectral measurements on spent reaction solutions proved that the reaction product is $Cr(NH_3)_5OH_2^{3+}$ as written in eq 1 and 2.

The effects of ionic strength and anion concentration on similar reactions at relatively high reactant concentrations have been considered in the earlier study of the related $Cr(OH_2)_5Cl^{2+}$ – Hg^{2+} reaction.² As a consequence of these results, our rate measurements on both Hg^{2+} and $HgCl^+$ were carried out in an ionic medium which preserves both constant ionic strength and constant perchlorate ion concentration. All the data reported here refer to a medium of ionic strength 2.00 M, consisting of 0.50 M divalent ions (Ba^{2+} , Hg^{2+} , $Cr(NH_3)_5Cl^{2+}$) and 0.50 M univalent ions (H^+ , Li^+ , $HgCl^+$); perchlorate ion remained constant at 1.50 M. Appropriate changes in $[Ba^{2+}]$ or $[Li^+]$, presumed to exert no specific effects other than electrolyte effects, compensated for changes in concentration of any other substance.

Results

The rate data obey the equation

$$-d[Cr(NH_3)_5Cl^{2+}]/dt = [Cr(NH_3)_5Cl^{2+}](k_0[Hg^{2+}] + k_1[HgCl^+]) \quad (3)$$

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(6) Our values for absorption maxima, A (molar absorbance index, $M^{-1}cm^{-1}$), for $Cr(NH_3)_5Cl^{2+}$ are 3760 (37.3) and 5120 (36.9). These values can be compared to 3750 (39) and 5120 (36),^{5a} 3760 (43.6) and 5140 (38.0),^{5b} 3750 (34.7) and 5120 (33.9),^{5c} 3750 (31.7) and 5080 (40).^{5d}

(1) (a) Work performed in the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1824; (b) Undergraduate research participant, summer 1965.

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